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Clusters in the adsorbates of vapours and gases: Zeta isotherm approach

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A procedure for determining the structure of vapour and gas adsorbates that is based on the Zeta adsorption isotherm is reported. For vapours and for gases, this isotherm supposes that an adsorbate consists of particle clusters with the number of particles in a cluster denoted ζ, where ζ can be $1,2,3\cdots$ up to a maximum of ζ_m, and predicts the isotherm constants are *independent* of pressure. For vapours, this allows the isotherm constants to be determined from isotherm measurements made at pressures less than the saturation-vapour pressure, P_s, but applied at pressures greater than P_s. Since ζ has an upper limit, we show that there are no singularities in the vapour or gas adsorption isotherms for any pressure. This allows the adsorption of vapours at pressures greater than P_s to be investigated: clusters with ζ_m molecules are predicted to increase in number as P^V is increased, until they form an adsorbed film with each adsorption site occupied by a ζ_m-cluster. We apply the same procedure to determine the value of ζ_m for gas adsorption. For CO adsorbing on Ni(100), ζ_m is predicted to be unity for all the cases considered, indicating that the adsorbate consists of adsorbed molecules without any clustering. For H_2 adsorption on the three different materials, ζ_m is found to be two: indicating the adsorbate consists of both adsorbed molecules and atoms. For each material considered, a pressure is predicted where the mole fractions of both are equal, and at higher pressure, the mole fraction of adsorbed molecules exceeds that of the adsorbed atoms.

1 Introduction

The presence of molecular clusters in the adsorbates of water vapour have been hypothesized for some time[1–6]. We propose a method based on the Zeta-adsorption isotherm[7] to predict the "structure" of vapour or gas adsorbates from their respective, measured adsorption isotherms. The structure of an adsorbate is determined by its cluster distribution, a_ζ: the number of clusters in an adsorbate that consists of ζ-particles (atoms or molecules), where ζ can be $1,2,3\cdots$ up to a maximum of ζ_m. We suppose the single-adsorbed particles react with larger sized clusters to form an equilibrium distribution. This imposes a condition on the chemical potentials of the adsorbed clusters, μ_ζ^A [7,8]

$$\zeta\mu_1^A = \mu_\zeta^A \qquad \zeta = 1,2\cdots\zeta_m. \tag{1}$$

We consider both vapour and gas adsorption and show ζ_m depends strongly on the isotherm temperature relative to the critical temperature of the adsorbing fluid.

When it is a vapour phase that is adsorbing and the vapour-phase pressures, P^V, is less than the saturation-vapour pressure, P_s of the adsorbing fluid, the Zeta adsorption isotherm has been successfully applied for 18 different systems[7,9–12]. As P^V approaches P_s, the Zeta isotherm does *not* predict an infinite amount is adsorbed. This allows the Zeta isotherm to be applied at $x^V (\equiv P^V/P_s)$ greater than unity. Adsorptions in this pressure range have not been previously explored, to our knowledge. All of the presently available isotherms indicate an infinite amount is adsorbed as x^V approaches unity[13]. Thus, those isotherms cannot be used to examine vapour adsorbates at pressures P^V greater than P_s.

For vapour adsorption, we use the expression for the cluster distribution and predict the adsorbate grows into an adsorbed film for x^V greater than unity. However, the film is susceptible to heterogeneous droplet formation, and therefore is metastable. We do not deal with the issue of droplet nucleation, but confine our attention to stable or metastable adsorbed films. We illustrate the procedure for determining the adsorbate structure using three hydrocarbon vapours: toluene, heptane and octane adsorbing on Cu at 298 K. The maximum number of molecules in the clusters are found to be 115, 130 and 60 respectively. All of the isotherm constants appearing in the expression for cluster distribution are determined from measurements made at x^V *less* than unity, but the derivation of the isotherm indicates they are independent of pressure[7]. Thus, they can be applied at x^V greater than unity. At these pressures, cluster distribution indicates adsorbed films form, and are estimated to have thicknesses of tens of nanometers,

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Table 1.

When the temperature, T, is raised above of the critical temperature, T_{cr}, of the adsorbing fluid, a remarkable change in the value of ζ_m is predicted from the measured isotherms. We consider two gases: CO adsorbing on Ni(100) and hydrogen adsorbing on Cu, on Ni(111) and on Si(111). For CO, ζ_m is predicted to have a value of unity, indicating that the adsorbate consists of adsorbed molecules, but no clusters. For hydrogen gas, the procedure indicates that, in contrast to the assumptions on which the second Langmuir isotherm is based, ζ_m has a value of two for all three substrates, indicating the adsorbates consist of both atoms *and* molecules. The second Langmuir isotherm shows no correlation with data reported by Raschke and Hofer for H_2 adsorbing on Si(111)[14]. By contrast, the Zeta isotherm accurately correlates their data and strongly supports the prediction obtained from the cluster distribution function that both adsorbed atoms and molecules are present in the adsorbates.

2 The Zeta adsorption isotherm and the isotherm constant

When a vapour or gas adsorbs, the amount adsorbed is denoted $n^A(x)$ where A is either SV or SG, and x is the pressure in the fluid phase. For vapours it is a dimensionless pressure ratio, but for gases it is dimensional because the data are expressed in terms of dimensional pressure. The amount adsorbed, n^A, as a function of x, can be expressed in terms of the cluster distribution of an adsorbate:

$$n^A = \sum_{\zeta=1}^{\zeta_m} \zeta a_\zeta. \tag{2}$$

Following the Zeta adsorption isotherm derivation, Ward and Wu[7] used eqn (1), and the condition for equilibrium between the single adsorbed particles and the fluid phase, μ^f:

$$\mu^f = \mu_1^A, \tag{3}$$

and constructed an expression for a_ζ that is equivalent to

$$\frac{a_\zeta}{M} = \frac{c(\alpha x-1)(\alpha x)^\zeta}{\alpha x(1+c((\alpha x)^{\zeta_m}-1))-1}, \quad \zeta = 1,2,3\cdots\zeta_m. \tag{4}$$

where M, c, α, and ζ_m are each constant along an adsorption isotherm. We determine their values from the measured isotherms for vapours and for gases.

The number of adsorption sites per unit area is denoted by M. It is related to the number of adsorption sites per unit mass, M_g, by the specific surface area, A_s:

$$M_g = A_s M, \tag{5}$$

as is the adsorption per unit mass of the substrate, n_g^A

$$n_g^A = A_s n^A. \tag{6}$$

The isotherm constant c is related to partition function for the clusters with different numbers of particles, q_ζ

$$q_\zeta = (q_1)^\zeta (c)^{1-\zeta} \qquad \zeta = 1,2,\cdots\zeta_m. \tag{7}$$

The derived expression for α may be written

$$\alpha = (\frac{q_1}{c})\exp\left[\frac{\mu(T,P_r)}{k_b T}\right], \tag{8}$$

where $\mu(T,P_r)$ is the chemical potential of the adsorbing fluid at the reference pressure P_r; the isotherm temperature is T; and the Boltzmann constant is denoted k_b. When eqn (4) is substituted into eqn (2), Ward and Wu showed that the series could be summed to obtain an analytical expression for $n^A(x)$:

$$n^A(x) = \frac{Mc\alpha x[1-(1+\zeta_m)(\alpha x)^{\zeta_m}+\zeta_m(\alpha x)^{1+\zeta_m}]}{(1-\alpha x)[1+(c-1)\alpha x - c(\alpha x)^{1+\zeta_m}]}; \tag{9}$$

however summing the series introduces an apparent singularity at αx equals unity, but application of l'Hôpital's rule indicates

$$\lim_{\alpha x^V \to 1} n^A = \frac{Mc\zeta_m(1+\zeta_m)}{2(1+c\zeta_m)}. \tag{10}$$

Since ζ_m is finite, $n^A[(\alpha)^{-1}]$ is finite, and there are no values of x where the Zeta isotherm indicates an infinite amount is adsorbed.

