Interactions between adsorbed molecules

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Abstract

We review recent work aimed at measuring and understanding interactions between adsorbed atoms and molecules separated by a few surface unit cells. At these distances, poorly understood phenomena associated with substrate mediation play a major role in determining both the sign and the magnitude of the lateral interactions. Our limited fundamental understanding of such interactions leads to limited predictive power in a broad range of important surface kinetic and thermodynamic phenomena, ranging from kinetic compensation to ensemble effects in catalytic reactions. © 1998 Elsevier Science B.V.

1. Introduction

The ubiquitous relevance of intermolecular potentials to gaseous and condensed phase chemistry and physics has provided an enduring research focus for many decades [1,2]. Our understanding of the potential energy surfaces governing interactions between adsorbed atoms and molecules, however, remains rudimentary at best [3–5]. A primary goal of our research program over the past decade has been to probe adsorbate lateral interactions using simple, coverage-dependent kinetic and thermodynamic measurements and to start to establish a rigorous framework within which the interactions between adsorbed particles can be understood. Our interest has focused predominantly in the 'intermediate range', where particles are separated by a few lattice sites and where the magnitude of the interparticle interaction energy is comparable to $k_B T$. While very weak compared to typical chemical bonds, these interactions nonetheless play an important role in all steps of a surface chemical process:

· The equilibrium desorption rate is proportional to the activity: $R_d \propto \lambda(\theta, T) = \exp\{\mu(\theta, T)/k_B T\}$ [5], where $\mu(\theta, T)$ is the coverage (θ)- and temperature (T)-dependent chemical potential. The interesting and sometimes unusual coverage dependence of the chemical potential can lead to important coverage-dependent phenomena in the adsorption and desorption steps such as kinetic compensation, phase separation, and enhanced or inhibited adsorption in coadsorption systems. While the nominal desorption temperature is related primarily to the adsorbate-surface bond energy, the equally important coverage dependence of the desorption rate is related to weaker lateral interactions upon which we will focus.

· Activation energies for diffusion are typically comparable to $k_B T$, so lateral interactions in the short and intermediate range will seri-

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ously modify microscopic diffusion rates and mechanisms [6]. Moreover, in the absence of correlated adsorbate motion, the ratio of the Fick's law diffusion constant to the tracer diffusion constant is given by the derivative $d[\ln\{\mu(\theta,T)/k_BT\}]/d\theta$. Techniques often measure the more macroscopic Fick's law diffusion constant, but the underlying goal is to probe microscopic diffusion mechanisms that are more closely related to the tracer diffusion constant. A better understanding of lateral interactions on a scale of k_BT is required to help develop a much-needed microscopic understanding of adsorbate diffusion.

· Lateral interactions play a key role in determining adsorbate local distribution functions. In turn, these distribution functions govern ensemble phenomena in catalytic reactions and film growth, steric factors in surface reactions, and the coverage dependence of recombinative desorption. These factors are particularly important in coadsorption systems which, viewed broadly, encompass catalytic poisoning, promotion, and selectivity enhancement. The long-range focus of our work will move toward coadsorption systems for this reason.

While some of these processes are understood at a phenomenological level in terms of lateral interactions between adsorbed particles, a fundamental understanding of the various factors that determine these interactions is certainly not available. The interactions between adsorbed particles provide a particularly interesting and challenging problem due to the role of 'substrate mediation' wherein a two-body potential between adsorbed particles is modified by the presence of a third body—the surface itself. There is at present little predictive power for how a particular substrate will mediate the interactions between two adsorbed particles. Similar systems can and do exhibit markedly dissimilar interactions.

In the following sections, we examine this problem in several contexts. We first discuss how coverage-dependent measurements relate to lateral interaction potentials. Numerous reviews

of such phenomena have appeared in the past [7–9], and many of the paradigmatic models have already entered textbooks [10–12]. Here we review recent work from our own laboratory. The emphasis is on nondissociative systems, since simple interactions can be probed adequately with these. We then distinguish the phenomenology of the processes governed by lateral interactions from the poorly understood quantitative aspects of the lateral interaction problem. Finally, we discuss some emerging trends in the area, both experimental and theoretical.

