Multisite Lateral Interactions and Their Consequences

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In a two-dimensional lattice–gas framework, the size and the effect of multisite (lateral) interactions between chemisorbed atoms (and between surface atoms in reconstruction systems) are assessed. The computation of such interactions, using relatively crude approaches, is surveyed. The effects of such interactions are discussed, in particular their role in producing asymmetries in temperature-coverage phase diagrams.

I. Introduction

For many adsorption systems, particularly chemisorbed atoms on transition metals, the adatoms are strongly bound to specific sites on the substrate. The barrier to diffusion is some moderate fraction of this energy, and the (lateral) interaction is a considerably smaller fraction. For such systems, it is a good approximation to describe the statistical mechanics of the adatoms in terms of a two-dimensional lattice–gas model. (These models are also useful in describing the reconstructions of some transition-metal surfaces.) In such models, the single-adatom binding energy can be absorbed into the chemical potential, so that the key energies in the 2-d systems are the interactions between adatoms on nearby sites. Most studies assume that only pairwise interactions are needed to describe the measurable properties of the adsorbates. The goals of this article are to assess how valid it is to neglect multisite interactions and to describe some of the consequences of such interactions when they are not negligible.

The first part of this article treats the computation of multisite interactions between chemisorbed atoms (or atoms in the top layer of a reconstructing surface). The low symmetry of the problem generally precludes the use of self-consistent, local-density calculations. Initially, crude tight-binding models gave some insight into the general behavior of such interactions. A variety of later schemes, using both one-electron theory and additional correlation effects, were applied to specific systems. After summarizing this work, we discuss more recent results using the semiempirical embedded-atom method, and related schemes.

The second part of the article considers the observable effects of these interactions, in particular on the equilibrium statistical mechanics of surface systems. Since the mapping between lattice models and spin models has proved very helpful in understanding adsorbate behavior, we detail the nonlinearity of the relationship between lattice–gas three-site interactions and three-spin interactions in their Ising model counterparts. Thus, a seemingly modest three-spin term can correspond to an unphysically large trio—i.e., trimer with constituent pairs subtracted—interaction. It is widely believed that any three-site interaction will break "particle–hole" symmetry in the lattice–gas model and so lead to gross asymmetries in the temperature-coverage phase diagram. We report specific results for systems with a coexistence region around the symmetry axis at half-saturation coverage; we also present a specific counterexample for a system with a pure phase around this coverage, in which two distinct trio configurations are required to produce noticeable asymmetry in the phase boundary. A simplistic argument rationalizes this behavior. We more generally describe many of the phase diagrams computed with the inclusion of trio interactions, using two methods that are reliable in two dimensions, Monte Carlo and transfer-matrix finite-size scaling. We also discuss evidence for trio interactions using field ion microscopy and scanning tunneling microscopy. Trios can determine whether small clusters of adatoms tend to be compact or linear.

II. Computation of Multisite Interactions

The computation of lateral interactions between atoms chemisorbed on metallic or semiconductor substrates has presented a stern challenge to solid-state theorists. With self-consistent-field, local-density, total-energy calculations, one must study ordered overlayers with a moderate fraction of a monolayer coverage. Such computations produce barely enough information to assess pair interactions—the total energy of a system with two adatoms in close proximity minus the corresponding energy with the adatoms widely separated. There is little hope of gauging multisite interactions. The most promising technique, discussed earlier by Feibelman, appears years away from being able to investigate multisite effects. To address these problems currently, we must therefore resort to either tight-binding models or semiempirical (or empirical) approaches, which give insight into qualitative behavior and suggestions of orders of magnitude but are incapable of providing reliable quantitative information. Readers who nonetheless find these approaches distasteful (as did some participants of the conference) should skim the latter part of subsection II.A, then skip to section III, and imagine the multisite interactions as phenomenological parameters. It is useful to begin by recapping relevant results reported over a decade ago (with some minor updates) in my review[1] of the general topic of indirect interactions.

A. Results as of a Decade Ago. For polar bonds, the dipolar interaction produces a pairwise repulsion (of size 1.25 eV times the two dipoles in debyes over the separation R cubed in angstroms) but no multisite contribution. For the weak van der Waals interaction, which dominates only in the physisorption case (but see ref 2), there is the Axilrod–Teller–Muto R^{-9} triple- (fluctuating-) dipole interaction, which is repulsive in all important cases. Its magnitude is at most 3% (for Ar) to 5% (for Xe) of the corresponding pair interactions if all distances are set at the equilibrium spacing. This effect is not of concern here, but for an interesting application, see ref 3.