The fraction of the adsorption sites that are empty, a_0/M, may now be obtained

$$a_0 = M - \sum_{\zeta=1}^{\zeta_m} a_\zeta, \tag{11}$$

and after combining eqn (4) with eqn (11), one finds

$$\frac{a_0}{M} = \frac{\alpha x - 1}{\alpha x^V(1+c((\alpha x^V)^{\zeta_m}-1))-1}. \tag{12}$$

The value of a_0^{SV}/M will be particularly important when H_2 adsorption is considered. Note that the method for determining ζ_m has not yet been stated.

3 Adsorption isotherms when T is less than T_{cr} of the adsorbing fluid

We now apply the Zeta isotherm to vapour adsorption. In this circumstance, there is no change in the meaning of M or c but

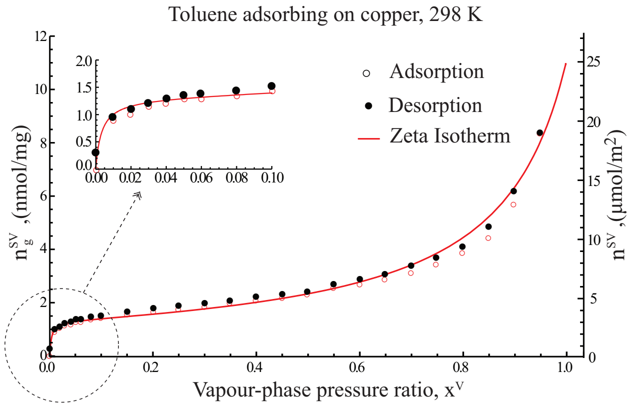

Fig. 1 Gravimetric measurements of the equilibrium adsorption and desorption isotherms of toluene were made on ∼130 mg of Cu powder (Sigma-Aldrich: particle size of 10 μm, purity 99%) following the procedure described by Zandavi and Ward[9]. After the Cu was placed in the adsorption instrument (Surface Measurements Systems), it was heated to 473 K, and held at this condition for four hours. The copper was cooled in the thermostated enclosure of the instrument to 298 K by dry N_2 flow, and the equilibrium adsorption-desorption isotherms measured with a gas-vapour mixture at flow rate of 1.67 cm^3/s. The solid line in Fig. 1 was calculated using n_g^{SV}, eqn (9). The isotherm constants at 298 K were determine from the measurements and are listed in Table 1.

n^A becomes n^{SV} and the reference pressure is chosen to be the saturation-vapour pressure, $P_s(T)$. α and x are replaced by α^{SV} by x^V respectively where

$$\alpha^{SV} = (\frac{q_1}{c})\exp\left[\frac{\mu(T,P_s)}{k_bT}\right]. \tag{13}$$

All of the Zeta adsorption isotherm constants are determined from the measured adsorption isotherms at $x^V < 1$. That is the only x^V range where adsorption measurements can be made at present. But since the derivation of the Zeta isotherm indicates M, c, α and ζ_m are constant along an isotherm, they may be used in n^{SV} for $x^V \geq 1$.

Gravimetric adsorption isotherms, n_g^{SV}, of toluene, heptane and octane adsorbing on a polycrystalline Cu surface at 298 K were measured for values of x^V up to 0.95. The isotherm measurements for each vapour were used to determine the value of the Zeta isotherm constants for that vapour.

All the isotherm measurements were similar to those of toluene that are shown in Fig. 1.

We define a function:

$$\Delta(\zeta_{mj}) \equiv \frac{\sqrt{\sum_{i=1}^{N_m}[n_g^{SV}(x_i^V,\zeta_{mj}) - n_m^{SV}(x_i^V)]^2}}{\sum_{i=1}^{N_m} n_m^{SV}(x_i^V)}, \tag{14}$$

to estimate the difference between the measured adsorption as a function of the measured pressures $n_m^{SV}(x_i^V)$, and that calculated, $n_g^{SV}[x_i^V, \zeta_{mj}]$ where

$$i = 1, 2, \cdots N_m, \tag{15}$$

and

$$j = 1, 2, 3 \cdots. \tag{16}$$

We examine a series of different ζ_m values, and determine the value that minimizes $\Delta(\zeta_m)$. If ζ_m is chosen to be ζ_{mj}, the isotherm data for $x^V < 1$ and eqns (6) and (9), may be used in the Nonlinear Regression package of Mathematica™ to determine the values of M_g, c and α^{SV} that minimizes the difference between the calculated isotherm and that measured.

For example, if ζ_{m1} is chosen to be 100, $\Delta(100)$ is found to be 11.12%, but if ζ_{m2} is chosen to be 115, $\Delta(115)$ is reduced 1.41%, a significant reduction in the calculated error. And if ζ_{m3} is chosen to be larger than 115, there is no further reduction in $\Delta(\zeta_m j)$. Thus, ζ_m for toluene adsorbing on Cu at 298 K is taken to be 115. The solid line shown in Fig. 1 was calculated using eqn (6) and the values of the other isotherm constants corresponding to ζ_m equal 115 are listed in Table 1.

The values of the isotherm constants, determined by this procedure, for heptane, and octane adsorbing on Cu are also listed in Table 1. The calculated errors for these vapours are even smaller than that for toluene.

3.1 Vapour adsorption when x^V is *greater* than unity

Once the values of the isotherm constants have been determined from measurements made for x^V *less* than unity, the isotherm constants determined, the number of molecular clusters in the adsorbate that have ζ-molecules, a_ζ, may be calculated from eqn (4) for the full x^V range, $0 < x^V < 2$. As seen in Figs. 2 and 3, when x^V is near zero, the adsorbate consists primarily of adsorbed molecules, a_1, but as also indicated in these figures, a monolayer never forms. As x^V is increased, clusters with a larger number of molecules begin to appear in the adsorbate, and when x^V reaches $(\alpha^{SV})^{-1}$, the number of molecular clusters becomes the same for all values of ζ:

$$\lim_{\alpha^{SV}x^V \to 1} \frac{a_\zeta}{M} = \frac{c}{1 + c\zeta_m}. \tag{17}$$

At this value of x^V, the fraction of the adsorption sites occupied by each sized cluster is the same: for toluene, heptane and octane these fractions are 0.0087, 0.0077, 0.017 respectively.

