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Pairing and clustering of hydrogen on Si(100)2×1: Monte Carlo studies

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Pairing and clustering of hydrogen on Si(100)2×1: Monte Carlo studies

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Abstract

We consider a generalization of the doubly-occupied dimer model we proposed recently to explain the near-first-order desorption kinetics of H_2 from Si(100)2×1, incorporating effective nearest-neighbor interactions between paired hydrogen atoms on adjacent dimers. We have performed Monte Carlo simulations of the generalized model, and compare the pairing and cluster-size distributions with those observed recently by scanning tunneling microscopy (STM). The agreement is reasonable but the cluster size distributions differ in shape, which we suggest is due to the nonthermal nature of the distributions observed by STM and/or inadequacies in the use of nearest-neighbor interactions to represent the physics of clustering. Implications of the results for the underlying physical interactions responsible for ordering of hydrogen on Si(100) and for the desorption kinetics are discussed.

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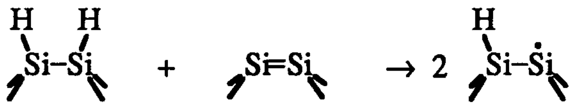
I. INTRODUCTION

Surface hydrogen plays a critical role in the growth of silicon and Si_xGe_{1-x} alloy films by chemical vapor deposition and atomic layer epitaxy and also comprises a prototypic semiconductor adsorbate. The discovery by Sinniah *et al.* that recombinative hydrogen desorption follows first-order kinetics on Si(100)2×1,[1] in contrast to the second-order behavior seen on metal surfaces, has prompted a great deal of recent work on the kinetics and dynamics of hydrogen desorption, including verification by George and co-workers.[2] The original proposal by Sinniah *et al.* that the first-order kinetics results from the rate-limiting excitation of hydrogen atoms to a band-like delocalized state[1] was contradicted by the near-second-order kinetics observed for desorption of hydrogen from Si(111),[2-4] by measurements of the diffusion kinetics of hydrogen on Si(111) which suggest conventional hopping,[5] and by dynamical measurements showing that desorbing H_2 is rotationally cold and vibrationally hot, implying a highly symmetric transition state.[6] Wise *et al.*[2] suggested that the desorption kinetics are first order due instead to pairing of hydrogen on the dimerized surface atoms, and Boland[7] and we[8] independently proposed that preferential pairing of H atoms is a consequence of the π bond[9,10] on "unoccupied" dimers. Boland obtained direct evidence for preferential pairing by scanning tunneling microscopy (STM) and estimated a π bond strength of ≈18 kcal/mol from tunneling spectra above un- and singly-occupied dimers.[7] We reviewed existing evidence for π bonding and preferential pairing and proposed a doubly-occupied dimer model to quantitatively describe the desorption kinetics.[8] The driving force for pairing, to which we will refer as ε, is defined as the energy required to un-pair the hydrogen atoms on a single surface dimer, that is, to move H from a doubly-occupied to an unoccupied dimer, creating two singly-occupied dimers, as indicated in Eq. (1):



(1)

It is easily seen that ε is also equal to the difference in Si-H bond strengths between hydrogen on doubly-occupied versus singly-occupied dimers. We identified ε with the π bond strength[8] by analogy to π bonds in molecules,[11] and estimated $\varepsilon \approx 7.5$ kcal/mol by comparing model predictions to evidence of a slight departure from first-order kinetics from temperature-programmed desorption (TPD) data. Höfer *et al.* demonstrated that the kinetics do indeed deviate from first-order at low coverage, and used our model to obtain a refined determination of 6±1 kcal/mol for ε.[12] Recent high-level *ab initio* calculations of Si-H bond strengths in a cluster analogue of Si(100)2×1 imply values of 2-5 kcal/mol for ε.[13,14] The chemistry of hydrogen on Ge(100)2×1 is very similar to that on Si(100)2×1, and we showed very recently that the desorption kinetics also exhibit near-first-order behavior and can be described quantitatively by the doubly-occupied dimer model with ε = 5±1 kcal/mol.[15]

A difficulty with the present state of understanding of the behavior of hydrogen on Si(100) is that Boland's STM images demonstrate not only preferential pairing of hydrogen atoms but also *clustering*, that is, that doubly-occupied dimers tend to occur in one-dimensional chains.[7] Such clustering demonstrates the existence of effective attractive interactions between the doubly-occupied dimers which are omitted from the original model[8] and are likely to perturb the desorption kinetics, thus necessitating a reassessment of the identification of the effective pairing energy inferred from desorption kinetics measurements with the surface π bond strength.[8,12] In the present paper we consider the effect of interactions between doubly-occupied dimers and the resulting pairing and clustering distributions by means of Monte Carlo simulations.