For chemisorption bonds, it is generally believed that once the adatoms are separated by about a couple substrate

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(3) Klein, J. R.; Bruch, L. W.; Cole, M. W. *Surf. Sci.* **1986**, *173*, 555.

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lattice constants, their atomic orbitals do not overlap significantly, so any interaction is indirect via the substrate. The basic idea, presented by Grimley nearly a quarter century ago,[4] is that the adsorbate orbitals couple to substrate orbitals by virtue of the adsorption bond. When the orbitals of two or more adatoms couple to the same extended state of the substrate, quantum-mechanical matching conditions may cause these orbitals to be in phase or out of phase, leading to attractions or repulsions, respectively. For the transition metals (or semiconductors) involved in most chemisorption systems, in contrast to jellium,[5] these wave functions are anisotropic, leading to anisotropic interactions. In general, one must consider the coupling to all the occupied states of partially filled bands to compute the indirect interaction, leading to interactions that decay very rapidly with increasing interadatom separation. Only in the asymptotic limit does the coupling simplify to a single state on the Fermi surface with wavevector parallel to the direction in real space between adatoms.[1,6,7] This simplification is usually applicable only at separations so large that the interaction is negligibly small.

In the framework of the Anderson–Newns model of adsorption and a single-band substrate in the tight-binding (TB) approximation, it is straightforward not only to write expressions for pairwise interactions, but also to write generalizations for multiparticle effects and for complete ordered overlayers. Assuming strong chemisorption bonds, this treatment essentially sums the changes in one-electron energies. Careful treatment of Coulomb-induced correlations on the adatom, which are important for weaker bonds, is glossed over in Hartree–Fock fashion. Readers interested in the formalism should consult ref 1. The hope that pair energies describe most of the interesting physics is encouraged by the (potentially deceptive) observation that the lateral interactions of an ordered overlayer are generally reasonably well approximated by the pair interactions of the shortest-separation pairs in the overlayer.[8,9] Nonetheless, "trio" interactions—the interaction energy of three adatoms *minus* the *three* associated pair interactions—do have a magnitude that is often some moderate fraction of the shortest-separation pairs. The good agreement between pairs and the ordered overlayer often results from partial cancellations of these higher-order terms, so that neglect of such contributions is often attributable less to any formal a priori justification and more to desperation to restrict the number of included interactions to a manageable set.

In this vein, it is worth reemphasizing the point that once one opens the Pandora's box of multiparticle interactions, there are many to consider. In an early study of their effect in deducing phase diagrams, noting the dependence of magnitude on the two shorter legs of the trio, I pointed out[10] that on a square lattice, a linear trio should have interaction energy comparable to a right triangle with the same legs. Moreover, if the binding is in bridge sites, there are two distinct linear configurations with comparable magnitude. A ramification of this result is that one must be careful in attributing features of temperature-coverage phase diagrams, e.g., asymmetries, to one or two trios. The underlying idea is that in a lattice-gas with purely pairwise interactions, the phase diagram should be *symmetric* about the coverage at which *half the adsorption sites* are filled. (Since coverage is conventionally expressed as adatoms per top-layer atoms, this criterion indicates, for example, that for a close-packed surface on which both kinds of 3-fold sites can be occupied, the special coverage is 1, not 1/2.) In section III.A we shall point out some subtleties in applying this argument to phase boundaries near half-saturation coverage. For O/W(110) a more flagrant asymmetry occurs, with an ordered phase at $^{3}/_{4}$ monolayer not reflected at $^{1}/_{4}$; for such asymmetries in the ground-state energy, simple energetic arguments place lower limits on the values of trio interactions. In studying this system, Ching et al.[11] assumed that two trio configurations produced the asymmetry and thereby estimated the average of their magnitude. If one considers all the various trio configurations of comparable magnitude, the size required of each can be substantially reduced.[10]

B. Progress in the Early 1980s by Use of Embedded Clusters. The philosophy behind the above single-band tight-binding calculations is that the d band is primarily responsible for the lateral indirect interactions. Burke[12] raised doubts about the adequacy of this idea by performing more realistic TB calculations with a 5-fold degenerate substrate band. For W/W(110) his computed attraction was too large by nearly a factor of 5 compared to results from field ion microscopy; for O/Ni(100) he could not explain the ordered phase[13] (and the strength was typically much too small, of order 1–10 meV, to account for disordering temperatures). Lau and Kohn[5] as well as Johansson[14] and Eguiluz et al.[15] showed that with a jellium substrate there were also indirect interactions of substantial magnitude.