For x^V greater than $(\alpha^{SV})^{-1}$, only the clusters with ζ_m molecules are predicted to increase in number. The formation of clusters with ζ_m molecules represents the initiation of an adsorbed film, but the film is not yet uniform. However, as indicated in Fig. 3A, once ζ_m-molecule clusters begin

Table 1 Zeta-isotherm constants for toluene, heptane or octane adsorbing on copper at 298 K

Vapour	v_f m^3/kmol	ζ_m	M_g (nmol/mg)	c	α^{SV}	$\Delta(\zeta)$ %	A_s(Cu) m^2/kg	M (μmol/m^2)	τ_{af} (nm)
Toluene	0.107	115	1.36 ±0.07	353 ±52	0.88 ±0.01	1.41%	410 ±22	3.10 ±0.16	38
Heptane	0.147	130	1.05 ±0.05	255 ±30	0.92 ±0.01	1.29%	462 ±32	2.39 ±0.11	46
Octane	0.163	60	0.83 ±0.02	70 ±9	0.73 ±0.01	0.84%	445 ±11	1.89 ±0.05	18
Mean ±SDV							439 ±6.0%		

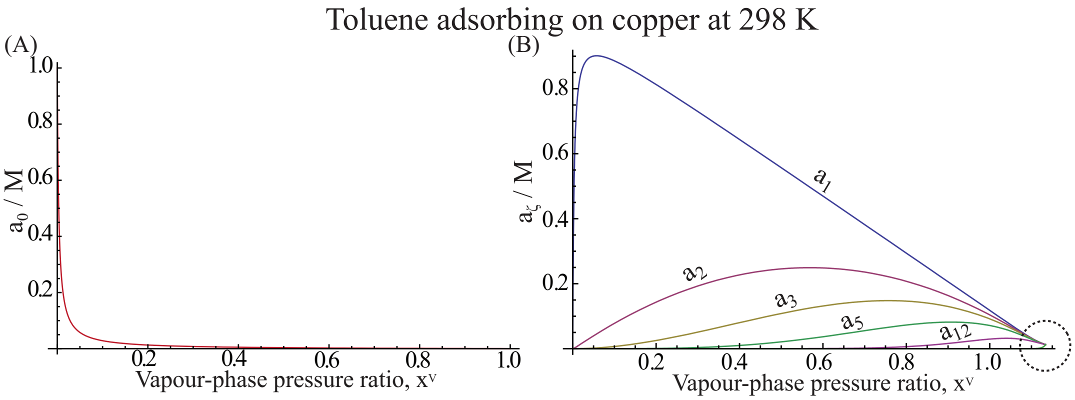

Fig. 2 A) For toluene adsorbing on Cu, the number of unoccupied adsorption sites goes to zero when x^V reaches 0.4. B) But there is never a monolayer formed: a_1/M reaches a maximum of 0.9. The adsorbate structure for the region indicated by the dashed circle is shown Fig. 3A.

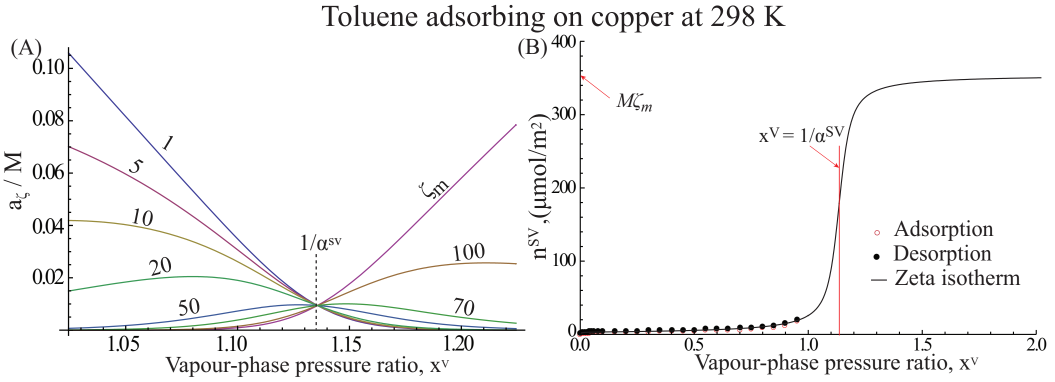

Fig. 3 The Zeta isotherm predicts the formation of an adsorbed film when x^V is greater than $(\alpha^{SV})^{-1}$. Each adsorption site is occupied by a molecular cluster with ζ_m molecules (Table 1).

to form, they increase in number monotonically as x^V is increased above $(\alpha^{SV})^{-1}$.

With further increase in x^V, the film becomes asymptotically uniform with each adsorption site ultimately containing a cluster with ζ_m molecules, and $M\zeta_m$ molecules adsorbed, Fig. 3B.

3.2 Specific surface area of Cu determined from molecular-cluster properties

In a recent study[9] the Zeta-adsorption isotherm was used with the measured isotherms of toluene, heptane and octane to determine the specific surface area of a non-porous *silica* powder (Aerosil 150) and of a porous silica, (MCM-41). Since the specific surface area is independent of the vapour used to determine it, the accuracy of the procedure could be assessed. The mean of the specific surface areas of the non-porous silica (±SDV) determined with the three vapours were 0.120 ± 2.5% and that of MCM-41 were 1.15 ± 1.7% m^2/mg. We use these results with a hypothesis to determine the specific surface area of the Cu powder used in this study.

In the derivation of the Zeta isotherm, it was assumed that one molecular cluster occupied one adsorption site. The average cross-sectional area of an adsorption site or of a molecular cluster of a particular vapour, say I, is denoted $\overline{\sigma(I)}$, then

$$\overline{\sigma(I)} M_g(I, silica) = A_s(silica), \qquad (18)$$

$$\text{I: toluene, heptane, or octane}$$

and combining eqns (5) and (18) gives

$$\overline{\sigma(I)} = \frac{1}{M(I, silica)}, \qquad (19)$$

where the values of $M(I, silica)$ for the different vapours are listed in Table 2. As an approximation to be evaluated, we assume $\overline{\sigma(I)}$ for a particular vapour has the same value on silica as it has on Cu. Then after making use of eqn (19), the value of A_s for Cu is given by

$$A_s(Cu) = M_g(Cu)\overline{\sigma(I)}. \qquad (20)$$

In Table 1, we show the result of calculating $A_s(Cu)$ from eqn (20) for each of the three vapours. The mean value of $A_s(Cu)$± SDV is 439 ± 6.0 % m^2/kg. This error is larger than that found for silica (i.e., 2.5%)[9], but the amount adsorbed on silica is approximately 300 times larger than that for these vapours adsorbing on Cu. Thus, making the measurement of the amount adsorbed on Cu more difficult. For example, M_g is directly determined from the adsorption measurements. The error in M_g for Cu ranges from 5.1% for toluene to 2.4 % for octane, Table 1. Clearly the indicated error in $A_s(Cu)$ is in part a reflection of the error in the measurement of M_g, see eqn (20).