II. GENERALIZED MODEL AND THEORETICAL METHOD

We begin by illustrating how clustering can affect the desorption kinetics. In the original model[8] we postulated that hydrogen atoms pair preferentially due to the existence of a weak π bond on unoccupied dimers but that adsorption is otherwise random. We also assumed that desorbing H_2 originates from H atoms paired on a single dimer so that the desorption rate is proportional to the coverage of doubly-occupied dimers, and that surface diffusion of hydrogen is fast compared to desorption so that quasiequilibrium between doubly- and singly-occupied dimers persists throughout a desorption experiment. Because the driving force for pairing is finite, the kinetic order for desorption becomes greater than one at low coverage as entropy causes a rising fraction of the surface hydrogen to be unpaired.

Consider for the moment a model where essentially *all* the hydrogen is paired up (as would occur if ε is as large as 18 kcal/mol[7]), that clustering results from a nearest-neighbor attractive interaction between adjacent doubly-occupied dimers of magnitude w, and that recombinative desorption occurs between hydrogen atoms adsorbed on *adjacent* dimers, as suggested by Wu and Carter.[14] The adsorbate-ordering portion of this model is precisely a one-dimensional lattice gas model with nearest neighbor interactions whose solution has been described by Hill.[16] Defining Θ and α as the surface hydrogen coverage and the fraction of "bonds" between adjacent dimers where one of the dimers is (doubly) occupied and the other is unoccupied, the solution to the maximization condition for the partition function can be written as[16]

$$\frac{\alpha^2}{(\Theta - \alpha)(1 - \Theta - \alpha)} = y \qquad (2)$$

where

$$y \equiv \exp\left[-\frac{w}{k_B T}\right]. \qquad (3)$$

and k_B is Boltzmann's constant. Defining

$$\Theta_{22} = \Theta - \alpha, \tag{4}$$

i.e., the fraction of nearest-neighbor pairs comprising two doubly-occupied dimers, Eq. (2) can be solved to yield

$$\Theta_{22} = \Theta - \frac{2\Theta(1-\Theta)}{\left[1 + 4(1/y-1)\Theta(1-\Theta)\right]^{1/2} + 1}. \tag{5}$$

Eq. (5) is *identical* to Eq. (4) of Ref. 8 except that Θ_2 is replaced by Θ_{22}, x is replaced by y (i.e., ε is replaced by w), and the algebraic form has been altered to be better behaved numerically. The assumption that desorption occurs between hydrogen atoms on adjacent dimers implies that

$$\text{desorption rate} = -\frac{d\Theta}{dt} = k\,\Theta_{22}. \tag{6}$$

It is clear from the identical mathematical form of Eqs. (5) and (6) to the corresponding equations in the original model[8] that this "clustered-dimer" model is equally capable of accounting for the near-first-order desorption kinetics. However, in this latter model the assumptions are very different: the effective pairing energy of 6±1 kcal/mol would be identified with the clustering energy w rather than ε ($\approx$ the π bond strength), which was assumed to be large. This model has been presented for the sake of illustration--we do *not* believe that desorption takes place between hydrogen atoms on adjacent dimers (Eq. 6) but rather that the desorption rate is equal to $k\,\Theta_2$ as proposed originally;[8] this question is discussed in detail elsewhere.[17]

Having shown that clustering can explain the desorption kinetics under restrictive assumptions, it seems clear that clustering must be taken into account in the description of the desorption kinetics if the effective pairing energy inferred from desorption kinetics measurements is to be related to the underlying physical interactions. We now generalize the clustering model described above, allowing for the possibility of both preferential pairing and clustering via nearest-neighbor interactions between adjacent doubly-occupied dimers. In this "clustered doubly-occupied dimer" model the total energy is ε times the number of "unpairings" of adsorbed hydrogen atoms (= half the number of singly-occupied dimers) minus w times the number of "bonds" between adjacent doubly-occupied dimers. We define Θ_1, Θ_2, and α to be the coverage of hydrogen on singly- and doubly-occupied dimers and the fraction of "bonds" between adjacent dimers where one of the dimers is doubly occupied and the other is either un- or singly-occupied, respectively. Maximization of the partition function leads to the two equations[17]

$$xy = \frac{(\Theta - \Theta_1)\,\Theta_1^2\,(1 - \Theta + \Theta_1 - \alpha)}{(\Theta - \Theta_1 - \alpha)(1 - \Theta + \Theta_1)^2(1 - \Theta - \Theta_1)} \tag{7}$$