2. Coverage-dependent adsorption phenomena

This section presents a simple model for relating fundamental interactions between molecules adsorbed on a surface and adsorption/desorption phenomena. It is at first surprising that it is possible to treat these two on equal footing. 'Adsorption' normally refers to adsorption isotherms or isobars, i.e., the equilibrium density of adsorbed particles as a function of applied pressure or temperature. Desorption refers to the rate at which molecules leave the surface at a given temperature and pressure and is normally measured under nonequilibrium conditions. We overcome this difficulty by making a quasi-equilibrium assumption which allows treatment of kinetic data using primarily statistical thermodynamics. We emphasize that our approach, while approximate, is logically consistent and avoids application of empirical paradigms such as coverage-dependent Arrhenius parameters. This is the simplest possible treatment which also captures much of the important conceptual chemical physics without delving into nonequilibrium thermodynamics or numerical simulations.

2.1. Equilibrium adsorption

Our goal is to evaluate a general expression for the fractional coverage of interacting ad-

sorbed molecules as a function of applied pressure and temperature. We consider the gas with which the adsorbed phase is in equilibrium to be ideal. At equilibrium both the temperature and chemical potential or activity of the 2D and 3D systems must be equal. The activity $\lambda_{3D}(P,T)$ of the ideal gas phase at equilibrium temperature T and pressure P is given by [13]:

$$\lambda_{3D}(P,T) = \exp\left[\mu_{3D}(P,T)/k_B T\right]$$
$$= P\Lambda^3/(q_{int} k_B T) \qquad (1)$$

where $\mu_{3D}(P,T)$ is the ideal gas chemical potential, $\Lambda = h/(2\pi M k_B T)^{1/2}$ is the thermal wavelength, M is the mass of the atom or molecule, and q_{int} is the partition function for the free atom's or molecule's internal degrees of freedom. For a single component system at equilibrium, $\mu(P,T)$ is equal to the Gibbs free energy per particle, including all interactions. If we select our zero of energy so that the chemical potential is zero for molecules at rest in vacuum, Eq. (1) can then be rewritten in the more common form:

$$P = \left[q_{int} k_B T/\Lambda^3\right]\exp\left[\mu(\theta,T)/k_B T\right]$$
$$= \left[q_{int} k_B T/\Lambda^3\right]\exp\left[\Delta S(\theta,T)/R\right]$$
$$\times \exp\left[\Delta H(\theta,T)/RT\right], \qquad (2)$$

where ΔS and ΔH are the molar entropy and enthalpy changes of adsorption, and R is the gas constant. Plots of the logarithm of the equilibrium pressure as a function of $(1/T)$ at constant coverage can then be used to derive the isosteric heat of adsorption (and sometimes also the entropy of adsorption) as a function of coverage [14]. We generally use the first part of Eq. (2) without resorting to this Clausius–Clapyron analysis. Since the chemical potential is a function of temperature and particle density, this relationship can be taken to relate the adsorbed particle density to the temperature and applied pressure.

One further limitation of this approach deserves special attention. Specifically, Eq. (2)

pertains to a single-component system, but in reality we have at least a two-component system since both an adsorbent and one or more adsorbates are present. This simplified approach treats the substrate as a static entity whose thermodynamic properties do not change upon adsorption. While this approximation is inherent, e.g., in the lattice gas approach discussed in Section 2.3, it clearly has some limitations. The substrate does in fact respond to adsorption, either with modest local relaxations or more serious reconstructions. These relaxations modify the single-particle adsorption energy and entropy and also can impact lateral interactions between adsorbed particles. At a minimum, we should consider the energetic parameters derived from this model to include, in an approximate way, the interactions between adsorbed particles and between local modifications to the substrate. We return to this issue in Section 3.4.3.

2.2. Unimolecular desorption

It is possible to model the desorption rate with similar ideas. However, an important approximation is necessary since the desorption rate may include nonequilibrium effects. The assumption is commonly made that a quasiequilibrium condition is maintained at the surface during the kinetic measurement [15,16]. This is often expected to be valid since the dynamical events occurring on the surface that establish equilibrium, particle and energy diffusion, occur on a time scale much faster than the average time required for a molecule to desorb from the surface. In this circumstance, a desorbing molecule has no memory of how it was initially adsorbed onto the surface, and the desorption rate in a nonequilibrium steady-state condition is the same as that at equilibrium. These statements are generally valid for simple adsorption/desorption systems that are far from phase boundaries and where the adsorption step is nonactivated. If either of these does not hold, then the desorption step is more complicated and our treatment is not valid.