Table 2 Zeta-isotherm constants for each vapour (toluene, heptane or octane) adsorbing on silica at 298 K[9]

Vapour	ζ	M_g (nmol/mg)	A_s(Si) m^2/mg	$M(I, silica)$ (μmol/m^2)	$\overline{\sigma_I}$ Å^2	τ_{af} (nm)
Toluene	120	399 ±12	0.117	3.32 ±0.10	50 ±2	43
Heptane	150	271 ±12	0.120	2.26 ±0.10	73 ±3	50
Octane	150	224 ±12	0.122	1.87 ±0.10	89 ±4	46
Mean ±SDV			0.120 ±2.5%			

The thickness of the adsorbed film may now be estimated. If the specific volume of the adsorbed film is approximated as that of the bulk liquid, v_f, then the thickness of the adsorbed film, τ_{af}, may be written as:

$$\tau_{af} = \frac{M_g \zeta_m v_f}{A_s}, \qquad (21)$$

and after combining with eqn (5)

$$\tau_{af} = M\zeta_m v_f. \qquad (22)$$

The values of τ_{af} for each vapour adsorbed on Cu and on silica are listed in Tables 1 and 2 respectively.

4 Adsorption when the temperature is greater than the critical temperature of the adsorbing fluid

When a nonporous solid surface is exposed to a gas, two types of adsorption can occur: molecular or dissociative. From the perspective of the Zeta adsorption isotherm, the type of adsorption is determined by the value of ζ_m, and as seen in the previous section for vapour adsorption, its value may be determined from a measured adsorption isotherm. In this section, we apply the same procedure as that used for vapours to determine the structure of CO and of H_2 adsorbates.

We suppose it is known from T and gas phase pressure, P^G, that only molecules are present in the gas phase. Equilibrium between the molecules in the adsorbed phase and those in the gas phase requires

$$\mu_1^{SG} = \mu^G(T, P^G), \tag{23}$$

and equilibrium between the *possibly* adsorbed clusters requires

$$\mu_\zeta^{SG} = \zeta \mu_1^{SG}, \quad \text{where} \quad \zeta = 1, 2 \ldots \zeta_m, \tag{24}$$

If the chemical potential of a gas in a reference state is denoted $\phi(T, P_r)$, where P_r is a reference pressure, then from eqn (23), the expression for the chemical potential of the adsorbed molecules becomes

$$\mu_1^{SG} = k_b T \ln(\frac{P^G}{P_r} \exp[\frac{\phi(T, P_r)}{k_b T}]). \tag{25}$$

We eliminate the isotherm constant α^{SV}, but introduce a new isotherm constant β^{SG} that depends on the reference state for the gas

$$\beta^{SG} = (\frac{q_1}{c}) \frac{\exp(\frac{\phi(T,P_r)}{k_b T})}{P_r}. \tag{26}$$

where c is only a function of T and β^{SG} has units of inverse pressure.

We introduce M_0, the number of substrate surface atoms per unit surface area, and define the coverage, Θ, as

$$\Theta \equiv \frac{n^{SG}}{M_0}. \tag{27}$$

After combining the eqns (24) to (27) with eqn (2), and following the same procedure as used with the vapour[7], one obtains the Zeta adsorption isotherm for a gas:

$$\Theta(P^G) = \frac{M}{M_0} \frac{c\beta^{SG}P^G[1 - (1+\zeta_m)(\beta^{SG}P^G)^{\zeta_m} + \zeta_m(\beta^{SG}P^G)^{1+\zeta_m}]}{(1-\beta^{SG}P^G)[1+(c-1)\beta^{SG}P^G - c(\beta^{SG}P^G)^{1+\zeta_m}]}. \tag{28}$$

The expression for Θ has an apparent singularity at

$$\beta^{SG}P^G = 1, \tag{29}$$

but the application of l'Hôpital's rule indicates

$$\Theta(1/\beta^{SG}) = \frac{Mc\zeta_m(1+\zeta_m)}{2M_0(1+c\zeta_m)}. \tag{30}$$

Thus, again since ζ_m is finite, there are no singularities in the expression for Θ given in eqn (28).

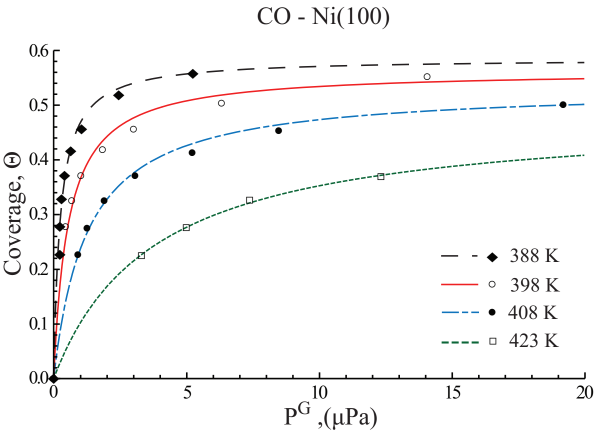

Fig. 4 The measured adsorption isotherms of CO adsorbing on Ni(100)[15,16]. The lines are the recalculated isotherms obtained with the isotherm constants listed in Table 3.

Table 3 Zeta-isotherm constants for CO on Ni(100)[15,16]

Temperature K	ζ_m	$\Delta_g(1)$ (%)	M/M_0	$c\beta^{SG}$ $(\mu\text{Pa})^{-1}$
388	1	1.54	0.585	3.99
398	1	1.22	0.563	1.82
408	1	0.87	0.532	0.80
423	1	0.48	0.485	0.26

When the error estimate, $\Delta_g(\zeta_{mj})$, is written in terms of the coverage, one obtains

$$\Delta_g(\zeta_{m_j}) \equiv \frac{\sqrt{\sum_{i=1}^{N_m}[\Theta(P_i^G, \zeta_{mj}) - \Theta_m(P_i^G)]^2}}{\sum_{i=1}^{N_m}\Theta_m(P_i^G)}. \tag{31}$$

We now use eqns (28) and (31) with the measured isotherms of CO adsorbing on Ni(100)[15,16], and determine the value of ζ_m and the other isotherm constants for each empirical isotherm. The procedure is similar to that used with vapours: a value of ζ_{mj} is assumed and the other corresponding isotherm constants that minimizes $\Delta_g(\zeta_{mj})$ are determined from the empirical isotherms. For each isotherm, as indicated in Table 3, the minimizing value of ζ_m is unity, and the error estimate is less than 2% for each isotherm.

Once the value of ζ_m has been determined to be unity, both the expression for $\Theta(P^G)$ and the cluster distribution, eqn. (4), can be simplified to

$$\Theta = \left(\frac{M}{M_0}\right) \frac{c\beta^{SG} P^G}{1 + c\beta^{SG} P^G}, \tag{32}$$

a Langmuir-type isotherm with only one isotherm constant!

The isotherms shown in Fig. 4 illustrate the type of isotherm obtained when the ζ_m is unity. Since the cluster distribution and adsorption isotherm coincide when ζ_m is unity, this means physically that an adsorption site has either one molecule adsorbed or is empty. It is important to recognized that it was the measured adsorption isotherms that were used to determine the value of ζ_m.