$$y = \frac{\alpha^2}{\left(\Theta - \Theta_1 - \alpha\right)\left(1 - \Theta + \Theta_1 - \alpha\right)} \tag{8}$$

where

$$x \equiv \exp\left[-\frac{\varepsilon}{k_{\mathrm{B}}T}\right]. \tag{9}$$

which must be solved numerically to obtain Θ_1 and α for specified values of Θ, ε, and w. Θ_2 and Θ_{22} are trivially obtained from

$$\Theta_2 = \Theta - \Theta_1 \tag{10}$$

$$\Theta_{22} = \Theta_2 - \alpha. \tag{11}$$

The quasi-analytic solution does not give the cluster-size distribution, however. In the present paper we report Monte Carlo simulations[18] of the clustered doubly-occupied dimer model and compare the resulting distributions with the STM image (Fig. 1(b) in Ref. 7(a)) obtained by Boland after annealing a partially-hydrogen-covered Si(100)2×1 surface to a temperature of 630 K.

We have performed Monte Carlo simulations of a lattice-gas model comprising a one-dimensional chain of dimers with periodic boundary conditions. Each dimer can be occupied by zero, one, or two adatoms; both the positions (dimer number, "left" or "right" side) of the adatoms and the state of each dimer (un-, singly-, or doubly-occupied) are monitored throughout the simulation. Particle moves are attempted sequentially, either "sideways" or to an adjacent dimer, and are accepted or rejected according to the standard criterion.[19] Because each attempted move can result in changes in both the number of unpairings and the number of "cluster bonds" of 0 or ±1 only, the change in energy corresponding to each possibility is evaluated at the beginning of each run, which enables most of the arithmetic necessary to generate the sequence of configurations to involve integers rather than real numbers.

III. RESULTS

Simulations of 40, 200, and 500 hydrogen atoms on a 1000-dimer (2000-site) lattice were performed to determine the effects of different values of ε and w on the pairing and cluster distributions, and additional simulations of 116 atoms on a 868-dimer lattice were performed specifically for comparison to the pairing and cluster distributions obtained by counting singly- and doubly-occupied dimers in Fig. 1(b) of Ref. 7(a). The number of passes (each adatom attempts a move once per pass) necessary for equilibration of the system and collection of adequate statistics varied between 8×10^5 and 1.1×10^7. Fewer configurations were needed at lower coverages and for smaller values of ε and w. For larger values of ε and w, particularly at higher coverages, clusters of considerable size form, decreasing the acceptance probability for particle moves (adatoms in the middle of a chain of doubly-occupied dimers cannot move) and necessitating longer runs for equilibration and adequate statistics.

Results for the fraction of hydrogen present on doubly-occupied dimers, Θ_2/Θ, obtained from simulations of a 1000-dimer lattice and from Eqs. (7)-(11) with various values of ε and w, are shown in Fig. 1. Corresponding results for the ratio of the number of "bonds" between doubly-occupied dimers to the number of doubly-occupied dimers, Θ_{22}/Θ_2, are shown in Fig. 2. In all cases the agreement between the quasi-analytic solutions and the Monte Carlo results is excellent.

Cluster-size histograms, plotted as the fraction of doubly-occupied dimers present in clusters of size N, as obtained from the 1000-dimer simulations, are shown in Fig. 3 for three coverages and five values of ε and w. The quantity plotted is the mean number of doubly-occupied-dimer clusters of size N multiplied by N divided by the total number of doubly-occupied dimers.

Fig. 1(b) from Ref. 7(a) is an STM image of a Si(100)2×1 surface with a small coverage of hydrogen which was annealed to 630 K and then cooled rapidly. If the cooling process is sufficiently rapid, one might hope that the distributions of singly- and doubly-occupied dimers approximate the equilibrium configurations at 630 K. To test the validity of this idea and to obtain at least rough estimates of the actual magnitudes of ε and w on Si(100), we have compared the distributions obtained from Boland's STM experiment[7] with Monte Carlo simulations of our model. We count 18 singly-occupied dimers, 48 doubly-occupied dimers, and 29 cluster bonds on a lattice comprising $\approx$ 868 dimers in the STM image, or $\Theta = 0.067$, $\Theta_2/\Theta = 0.85$, and $\Theta_{22}/\Theta_2 = 0.50$. A comparison of the predicted cluster-size histograms of the generalized model with nearest-neighbor clustering interactions with the distributions extracted from the STM data is shown in Fig. 4. The values of Θ_2/Θ and Θ_{22}/Θ_2 obtained in the simulations were 0.83 and 0.42 for ε/k_BT and w/k_BT = (5, 3), 0.84 and 0.57 for (4.5, 4), and 0.86 and 0.71 for (4, 5), respectively.