Consider again the equilibrium situation discussed above [17,18], an ideal 3D gas phase in thermal and diffusive equilibrium with an adsorbed phase of N molecules on a surface of area A with N_o adsorption sites, so that $\theta = N/N_o$. For simple unimolecular systems the desorption rate can be written

$$r_d(\theta,T) = k_d(\theta,T)\theta \qquad (3)$$

i.e., the desorption process follows a pseudo-first-order rate equation. Note that Eq. (3) is experimentally important, since it implies that the unimolecular desorption process can be linearized if small coverage perturbations are applied. This statement has been tested for several simple systems that are far from phase boundaries and where adsorption is not activated, and in all cases it has been shown to be valid [17–21]. From the kinetic theory of gases [22], the equilibrium adsorption rate can be written $r_a = S(\theta,T)PA/(2\pi m k_B T)^{1/2} = S(\theta,T)PA\Lambda/h$, where $S(\theta,T)$ is the equilibrium thermally-averaged sticking coefficient. Again express the pressure in terms of the chemical potential. At equilibrium this chemical potential is equal to that of the adsorbed phase. The equilibrium adsorption rate is by definition equal to the equilibrium desorption rate, which is assumed in the quasi-equilibrium model to be equal to the desorption rate measured under nonequilibrium conditions. In this way, the activity or chemical potential can be related to the pseudo-first-order rate constant $k_d(\theta,T)$:

$$r_d(\theta,T) = k_d(\theta,T)\theta$$
$$= \left[S(\theta,T) A q_{int} k_B T / \left(N_o h \Lambda^2 \right) \right]$$
$$\times \exp\left[\mu(\theta,T)/k_B T \right] \qquad (4)$$

Eq. (4) is remarkably similar to the result obtained from transition state theory (TST) [23]. TST is normally applied to systems having a saddle point in configuration space and thus the relevant energy and entropy are the activation energy and entropy pertaining to a single reaction center. In nonactivated adsorption systems, these become essentially a thermodynamic quantity, $\mu(\theta,T)$, which is the free energy needed to remove one molecule from N molecules, including all interactions. Thus, the quasiequilibrium model includes energetic, intramolecular entropic, and configurational entropic contributions through the chemical potential. The last of these contributions is normally not specifically treated in TST.

In the quasiequilibrium model, the dynamics of desorption are entirely included in the thermally averaged sticking coefficient in Eq. (4). Aside from this, the information contained in desorption experiments is seen to be very similar to equilibrium adsorption, assuming that the quasiequilibrium approximation is valid. If we know or can calculate the chemical potential and the sticking coefficient as a function of coverage and temperature, we can predict both the coverage and the desorption rate. Note that $S(\theta,T)$ is the average sticking coefficient at equilibrium. This is rarely measured, since it would require ensuring that the temperature of the gas phase is identical to that of the surface, and also that the departure from equilibrium be very small. Generally, $S(\theta,T)$ is a smooth function, and it does not seriously inhibit our ability to understand adsorption and desorption phenomena starting from molecular interactions.

The above discussion seems to imply that adsorption is a 'better' measurement for estimating molecular interactions than desorption. It does not require the quasiequilibrium assumption, and it also does not require knowledge of a sticking coefficient. In actual fact, adsorption is not really better since adsorption isotherms or isobars are rarely measured at a true equilibrium. The temperature of the 3D gas phase is normally not the same as that of the surface. These nonequilibrium problems can be treated approximately using the same sort of quasiequilibrium assumption used to treat desorption, and some dynamical information in the form of sticking coefficients must also be known [8].

2.3. Models for the chemical potential

Eqs. (2) and (4) indicate that we need to calculate $\mu(\theta,T)$ starting from fundamental interactions on the surface to model adsorption and desorption data. This is clearly a difficult task if an exact treatment is desired, and we will rely on models which attempt to capture the important interactions [13,22,24]. We really should only hope to determine some of the general features of the lateral interaction potential (e.g., the position of the repulsive barrier, the existence and magnitude of an attractive well, etc.) rather than its precise spatial character. The first step in this process is to choose a model which most closely fit the system being studied. For example, a physisorbed layer might be modeled as a 2D imperfect gas. Starting from the full potential energy surface between molecules, we could then evaluate the chemical potential using classical statistical mechanics. Alternatively, for localized bonding characteristic of chemisorption systems, it is common to apply the lattice gas approximation wherein the potential is discretized, and we use neighbor interaction energies as free parameters. The validity of these models can clearly limit the precision of our approach.