4.1 Hydrogen gas adsorption on different materials

The isotherms of hydrogen adsorbing on polycrystalline Cu at 298 K are shown in Fig. 5[17], on Ni(111) at 314 K in Fig. 6[16,18] and on Si(111) at 876 K in Fig. 7[14]. As will be seen, the analysis of these data with the Zeta adsorption isotherm indicates the adsorbates consist of both hydrogen atoms and *molecules*. To our knowledge, only the Zeta adsorption isotherm predicts the presence of both hydrogen atoms and molecules in hydrogen adsorbates. The dissociative Langmuir isotherm (DLI)[13,19–21] assumes the adsorbate consists only of adsorbed atoms. The importance of the molecules in the adsorbate will be investigated by comparing the analysis of the data in Figs. 5 to 7 with the Zeta and with DLI isotherms.

The Zeta isotherm constants are determined using the same procedure as that used earlier for vapours and for molecular gas adsorption. As the condition for equilibrium of the adsorbed hydrogen, we may write

$$\mu_\zeta^{SH} = \zeta \mu_1^{SH}, \qquad \zeta = 1, 2 \ldots \zeta_m, \tag{33}$$

where μ_ζ^{SH} is the chemical potential of atomic clusters in the adsorbate that contain ζ atoms. Since no atoms are expected in the gas phase, the conditions for equilibrium between the gas phase and the adsorbed phase is

$$\mu_2^{SH} = \mu^G. \tag{34}$$

From eqn (33) for ζ equal 2,

$$\mu_2^{SH} = 2\mu_1^{SH}. \tag{35}$$

Combing eqns (34) and (35):

$$\mu_1^{SH} = \frac{1}{2}\mu^G. \tag{36}$$

After introducing the expression for the chemical potential of the hydrogen gas which we approximate as ideal, one finds from eqn (36)

$$\mu_1^{SH} = k_b T \ln\{(\frac{P^H}{P_r^H})^{1/2} \exp[\frac{\phi(T, P_r^H)}{2k_b T}]\}, \tag{37}$$

where the pressure in the hydrogen gas is denoted P^H, and the reference pressure as P_r^H.

The isotherm constant α^{SV}, introduced in the derivation of the Zeta isotherm for vapours[7], is replaced by κ^{SH}:

$$\kappa^{SH} = (\frac{q_1}{c})^2 \frac{\exp(\frac{\phi(T, P_r^H)}{k_b T})}{P_r^H}. \tag{38}$$

After combining the eqns (33) to (38) with eqn (2), and following the same procedure as used with the vapours and with CO, one obtains the expression for the Zeta isotherm for hydrogen adsorption on a polycrystalline material per unit mass of the material:

$$n_g^{SH}(P^H) = \frac{M_g c(\kappa^{SH} P^H)^{\frac{1}{2}} [1 - (1+\zeta_m)(\kappa^{SH} P^H)^{\frac{\zeta_m}{2}} + \zeta_m (\kappa^{SH} P^H)^{\frac{1+\zeta_m}{2}}]}{(1 - (\kappa^{SH} P^H)^{\frac{1}{2}})[1 + (c-1)(\kappa^{SH} P^H)^{\frac{1}{2}} - c(\kappa^{SH} P^H)^{\frac{1+\zeta_m}{2}}]}, \tag{39}$$

or the hydrogen coverage on a single-crystal material is given by

$$\Theta^{SH}(P^H) = \frac{M}{M_0} \frac{c(\kappa^{SH} P^H)^{\frac{1}{2}} [1 - (1+\zeta_m)(\kappa^{SH} P^H)^{\frac{\zeta_m}{2}} + \zeta_m (\kappa^{SH} P^H)^{\frac{1+\zeta_m}{2}}]}{(1 - (\kappa^{SH} P^H)^{\frac{1}{2}})[1 + (c-1)(\kappa^{SH} P^H)^{\frac{1}{2}} - c(\kappa^{SH} P^H)^{\frac{1+\zeta_m}{2}}]}. \tag{40}$$

As was found for vapours and for molecular gas adsorption, the apparent singularity in the hydrogen isotherms, eqns (39) and (40), at

$$P^H = (\kappa^{SH})^{-1}, \tag{41}$$

is not a singularity. The values of n_g^{SH} and Θ^{SH} at the apparent singularity are

$$n_g^{SH}[(\kappa^{SH})^{-1}] = \frac{M_g c \zeta_m (1+\zeta_m)}{2(1+c\zeta_m)}; \tag{42}$$

and

$$\Theta^{SH}((\kappa^{SH})^{-1}) = \frac{M_g c \zeta_m (1+\zeta_m)}{2M_0(1+c\zeta_m)}. \tag{43}$$

Note that no assumptions were made regarding the value of ζ_m. We can now determine its value.

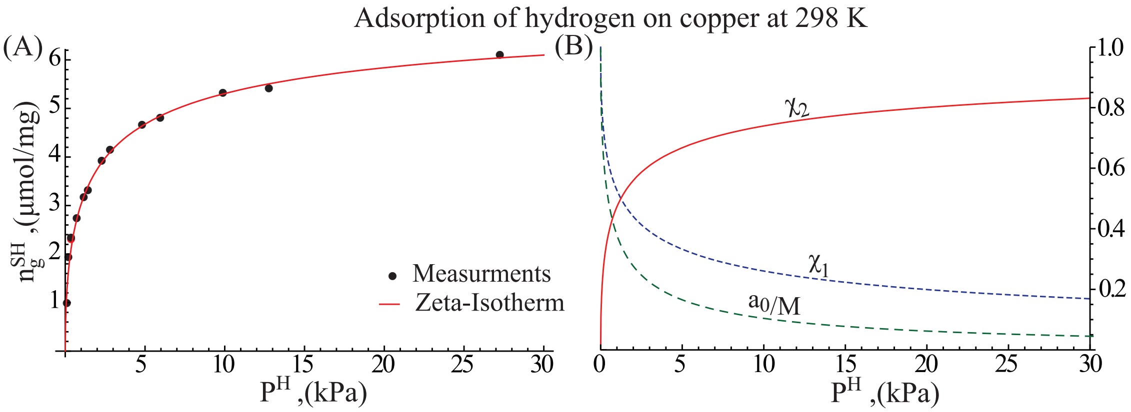

Fig. 5 In figure A, the measured isotherm for H_2 adsorbing on Cu at 298 K and up to 30 kPa is shown [17]. The solid line was calculated using the Zeta isotherm and the isotherm constants listed in Table 4. The error in the calculated isotherm, as indicated by $\Delta_g(\zeta_m)$, is 1.02 %, Table 4. In figure B, the mole fractions of the adsorbed hydrogen atoms, χ_1, of the adsorbed molecules, χ_2, and the fraction of the adsorption sites that are empty, a_0/M, are shown. The pressure at which the mole fraction are predicted to be equal, P_{χ_2,χ_1}, is 1.24 kPa. At pressures above this pressure, χ_2 increases, χ_1 deceases, but there is continued accumulation of hydrogen on the surface, as indicated by the decrease in the number of empty sites a_0/M in this pressure range.