IV. DISCUSSION

As discussed previously,[8] in the absence of a clustering interaction the ratio Θ_2/Θ increases from Θ to 1 as the dimensionless pairing energy ε/k_BT is raised from 0 to ∞, associated with a transition between second- and first-order desorption kinetics. This trend is also apparent in Fig. 1, as the (5, 0) curve is significantly greater than the (3, 0) curve. Fig. 1 also shows that clustering interactions facilitate pairing: as w/k_BT is raised from 0 to 6 the fraction of adsorbate present as doubly occupied dimers increases significantly, particularly at coverages above 0.1. This effect has an obvious explanation: the energetic cost for a hydrogen atom in a doubly-occupied dimer at the end of a cluster to diffuse to the adjacent unoccupied dimer is not ε but $\varepsilon+w$. The result is an effectively larger pairing energy and higher fraction of doubly-occupied dimers which depends, however, on the prevalence of clusters.

In the absence of an attractive interaction between doubly-occupied dimers very little clustering takes place at low coverage, as is evident from the (5, 0) and (3, 0) results in Fig. 2. As w/k_BT is raised the fraction of doubly-occupied dimers present in clusters increases markedly. However, at low coverage the ratio Θ_{22}/Θ_2 decreases to zero for all values of w, which explains why the effect of w on pairing (Θ_2/Θ) diminishes at low coverage (Fig. 1).

Fig. 3 shows that clustering interactions also greatly increase the mean size of clusters, as would be expected. For $w = 0$ the cluster-size histograms peak at N=1 at coverages as high as 0.25. However, as w increases the distributions shift to larger N to a considerable extent, so that for $w/k_BT = 6$ most doubly-occupied dimers are present in clusters of substantial length.

Fig. 4 represents an attempt to match the observed cluster distribution with predictions from the model. While there is qualitative agreement between the clustering visible in the STM images and that predicted by the model, the agreement is not quantitative and the shapes of the distributions differ. While the scaled parameters ε/k_BT=4.5 and w/k_BT=4 approximately reproduce the values of Θ_2/Θ and Θ_{22}/Θ_2 obtained from the STM image, the model predicts a substantially broader cluster distribution than that seen experimentally. Decreasing w narrows the distribution while increasing w broadens it, as is evident from Fig. 4 (the value of ε/k_BT was adjusted in the opposite direction as w so as to maintain a nearly constant value of Θ_2/Θ). However, there appears to be no set of (ε, w) parameters that predicts a maximum at N=2 and a relatively narrow distribution.

We suggest that the discrepancy between the model predictions and experiment results from two factors, whose effects cannot be separated at present. First, the experimentally-observed distribution probably does not represent an equilibrium distribution at all. A rough estimate of the average distance adsorbed H atoms diffuse on Si(100) may be made using the diffusion constant for H on Si(111).[5] Assuming a two-dimensional random-walk process (also an oversimplification), the diffusion constant D of 1×10^{15} cm^2 s^{-1} at 630 K and the 10 s annealing time[7] lead to an estimated root-mean-square displacement of $(4Dt)^{1/2}$ = 20 Å. This value is large enough to expect substantial ordering to occur, as seen experimentally,[7] but probably not large enough for the hydrogen atoms to reach an equilibrium configuration at this temperature. In addition, the hydrogen atoms would continue to be somewhat mobile as the substrate was cooled and so would begin to move toward a new distribution characteristic of a lower temperature, becoming quenched at the point where the time constant for hopping becomes large in comparison to the time scale for cooling. However, hydrogen in clusters of different size will quench at different rates: large clusters will become immobile at higher temperatures than small clusters, which in turn will be less mobile than hydrogen in isolated doubly-occupied dimers and, particularly, singly-occupied dimers. The peak in the cluster distribution at N = 2 and 3 may therefore be due to insufficient annealing and/or the quenching dynamics of the hydrogen atoms upon cooling. A second possible effect is the inadequacy of the assumed nearest-neighbor interactions to describe the driving force for clustering. If the primary driving force for clustering is lattice strain associated with the different dimer bond lengths in un- and doubly-occupied dimers, as suggested by Boland,[7] there is no guarantee that the energetic stabilization of the strain field associated with a cluster of length N will be proportional to (N-1), as is implicit in the assumption of nearest-neighbor interactions. It is also possible that *electronic* interactions between *un*occupied dimers provide a significant or perhaps even dominant contribution to the driving force for clustering. The dispersion in the valence band structure on clean Si(100)2×1 in the $\bar{\Gamma}$-$\bar{J}'$ direction (parallel to the dimer rows) is 0.8 and 0.7 eV in occupied and unoccupied states, respectively.[20-23] The magnitude of these dispersions indicates a quite substantial overlap between the dangling bond orbitals on adjacent dimers; since delocalization always leads to a lowering of electronic energy levels it is clear that longer chains of unoccupied dimers will be energetically favored due to purely electronic effects. An energetic preference for "clustering" of unoccupied dimers will give rise to an apparent driving force for clustering of surface hydrogen, which may be difficult to distinguish unambiguously from effective clustering interactions due to lattice strain. Further work will be necessary to make more definitive statements of the relative importance of these effects and the adequacy of a nearest-neighbor representation of the net effective clustering interactions.