A better method for describing the thermodynamic properties of the adsorbed phase at low density is in terms of a virial series expansion [13,22,24,25]. The thermodynamic virial coefficients then form a useful bridge between intermolecular forces in a statistical mechanics formulation and the desorption rate and adsorption isotherms through Eqs. (2) and (4). Its primary limitation is that it is valid only at low coverage. The virial expansion for the adsorbed phase chemical potential of a single-component system is [13,24]:

$$\mu(\theta,T)/k_B T = -E_d + \ln(\theta N_o/Q_1)$$
$$+ 2B_2(T)\theta + (3/2)B_3(T)\theta^2$$
$$+ \ldots \qquad (5)$$

E_d is the isolated molecule adsorption energy, and Q_1 is the partition function for one molecule interacting with N_o adsorption sites on the surface. The virial coefficients B_j can be written in terms of the partition functions Q_j for j particles interacting upon the potential energy surface under consideration, e.g., $B_2(T) = N_o(1/2 - Q_2/Q_1^2)$ [13,22,24,25]. The underlying physics is determined by the potential energy surfaces used to calculate the j-particle partition functions.

A fairly general technique for calculating the properties of an interacting lattice gas is based upon so-called transfer matrices [24,26–28]. These were originally introduced in the 1940s as a method for solving the 1D and 2D Ising models. Their use has expanded dramatically in the last 10–20 years because even though they are analytically cumbersome, they are readily implemented on computers [29–38]. Essentially, the grand partition function is written in terms of a product of matrices which couple finite strings of sites. It can be shown that the largest eigenvalue of this matrix is the grand partition function from which the coverage as a function of activity can easily be calculated. The limitation of the technique is that the matrix is of dimension 2^n where n is the number of atoms in the string. This limitation, which leads to finite size effects, can be overcome using accurate finite-sized scaling techniques [39–41]. This has allowed calculation, for example, of first- and second-order phase boundaries [31–36]. Also, there are two important simplifications which reduce the dimension of the transfer matrix substantially. The first is a symmetrization technique developed by Rikvold et al. [31] which block-diagonalizes the matrix, the largest block being $\sim 1/3$ the size of the full matrix. The second simplification is particularly relevant to molecules. For essentially all molecules, the nearest neighbor interaction energy w_1 is very large compared to $k_B T$; near neighbors can only be occupied under relatively high pressure. Since the ith interaction always enters as $\exp[-w_i/k_B T]$, the fact that $w_1 \gg k_B T$ implies that it is a very good approximation to set $w_1 = \infty$. This fact can be built into the transfer

matrix, leading to further substantial reduction in dimension.

3. Phenomenological vs. quantitative aspects of lateral interactions

Our goal in this section is to describe and differentiate the phenomenological and quantitative aspects of the intermediate-range lateral interaction problem. This will serve to delineate accurately the current status of the field.

3.1. Microscopic adsorbate islands and non-monotonic lateral interactions

CO adsorption onto Pt (111) is perhaps the best-studied molecular adsorption system. One might thus hope to have achieved a relatively sound understanding of lateral interactions in this system. Despite this, there have been at least three modeling studies that assumed simple but demonstrably wrong lateral potential energy surfaces [42–45]. An important step in clarifying the lateral potential in this system was the observation of low-coverage (4×4) and (8×8) diffraction patterns [46], with proposed real-space structures given in Fig. 1. While not proven, these structures are quite probably correct, since they have the correct coverage–periodicity relationship while occupying only atop sites. These structures are made up of microscopic islands, and one is tempted to seek an exotic interaction potential to explain their existence. Actually, at a phenomenological level, the interactions are quite simple. Aside from the dominantly repulsive near-neighbor interaction, these structures suggest a tendency to avoid third-neighbor site occupation. We have thus proposed that the interaction at third neighbor sites is relatively more repulsive than that at second neighbor sites [48]. Neither interaction can be attractive and the magnitude of the repulsive interactions beyond the first neighbors must not be terribly large. These microscopic island
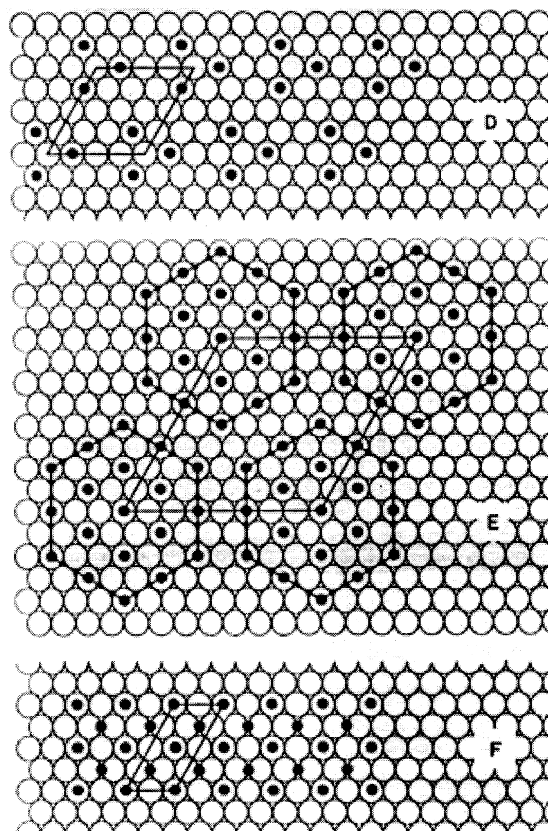