Following the Zeta adsorption isotherm procedure for vapour and molecular gas adsorption, the expression for the atomic cluster distributions in the adsorbate of hydrogen, a_ζ^{SH}, becomes

$$\frac{a_\zeta^{SH}}{M} = \frac{c((\kappa^{SH}P^H)^{\frac{1}{2}}-1)(\kappa^{SH}P^H)^{\frac{\zeta}{2}}}{(\kappa^{SH}P^H)^{\frac{1}{2}}(1+c((\kappa^{SH}P^H)^{\frac{\zeta_m}{2}}-1))-1}, \quad \zeta = 1,2\cdots\zeta_m, \tag{44}$$

and the fraction of the adsorption sites that are empty, a_0^H/M, is given by

$$\frac{a_0^{SH}}{M} = \frac{(\kappa^{SH}P^H)^{\frac{1}{2}}-1}{(\kappa^{SH}P^H)^{\frac{1}{2}}(1+c((\kappa^{SH}P^H)^{\frac{\zeta_m}{2}}-1))-1}. \tag{45}$$

We now use

- the measurements shown in Figs. 5 to 7;
- the Zeta isotherms for hydrogen adsorption, eqns (39) and (40);
- the error estimate, $\Delta_g(\zeta_{mj})$

and follow the same procedure as that used for vapour and for molecular gas adsorption to determine the value of ζ_m. The results are listed in Table 4. In each case, ζ_m was found to be two; thus, ζ can have values of two or one. The "clusters" with the largest number of particle has two atoms: i.e., it is a molecule; the other type of "cluster" has one atom.

The recalculated isotherms are shown in Figs. 5 to 7 as solid lines where they may be compared with the measurements. The largest value of $\Delta_g(\zeta_m)$ is for H_2 adsorbing on Cu: 1%. For the two single crystal surfaces, the maximum value of $\Delta_g(\zeta_m)$ is 0.7%. It is not clear that there is any measurable difference between the recalculated isotherms and the measurements.

4.2 Mole fractions of the adsorbed hydrogen atoms and the hydrogen molecules

Since ζ_m for H_2 adsorbing on each of the three surfaces was found to be two, the expression for the Zeta adsorption isotherms, eqns (39) and (40), can be simplified to

$$n_g^{SH} = \frac{M_g c\left[(\kappa^{SH}P^H)^{1/2}+2\kappa^{SH}P^H\right]}{1+c\left(\kappa^{SH}P^H\right)^{1/2}+c\left(\kappa^{SH}P^H\right)}. \tag{46}$$

and

$$\Theta^{SH}(P^H) = \frac{M}{M_0}\frac{c\left[(\kappa^{SH}P^H)^{1/2}+2\kappa^{SH}P^H\right]}{1+c\left(\kappa^{SH}P^H\right)^{1/2}+c\left(\kappa^{SH}P^H\right)}. \tag{47}$$

The fraction of the adsorption sites that are empty, eqn (45), becomes

$$a_0^{SH} = \frac{M}{1+c(\kappa^{SH}P^H)^{1/2}+c(\kappa^{SH}P^H)}. \tag{48}$$

The expressions for the adsorbed atoms and molecules can be obtained from eqn (44). The expression for the atoms is

$$a_1^{SH} = \frac{Mc(\kappa^{SH}P^H)^{1/2}}{1+c\left(\kappa^{SH}P^H\right)^{1/2}+c\left(\kappa^{SH}P^H\right)}, \tag{49}$$

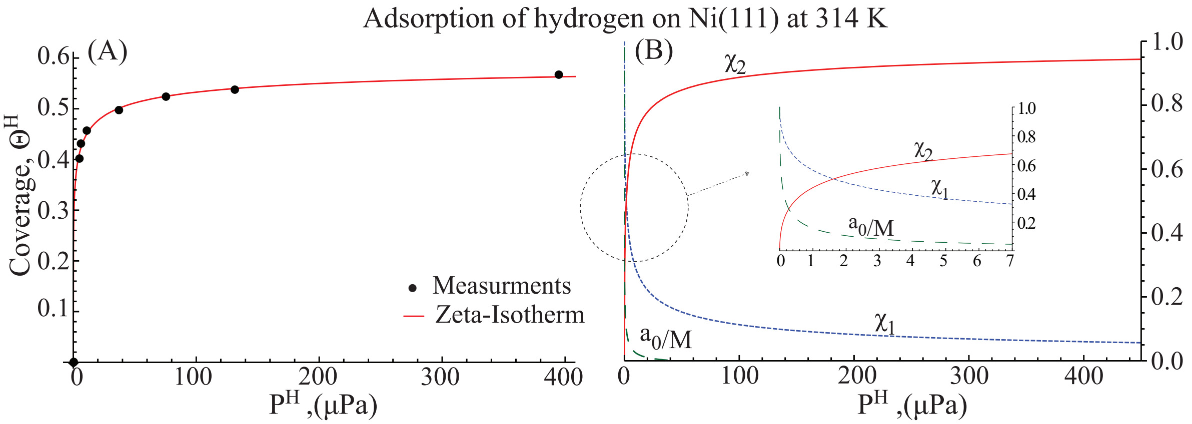

Fig. 6 The measured isotherms for H_2 adsorbing on Ni(111) at 314 and up to a pressure of 0.4 mPa are shown in figure A [16,18]. The recalculated isotherms obtained with the Zeta-isotherms and the isotherm constants listed in Table 4 are shown by the line. The error in the recalculated isotherm, as indicated by $\Delta_g(\zeta_m)$, is 0.52 % (Table 4). In figure B, the mole fractions of the atoms, χ_1, and the molecules, χ_2 are shown, along with the fraction of empty adsorption sites, a_0/M. The mole fractions of the adsorbed atoms and molecules are equal at 1.62 μPa, and full coverage is approached at 30 μPa, as indicated by a_0/M going to zero at this pressure, but note that at pressures greater than at 30 μPa there is still a decrease in the χ_1 at near full coverage, suggesting a recombination reaction and further molecular adsorption from the gas phase.

and for the adsorbed molecules

$$a_2^{SH} = \frac{Mc(\kappa^{SH}P^H)}{1+c\,(\kappa^{SH}P^H)^{1/2}+c\,(\kappa^{SH}P^H)}. \qquad (50)$$

Note that neither eqn (46) nor the eqn (47) is of the DLI form [13,19].

From eqns (49) and (50), the mole fraction of the adsorbed atoms is given by

$$\chi_1 = \frac{1}{1+2(\kappa^{SH}P^H)^{1/2}}, \qquad (51)$$

and that for the adsorbed molecules by

$$\chi_2 = \frac{2(\kappa^{SH}P^H)}{(\kappa^{SH}P^H)^{1/2}+2(\kappa^{SH}P^H)}. \qquad (52)$$

For a given value of ζ_m, the mole fractions are determined by a single isotherm constant, κ^{SH}. The value of this constant for each system is listed in Table 4. The values of κ^{SH} for hydrogen adsorbing on Cu at 298 K and on Ni(111) at 314 K differ by nine orders of magnitude. This isotherm constant multiplies the hydrogen pressure in the isotherm expressions; thus, the predicted mole fractions of the different materials depend strongly on pressure.