Despite the uncertainty in the fine details of the clustering interactions and the extent to which the STM image approximates a thermal distribution, the comparison between the model predictions and the STM image allows the semiquantitative estimate that $\varepsilon \gtrsim w \gtrsim \varepsilon/2$, i.e., that w is probably slightly smaller than ε but is of the same order of magnitude. As discussed in detail elsewhere,[17] the presence of a clustering energy requires a slight downward revision of the estimate of ε made by fitting the desorption kinetics, since a nonzero w causes an increase in Θ_2/Θ for a given ε (Fig. 1). However, the picture proposed originally for desorption[8] remains the same: desorption occurs between hydrogen atoms paired on a single dimer and preferential pairing occurs due to the π bond on unoccupied dimers. The essential reason why a nonzero w yields only a minor perturbation to the value of ε is that the estimate is based on the departure from first-order kinetics at low coverage[8,12] and that the effect of w on Θ_2 is very small below 0.01 monolayer (Fig. 1).

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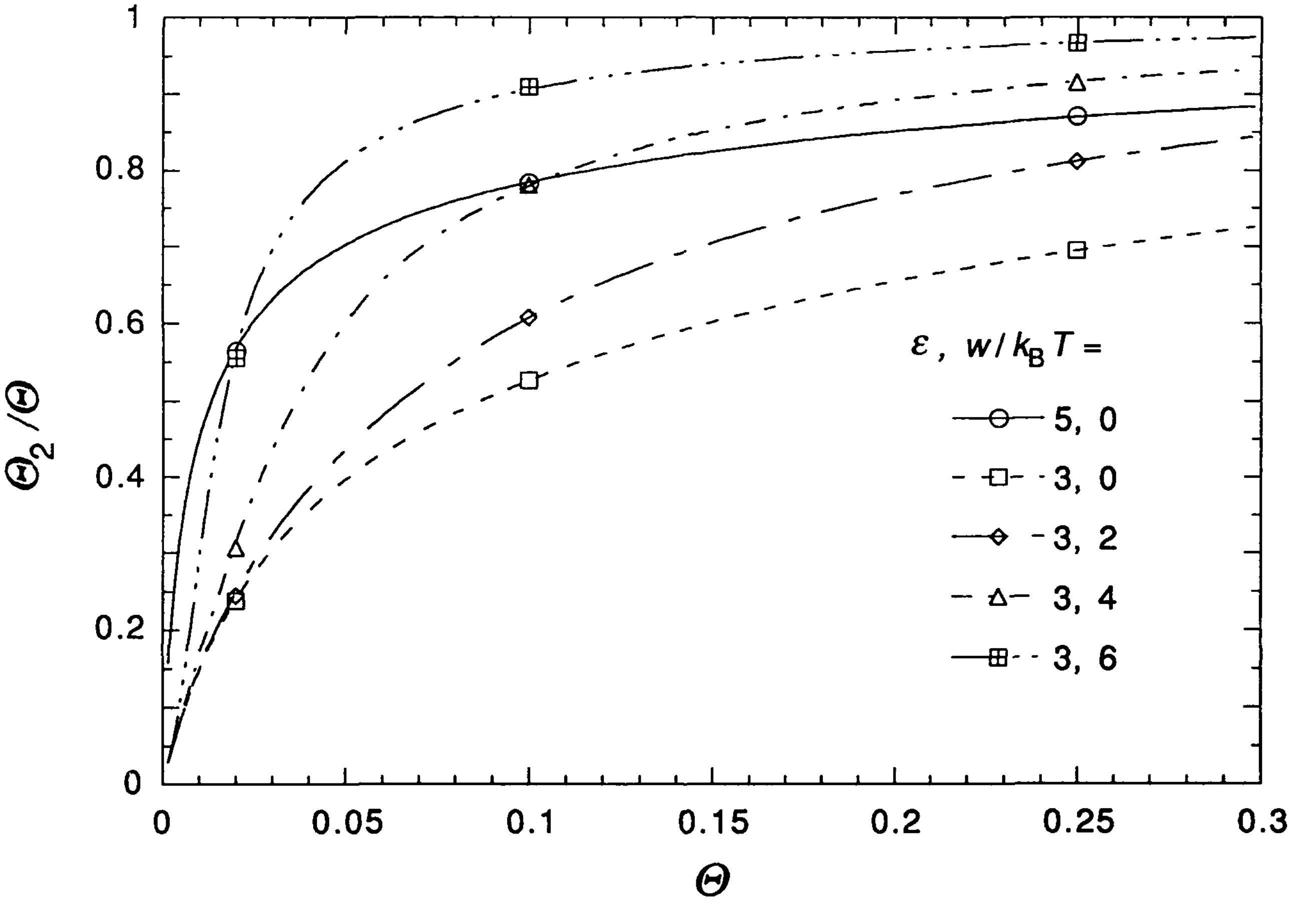