Fig. 1. Proposed real-space superlattice structures for CO/Pt (111), from Ref. [47]. Top: (4×4); middle: (8×8); bottom: $c(4 \times 2)$.

structures can always occur when uniformly repulsive interactions do not decay monotonically as a function of neighbor distance. To substantiate this model, we analyzed existing, high quality adsorption isotherms (see Fig. 2). Approximating the system as a lattice gas and calculating thermodynamic properties using a transfer matrix technique, we found that the third-shell interaction was indeed more repulsive than that of the second. We also obtained rough estimates for the magnitudes of the interactions, and those in the second, third, and probably also fourth neighbor shells were of order $k_B T$. Precise quantification of this result was not possible, however, since the interactions were found to be statistically coupled. We will return to this uniqueness issue shortly. The
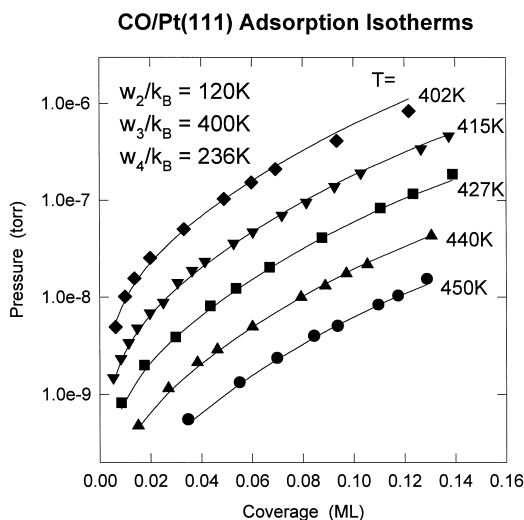
Fig. 2. Fits to adsorption isotherms for CO/Pt (111) from Ref. [49]. Curves applied the quasi-equilibrium model and used the transfer matrix technique to evaluate the chemical potential (from Ref. [48]).

latest attempt to assess the lateral interactions in this system comes from a massive total energy calculation of several CO molecules adsorbed onto a Pt (111) cluster [50]. The results suggest that our analysis was right for the wrong reason (or possibly wrong for the right reason). If broken into pair interactions, the calculation confirmed our nonmonotonic energetic ordering. However, this result was found to derive significantly from nonpairwise additive interactions—the 'bare' pair interactions do not follow this trend. The calculation is not without its own limitations, and it is certainly possible that this system will provide more surprises in the future.

3.2. Lateral interactions and kinetic compensation

Kinetic compensation (KC) is observed, though rarely understood, in a variety of condensed phase kinetic processes [15,51–53]. KC refers to the observation in some systems that the Arrhenius activation energy and preexponential factor exhibit very similar functional dependencies on some experimental parameter.

In desorption kinetics, this parameter is the surface coverage. At first sight, it is not obvious how this kinetic phenomenon could have a statistical thermodynamic origin, but we have shown that it can [18,54]. This is most easily seen by noting that, when KC is observed, the desorption rate constant is roughly coverage-independent. While this is often taken to imply weak lateral interactions, in reality such an observation implies balance between repulsive and attractive portions of the interaction potential. This is formally analogous to the Boyle temperature of an imperfect gas, as discussed further below.