For each material, as seen in Figs. 5 to 7, in the limit of the H_2 pressure going to zero, the number of empty sites approaches M, and the atomic mole fraction approaches unity while the molecular mole fraction approaches zero. But as the H_2 pressure is increased, a pressure is reached, $P_{\chi_1\chi_2}$, where the mole fractions are equal. At H_2 pressures above $P_{\chi_1\chi_2}$, each material is found to have different characteristics. These characteristics are discussed in the captions of Figs. 5 to 7.

The agreement between the measured and recalculated Zeta isotherms for each system is excellent. The estimated error, $\Delta(\zeta_m)$, is 1.02% or less, Table 4.

When the DLI is used to analyse the data shown in Figs. 5 to 7, one simply assumes the adsorbates consist only of adsorbed atoms, and writes the DLI so its constants can be determined by linear regression [19,22]

$$\frac{\sqrt{P^H}}{\Theta_L^H} = \frac{\sqrt{P^H}}{\frac{M}{M_0}} + \frac{1}{\left(\frac{M}{M_0}\right)\sqrt{K_L^d}}. \qquad (53)$$

Raschke and Höfer [14] assumed the adsorption they measured was dissociative, but did not examine their data with the DLI or any other theoretical isotherm. Their data are shown in Fig. 8 where it has been plotted on the linear regression coordinates of the DLI, eqn (53). The result obtained from the DLI analysis of all three system are listed in Table 5. Although the DLI correlates the data for H_2 adsorbing on Cu and on Ni(111)—the coefficient-of-determination, R^2— is near unity (Table 5), it does not correlate the data for the H_2–Si(111). Since the Zeta-isotherm correlates the data for this system very well (Fig. 7 and Table 4), a possible reason for the failure of the DLI is that it neglects the presence of adsorbed molecules.

Others have reported the presence of adsorbed molecules on different surfaces using electron energy-loss spectroscopy (EELS) at low temperatures, ∼10 K [23–26], but there are no measured isotherms available at these temperatures. So the

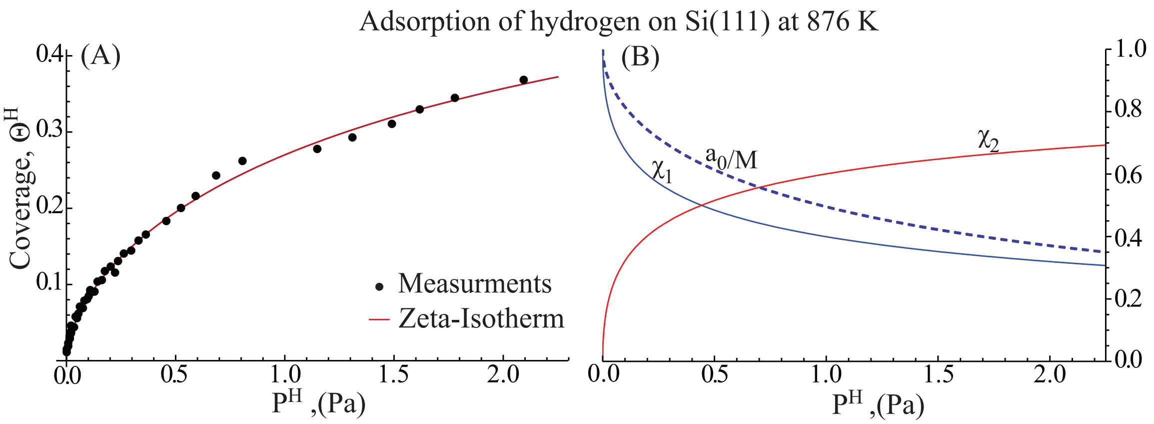

Fig. 7 The isotherm for H_2 adsorbing on Si(111) at 876 K and up to a pressure 2 Pa is shown in figure A [14]. The recalculated isotherm obtained with the Zeta-isotherms and the isotherm constants listed in Table 4 are shown by the solid line. The error in the calculated isotherm, as indicated by $\Delta_g(\zeta_m)$, is 0.69 % (Table 4). In figure B, the mole fractions of the hydrogen atoms, χ_1 and molecules, χ_2, along with the fraction of empty adsorption sites, a_0/M at 876 K are shown. The mole fractions of the adsorbed atoms and molecules are equal at 0.43 Pa, and full coverage is never approached even at the highest pressure considered, 2 Pa.

Table 4 Zeta isotherm constants for H_2 adsorbed on Cu, on Ni(111) or on Si(111)

Solid	Temp. (K)	ζ_m	M_g $(\frac{\mu mol}{mg})$	$\frac{M}{M_0}$	c	κ^{SH} $(kPa)^{-1}$	$\Delta(\zeta_m)$ (%)	$P_{\chi_1\chi_2}/P^H_{max}$
Cu	298	2	3.732	-	2.514	0.202	1.02	0.045
Ni(111)	314	2	-	0.298	9.84	$0.154\times10^{+9}$	0.52	0.004
Si(111)	876	2	-	0.375	0.777	560	0.69	0.22

Table 5 Langmuir isotherm constants for H_2 adsorbed on Cu, on Ni(111) or on Si(111)

Solid	Temp. (K)	M_g $(\frac{\mu mol}{mg})$	$\frac{M}{M_0}$	K_L^d $(kPa)^{-1}$	R^2	$\Delta_g^d(1)$ (%)
Cu	298	8.375	-	0.294	0.9596	1.18
Ni(111)	314	-	0.590	$0.946\times10^{+9}$	0.9997	0.58
Si(111)	876	-	-2.421	Imaginary	0.134	

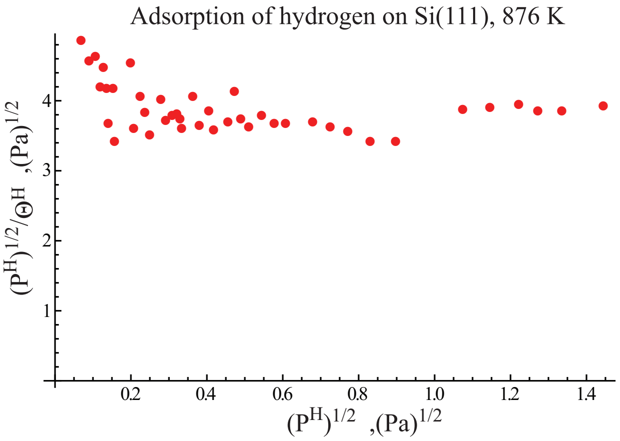

Fig. 8 As may be seen, the data do not support the predictions of the DLI, but the Zeta isotherm is in excellent agreement with the data ($\Delta_g(2) = 0.69\%$). The Zeta isotherm indicates that the adsorbate consists of both adsorbed atoms and molecules (Fig. 7), the presence of molecules in the DLI is neglected.