FIG. 1. Fraction of hydrogen present on doubly-occupied dimers as a function of total hydrogen coverage, for several values of the pairing energy ε and the clustering energy w. Symbols: results from Monte Carlo simulations. Curves: quasi-analytic solution.

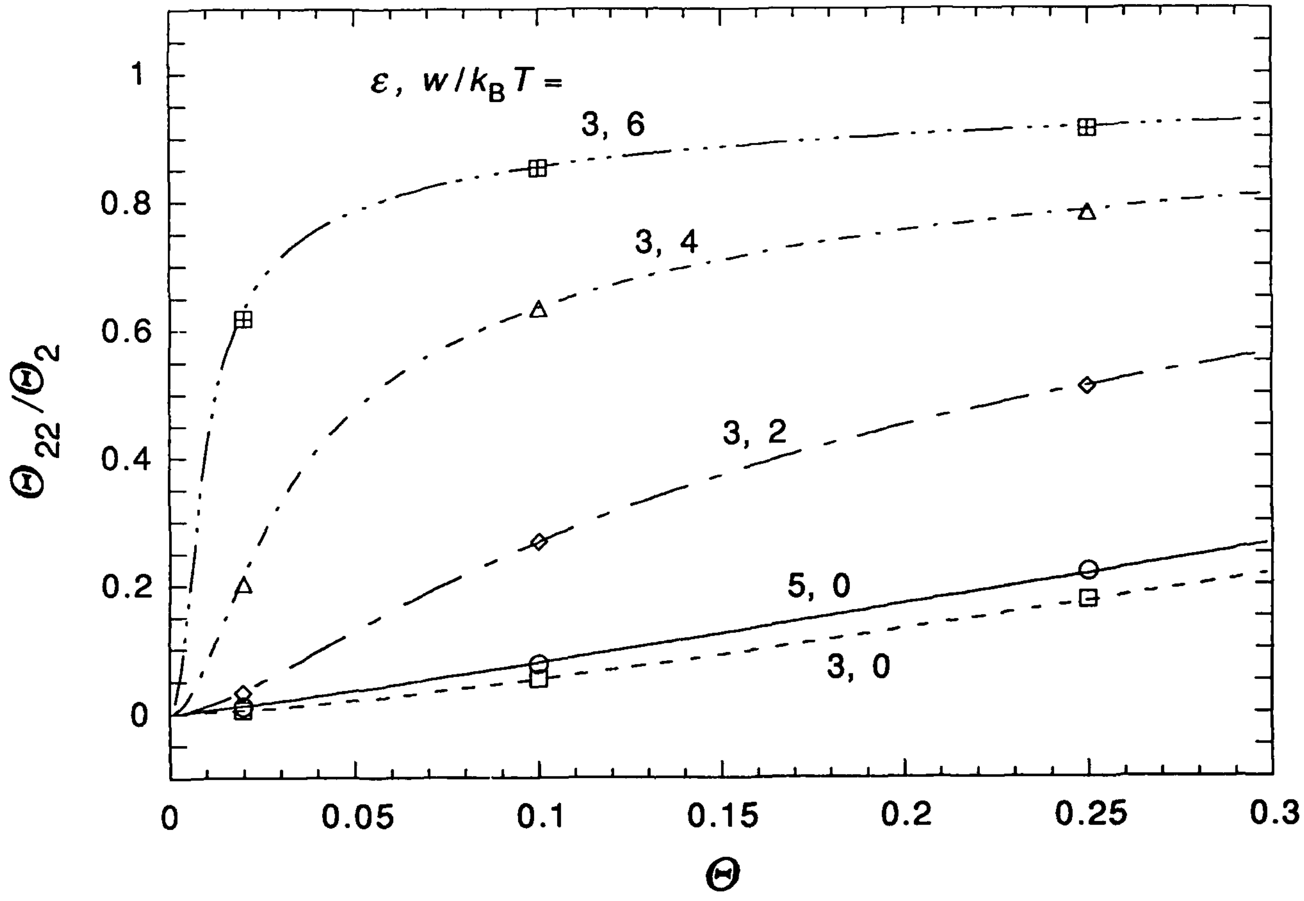