An example is offered by CO desorption from Cu (011), the results and analysis of which are given above [55]. The shallow slope of the desorption isotherms for this system at lower temperatures is the signature of kinetic compensation (see Fig. 3). The analysis, based upon a quasi-equilibrium model and employing a transfer matrix technique to evaluate thermodynamic quantities [38,56], requires that there be an attractive well in the second neighbor shell of magnitude ~ 100K. Again, the parameters in this fit are statistically coupled. Finally, the most interesting aspect of these results comes from comparing them to similar results for CO
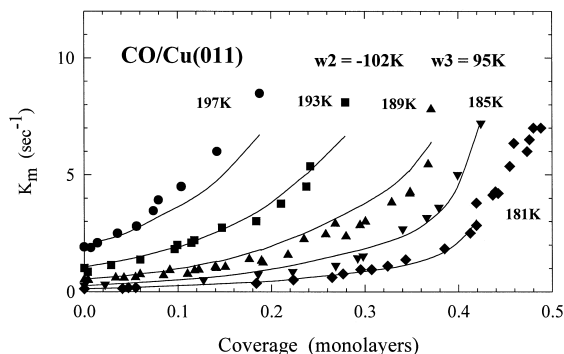

Fig. 3. Desorption isotherms for CO/Cu (011). Data are from Ref. [23]; fits are from Ref. [25] and employ a transfer matrix technique coupled to the quasi-equilibrium assumption. The shallow slope in the lower temperature isotherms is the signature of kinetic compensation.

desorption from Cu (001) and Cu (111). The magnitude of the attractive well is systematically smaller in this order, and actually vanishes for Cu (111). Once again, although the final parameters are statistically coupled, a useful trend can be distinguished—the closer packed surface mediates interactions in a way that produces relatively larger repulsion.

3.3. Cooperative effects in coadsorption systems

Coadsorption systems can exhibit cooperative effects that are not accessible in single-adsorbate systems. Obvious examples that clearly have a basis in lateral interactions are competitive and enhanced adsorption [57]. In the former, adsorption of one species reduces the equilibrium coverage of another by 'competing' for space on a surface, while in the latter the opposite would be observed. We have recently extended our efforts to coadsorption systems to try to understand, at least phenomenologically, the relationship between lateral interactions and such cooperative effects [54].

To isolate the interactions as best as possible, we have measured the low-coverage desorption rate of NO or NH_3 from Ni (111) and Pt (111) as a function of CO precoverage. In one instance, $NO + CO/Pt$ (111), we observe KC (see Fig. 4). We have extended the transfer matrix technique to handle coadsorption systems and find, in this case, that an attractive component to the CO–NO interaction is required to fit the data. In the other systems, the interactions are generally repulsive and we thus do not observe KC. Again, while these semi-quantitative conclusions are well-grounded, the lattice interactions are statistically coupled so that precise energies cannot be deduced. Finally, while our results have recently been compared favorably to the results of first principles computations for some of these systems (D.R. Jennison, private communication, 1996), it is still fair to say that our qualitative understanding of even the trends in lateral interactions in these simple coadsorption systems remains elusive at best.
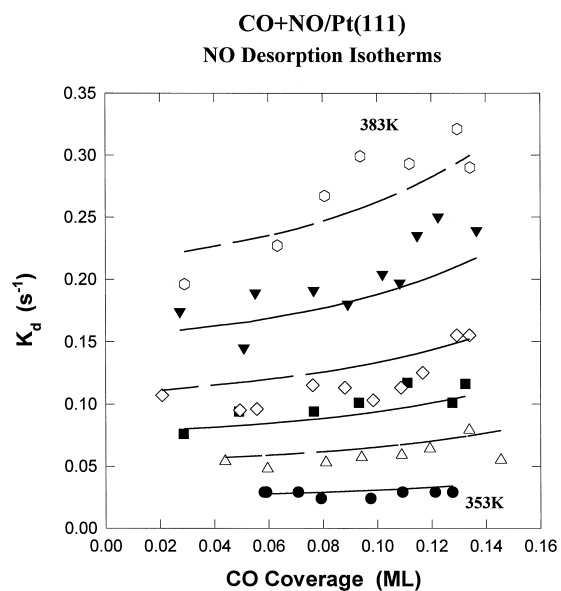

Fig. 4. Desorption isotherms for the low-coverage NO desorption rate constant as a function of CO pre-coverage for the system $CO + NO/Pt$ (111). Lines result from a fit that employed a quasi-equilibrium assumption and extended the transfer matrix technique to two-component systems.