Zeta adsorption isotherm cannot be applied at these conditions.

5 Discussion

A method based on the Zeta adsorption isotherm has been proposed for determining the structure of vapour and gas adsorbates. In the original formulation of this isotherm for vapours, an adsorbate was assumed to consist of molecular clusters and the canonical ensemble was used to construct the expression for both the cluster distribution, eqn (4), and for the Zeta isotherm, eqn (9)[7]. Hill had explored using the *grand canonical* ensemble to formulate an adsorption isotherm for vapours[27]. This particular ensemble assumes there are no special values of ζ and takes the limit of eqn (9) as ζ goes to infinity to construct the grand canonical partition function. This eliminates ζ_m as a isotherm constant in the isotherm expression, and leads to the BET isotherm[28], but it introduces a singularity in the isotherm expression at x^V equals unity. Hill noted the singularity in the BET isotherm expression that he had obtained, and called it a “serious fault of the BET theory”[27].

Since a canonical ensemble was used to construct the Zeta cluster distribution and isotherm, it was *not* necessary to sum eqn (9) over all ζ, leaving the upper limit, ζ_m, as a isotherm constant in the expression for cluster distributions and for the isotherm. For both vapour and gas adsorption, we have demonstrated herein that

1. the Zeta isotherm can be extended to include gas adsorption. There are special values of ζ_m, and for both vapours and gases, these values can be chosen by minimizing the difference between the measured and the calculated isotherms. The calculated error, $\Delta(\zeta_m)$, is less than 2% for each of 10 different isotherms considered herein.

2. Since ζ_m is finite, there are no singularities in the Zeta isotherms for vapours or gases. Once ζ_m has been determined from a measured isotherm for x^V less than unity, the Zeta isotherm can be applied for values of x^V greater than unity. For toluene adsorbing on Cu, the adsorbate structure is shown in Fig. 3. For x^V less than $(\alpha^{SV})^{-1}$, a large number of cluster-types are predicted to be present, but when x^V is greater than $(\alpha^{SV})^{-1}$, the clusters with ζ_m molecules are predicted to grow into an adsorbed film with each adsorption site occupied by clusters with ζ_m molecules. The results for other vapours are similar.

3. When x^V is increased above unity, it is thermodynamically possible for the system to form droplets heterogeneously. Our assumption is that at least some supercooling is required before droplets would form heterogeneously. Thus, we would expect the heterogeneous droplets to form on the already formed adsorbed film.

4. The role of ζ_m was illustrated using CO adsorbing on Ni(1 00) at different temperatures. When the proposed method for determining ζ_m was applied, it was found to be unity. This indicates no clustering occurs during CO adsorption. Also, when this value of ζ_m was used in the expression for the full Zeta isotherm, eqn (28), the Zeta isotherm reduced to the Langmuir isotherm for molecular gas adsorption.

5. The other gas adsorption systems considered were hydrogen adsorption on Cu, on Ni(111) and on Si(111). When ζ_m was determined from the isotherms shown in Figs. 5 to 7, it was found to have a value of two for each of the systems. This means the adsorbate consisted of both adsorbed atoms and adsorbed molecules. When this value of ζ_m was used in the expressions for n^{SH} or Θ^{SH}, the recalculated isotherms deviated from the measured isotherms by 1% or less in each case, Table 4.

   The mole fractions of each were predicted. The predictions indicate that above a certain pressure for each system, the number of adsorbed molecules exceeds the number of adsorbed atoms. This suggests that hydrogen adsorbates are very different than what had been assumed—only adsorbed atoms—and suggests strategies for using hydrogen catalyst could be developed.

   The Si(111) data reported by Raschke and Hofer[14] is not correlated at all by the DLI, as indicated in Fig. 8. This suggests that including the molecules in the adsorbate is essential for some systems.

6 Summary and Conclusion

The Zeta adsorption isotherm has been extended so it may be applied to describe the adsorption of molecularly adsorbed gases, of dissociatively adsorbed gases, and of vapours. This isotherm assumes, as a hypothesis to be tested, that the adsorbates of these fluids consist of clusters of ζ particles, where ζ can be $1, 2\cdots$ up to a maximum of ζ_m. The Zeta isotherm expression depends on ζ_m and on up to three isotherm constants. One constant is the number of adsorption sites, M, and the others arise from partition function. Once these isotherm constants have been determined, they may now be used with the Zeta isotherm theory to predict cluster distributions, eqn (4). Cluster-distribution predictions are a unique feature of Zeta isotherm. They are not available from other isotherms.

We illustrate the procedure using CO adsorbing on Ni(111). From the measured adsorption isotherm, the value of ζ_m is found to be unity. The cluster distribution and the Zeta adsorption isotherm then coincide, meaning there are no clusters in the adsorbate. There are then only two isotherm constants to be determined from the isotherm measurements, the same number as the classical Langmuir isotherm. These constant arise from M and the partition function for one particle, q_1.

When the same procedure was applied to H_2 adsorption on three different substrates, ζ_m was found to be two from the isotherm measurements for each substrate. There were then three isotherm constants to be determined from the isotherm measurements. The additional isotherm constant (compared to molecular gas adsorption) arises from the fact that the partition function for the adsorbed atoms is different than the partition function for the adsorbed molecules. Once the values of these constants were determined from the isotherm measurements, the cluster distribution could be calculated. This distribution indicates that each of three adsorbates consists of both atoms and molecules. The cluster distribution expression was used to predict mole fractions of *both* the adsorbed atoms and the adsorbed molecules throughout the pressure range of the measured isotherms.

The expression for the cluster distribution for hydrogen adsorption receives experimental support from the data reported by Raschke and Hofer[14]. Firstly, the Zeta adsorption closely correlates their data. The error estimate, $\Delta(\zeta_m)$, is less than 1%. Secondly, using the values of isotherm constants determined from the adsorption measurements, the cluster distribution expression was used to predict the mole fractions of the adsorbed atoms and molecules, see Fig. 7. At the highest pressure considered, the mole fraction of the molecules was predicted to be twice that of the adsorbed atoms. When the dissociative-Langmuir isotherm is applied, it is assumed there are no hydrogen molecules in the adsorbate, but an attempt to correlate the hydrogen adsorption data reported by Raschke and Hofer[14] with the dissociative-Langmuir isotherm showed no correlation, see Fig. 8.

The same procedure was applied to determine the value ζ_m for toluene, heptane and octane vapours adsorbing on Cu. Using only the data for $x^V < 1$, ζ_m values of 115, 130 and 60 were inferred respectively, along with values of three isotherm constants in each case. The reason there are only three isotherm constants rather than one for each type cluster is that the partition function for the clusters was assumed to be of the form given in eqn (7) that contains two isotherm constants, c and q_1 The third isotherm constant depends on the number number of adsorption sites, M. Using the values isotherm constants in the expression for the cluster distribution, cluster distributions for toluene shown in Figs. 2 and 3 were calculated. As seen there, the cluster distribution predicts the formation of an adsorbed film at vapour phase pressure greater than P_s. Similar predictions are found for the other vapours.

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