FIG. 2. Ratio of cluster bonds between doubly-occupied dimers and number of doubly-occupied dimers, for several values of ε and w. Symbols: results from Monte Carlo simulations. Curves: quasi-analytic solution.

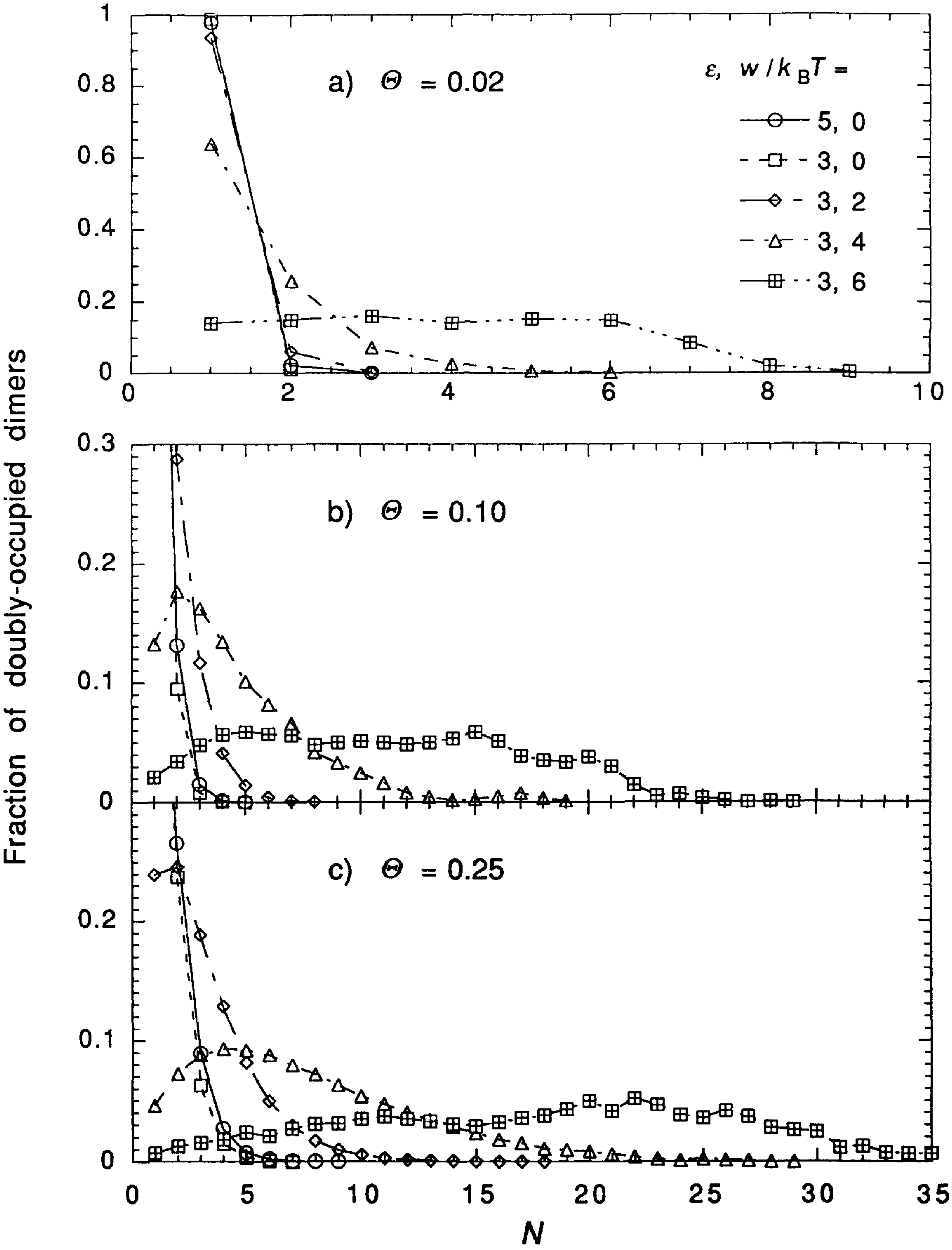

FIG. 3. Cluster size distributions obtained from Monte Carlo simulations using several values of ε and w.