3.4. What has been learned?

The preceding pages have provided a diverse and seemingly disconnected set of results—a fraction of those obtained by our group over the past 7–8 years. What unifying themes, if any, can be deduced from these experiments and the analysis? We discuss three themes: one technical, one phenomenological, and one pointing toward a more quantitative understanding of substrate-mediated lateral interactions. These themes form the basis for the proposed research in the following sections.

3.4.1. Statistical coupling of parameters

Beyond the obvious approximation of treating an adsorbed layer like an interacting lattice gas, the single largest technical limitation in analyzing essentially all these experiments is the statistical coupling between lattice parameters. The source for this coupling can be seen easily in the low-density limit by writing an expression for the equilibrium desorption rate constant

k_d in terms of a virial expansion truncated at the second virial coefficient, $B_2(T)$ [18]:

$$\ln(k_d) = \ln(A) - \frac{E_d}{k_B T} + 2 B_2(T)\theta \qquad (6)$$

where A is a prefactor that depends nonexponentially on temperature, E_d is the binding energy of a single molecule to the surface, and θ is the coverage. For example, considering only first and second nearest neighbors on a square lattice, $B_2(T)$ is given by [18]

$$B_2(T) = 9 - 4 x_1 - 4 x_2$$

$$= 9 - 4 e^{-\frac{w_1}{k_B T}} - 4 e^{-\frac{w_2}{k_B T}} \qquad (7)$$

In this limit, w_1 and w_2 are seen to be perfectly correlated—they can be interchanged and the value of B_2 is unchanged. This perfect correlation is removed at finite coverage, e.g., by modeling the phase diagram, but our results show that it remains a serious problem nonetheless.

The primary conclusion to be drawn from this is that, while the phenomenological aspects of the lateral interaction problem can be fairly well-studied with existing techniques, the quantitative accuracy with which interaction potentials can be deduced, even within the gross context of lattice gas theory, is minimal at best. The thermodynamic measurements used so far to probe lateral interactions are simply too macroscopically averaged and too limited in coverage/temperature dynamic range for robust, quantitative results to be available. This conclusion points to the need for a new experimental approach that combines the strengths of the thermodynamic data discussed above with more microscopic information.

3.4.2. Coverage-dependent desorption phenomenology

While the virial expansion is limited in validity to the zero coverage limit, we have shown that it nonetheless provides a good conceptual method for categorizing apparently disparate desorption phenomena. In analogy with the Boyle temperature for an imperfect gas, we can define a compensation temperature T_C such that $B_2(T_C) = 0$. The above expression for B_2 shows the interplay between repulsive (e.g., $w_1 > 0$) and attractive ($w_2 < 0$) interactions that can lead to this condition. With such interactions, at low temperature, B_2 is less than zero but increases monotonically with temperature. At high temperature, B_2 is greater than zero and is roughly constant. There are then three paradigmatic behaviors that may be observed, depending on the relative values of T_C and T_D, the nominal desorption temperature [18].

(1) When $T_D \gg T_C$, the activation energy is nearly independent of coverage, but the prefactor depends approximately exponentially on coverage. We have observed this behavior for adsorbates with strongly repulsive lateral interactions, e.g., NH_3 [5,20].

(2) When $T_D \sim T_C$, the system exhibits kinetic compensation and a weak coverage-dependence in the desorption rate constant ensues [18,54]. A significant fraction of CO/transition metal systems falls into this class.

(3) When $T_D \ll T_C$, the system will condense into a two-phase adsorbate and will exhibit zero or fractional order desorption kinetics, at least at high coverage. We have characterized this regime extensively in physisorption systems [58–60].

We have deduced a similar phenomenological relationship between KC and the enhanced vs. competitive adsorption issue in coadsorption systems [54]. In coadsorption, $T_D \ll T_C$ implies enhanced adsorption, while $T_D \gg T_C$ implies competitive adsorption.

A key feature of this analysis is the limited dynamic range available from measurements of adsorption or desorption isotherms or, in most cases, of adsorbate phase diagrams. The problem is that equilibration times are determined by the desorption rate. This rate is activated and thus changes rapidly as a function of temperature. A narrow temperature range, where the

rate constant is typically within a few orders of magnitude of 1 s^{-1}, is all that is experimentally accessible. One measures with best sensitivity that part of the lateral potential of magnitude $k_B T_D$ and the rest of the potential is much more poorly determined. With a much larger dynamic range in temperature, one would observe, for example, a system that exhibits KC slowly to transform to one that exhibits an exponentially dependent desorption prefactor as the temperature is raised. This observation points to the need for a new experimental approach that offers a much larger dynamic range in temperature than existing probes.

3.4.3. Tensile stress and substrate-mediated lateral interactions

The primary goal of this research has been to understand substrate-mediated interactions at a level where reasonable predictive power is possible. Given the limitations and approximations inherent in lattice gas theory combined with the statistical coupling of lattice interactions and limited dynamical range discussed above, terribly precise conclusions should not be expected at this time. However, we have studied about a dozen different systems, and a useful trend is apparent.

An apparently important source of substrate-mediated lateral interactions lies in the fact that most unreconstructed surfaces are under tensile stress [61–65]. Adsorbing a particle will alter the strain field in some way so as to reduce locally the tensile stress. When two adsorbates are located in the vicinity of one another, these strain fields overlap, leading to a substrate-mediated interaction. We have discussed qualitatively the impact of tensile stress upon the trends in lateral interactions [55]. For example, the trend observed for CO/Cu of relatively more repulsive interactions for closer-packed surfaces is naturally explained [55]. Also, the nonmonotonic lateral interactions observed on Pt (111) is at least consistent with the influence of tensile stress [48]. In the dozen or so systems we have studied, only a few have presented

evidence contrary to this stress hypothesis and often the results are consistent with it. This is not to say that electronically mediated interactions [3,4,66] can be excluded from consideration, and indeed we feel that they play a crucial albeit unpredictable role in the lateral interaction problem. The above observations about tensile stress are largely qualitative, and the overall interaction on metal surfaces might still be largely determined by electronic mediation. Moreover, recent advances in computing lateral interactions from nearly first principles, using methods that freeze the substrate so that the tensile stress component is not included, come surprisingly close to matching semiquantitatively our experimentally derived interactions [50] (D.R. Jennison, private communication, 1996). This is true even in relatively complex multicomponent adsorption systems like CO + NO/Pt (111) and CO + NH$_3$/Pt (111). These results serve to indicate firstly, that much remains to be done to achieve a general understanding of lateral interactions, and also that experiment and first-principles theory can, for the first time, attack this problem in concert.

4. Conclusions

The conclusions from the previous section suggest application of a new probe to the lateral interaction problem that (i) provides better microscopic information than that available from thermodynamic data so that the uniqueness problem can be solved, (ii) can be applied over a larger range of temperature so that a broader energy range of interactions can be probed efficiently, and (iii) achieves high enough accuracy that both simple phenomenological and emerging first-principles calculations can be seriously tested. If we loosely relate a disordered adsorbate layer to a liquid or glass, an obvious starting point is to probe adsorbate distribution functions since these have been particularly useful in quantifying the structure of noncrystalline materials. The distribution function measures

the probability of finding a particle at a given position on the surface relative to one at the origin. This clearly is 'microscopic' and would decouple the statistical correlation between lattice parameters discussed above. Also, in principle, these should be measurable over a temperature range that is not limited by proximity to the nominal desorption temperature or phase boundary.

There are two methodologies for determining adsorbate distribution functions, those that operate in real space and those that operate in momentum space. In the former, an atomic resolution snapshot of the surface would be taken to map the distribution of adsorbed molecules. Implementation of this approach using the scanning tunneling microscope has recently been proposed [67,68]. The dynamic range in temperature would be limited, since one would need to operate at high enough temperature that surface diffusion is fast enough that equilibrium can be achieved on a reasonable time scale, yet at low enough temperature that diffusion is slow on the time scale required to acquire an image.

The methodology that operates in momentum space is based upon the classic techniques for determining the distribution functions in gaseous and condensed phases [69,70]. These measure the flux of diffuse quasi-elastically scattered particles—typically neutrons or X-rays—as a function of scattering momentum. In the single, independent scattering limit, the scattering rate in reflection from a surface at parallel momentum transfer $\vec{q}$ and frequency ω is related to the dynamical structure factor. This quantity is just the space–time Fourier transform of the adsorbed particle correlation function, which is related to the desired information.

To what extent can these general concepts be applied to the adsorption problem? To a degree this has already been accomplished, though much remains to be done. Measurements using high-resolution helium scattering have probed surface diffusion in this way [71–73]. In principle, similar experiments will also provide spatial distribution functions, though this has not yet been accomplished.

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