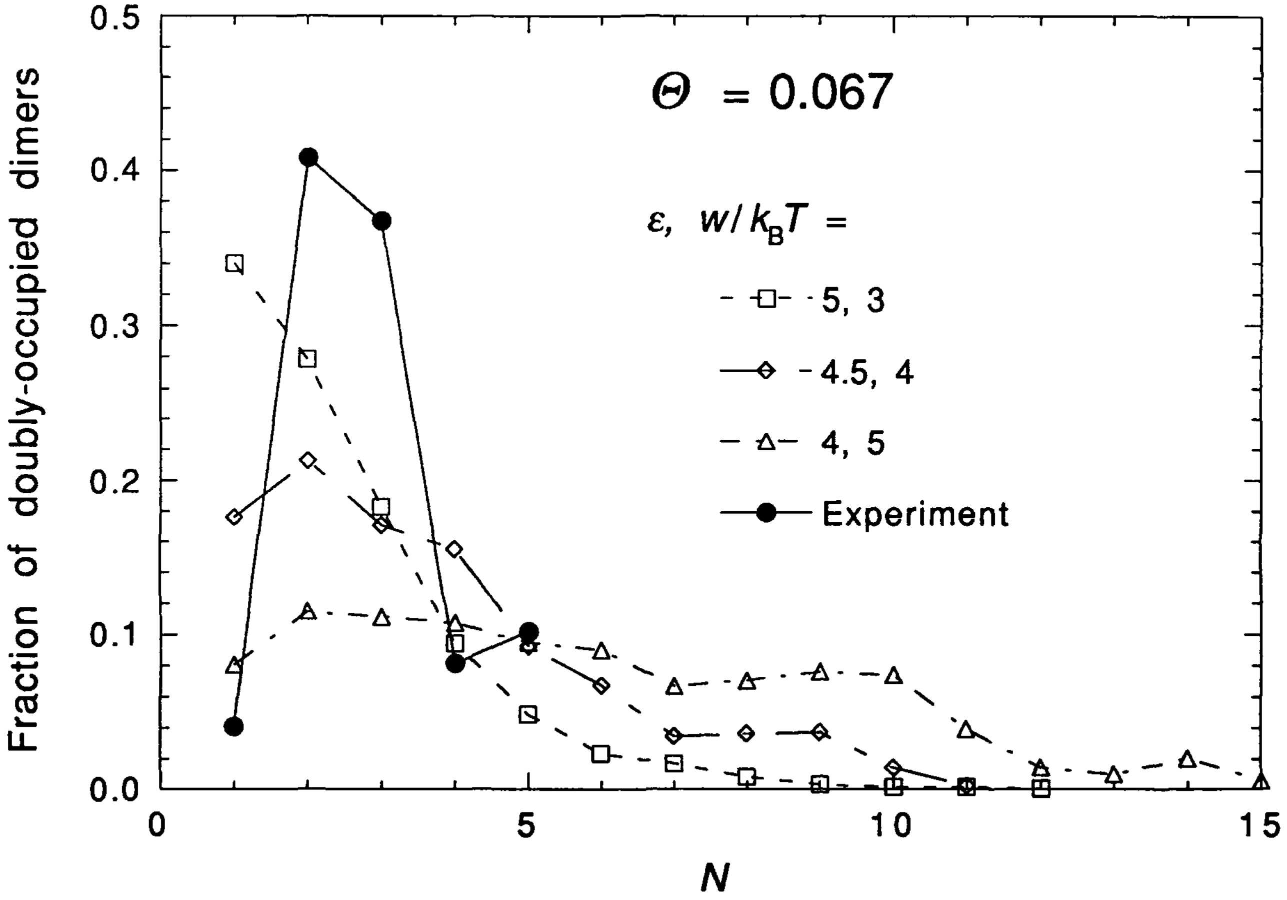

FIG. 4. Comparison of cluster size distribution extracted from STM image (Fig. 1(b), Ref. 7(a)) with results from Monte Carlo simulations.