Muscat[16] was the first to allow explicitly for contributions of both free and d-like electrons in producing lateral interactions between adatoms, in his case H atoms. In his embedded-cluster model, spheres are centered on the sites of the H adatoms as well as on a cluster of nearby metal atoms in the substrate. Within the latter muffin-tin spheres, he places self-consistent bulk band-structure potentials.[17] The spheres are then embedded in some model of a free-electron gas, usually infinite-barrier jellium. (In some later work, the jellium contribution is taken from effective medium theory.)[18,19] The d-wave contribution comes from the $l = 2$ solutions. Again, interaction energies are calculated from changes in all the one-electron energies. The technique was applied to a wide variety of late-transition and noble metal substrates. Pair interactions generally have the correct sign and order of magnitude to corroborate the energies deduced from Monte Carlo simulations of the experimental phase diagram (but were often off by factors of very roughly 3). Here, however, we limit our coverage to instances in which trio interactions are deduced.[20-23] In all these papers, Muscat places various

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clusters of H atoms on the surface. In these calculations the distance *d* between the H proton and the jellium edge (taken as a plane halfway between the surface atoms and what would have been the next plane above the surface[23]) is an input parameter. By quoting the results for a few values of *d*, Muscat gives some idea of an intrinsic uncertainty in this approach. While the variation is not negligible, the qualitative and usually semiquantitative results are not overly sensitive.

Reference 23, an extension of refs 21 and 22, gives the most comprehensive results, treating the close-packed faces of seven substrates: Ti, Co, Ni, Cu, Ru, Rh, and Pd. In addition to six configurations of pairs, three trio configurations and four hexagonal configurations are considered and their lateral interaction energies evaluated. The principal goal was to evaluate the relative stabilities of the ground states of various possible ordered overlayers. In this regard, pairwise interactions alone were found sufficient. Hence, equilateral-triangular trio and hexagonal-ring six-adatom interactions are presented only for the case H/Ni(111). Indeed, these trios typically have magnitude 1 meV and never exceed 2 meV. On the other hand, the second- and fifth-neighbor pair interactions of the sides of the first and second triangles are 4 ± 2 and 1 meV, respectively, so that the *fractional* contribution is comparable to that found in single-band tight-binding calculations. The third trio has sides that are sixth neighbors. Here Muscat deduces a very strong attraction—unreasonably strong in comparison to shorter-range interactions—which produces a reasonable disordering temperature (compared with experiment[24]) but poorly reproduces the topology of the phase diagram.[25] Muscat's most extensive tabulation of trio energies is in his treatment of H/Fe(110).[20] Experimental determination of the adsorption site was problematic. Initial suggestions of the long-bridge site (based on LEED[26]) and of the short-bridge site (based on EELS[27]) were eventually supplanted by the conclusion from detailed LEED work[28] that H sits in the quasi 3-fold site. Since Muscat's calculations supported the short-bridge site, it seems inappropriate to reproduce the details, but his general finding was again that trio interactions were sufficiently small in magnitude—on the order of 1 meV—to be insignificant [except for the smallest (linear) configuration, for which the H atoms are unphysically close to each other]. For the eight computed configurations, the trio energy was roughly 1 order of magnitude smaller than the shorter-range constituent pair energies, i.e., somewhat smaller than predicted with tight binding.

C. Recent Progress, Mostly with Embedded Atom and Tight-Binding Methods. Further interest in the problem of trio interactions was spurred by the observation, by several groups using field ion microscopy (FIM), of adsorbed trimers. By collecting statistics from large numbers of micrographs, one can deduce the interaction energies of configurations of adsorbates, as reviewed here by Ehrlich and Kellogg. To account for the trends of the 5-d series (Ta, W, Re, Os, Ir) on W(110)—in particular, the striking minimum of the lateral interactions for Re[29]—Bourdin et al.[30] proposed a very simple analytical model. They claimed that Burke's excessively large energies were due to his neglect of both core–core repulsions and electronic correlations, which they computed to second order in U/w, where U is the Hubbard-like intraatomic Coulomb repulsion and w the bandwidth. (A decade earlier, correlation was found to make a negligible change from the Hartree–Fock energy for H on a single-band tight-binding substrate.[31]) Bourdin et al. considered *linear* trimers at nearest-neighbor separation. They made several simplifying assumptions: (1) The substrate is rigid and the adatoms sit exactly at high-symmetry sites. (2) The core–core repulsion is the same for all the adsorbates. (3) The one-electron, "band" contribution comes solely from broadening of the adsorbate levels. Thus, the dominant interaction is directly between adsorbates rather than through the substrate. This ansatz is only reasonable at short spacings. Burke[12] also

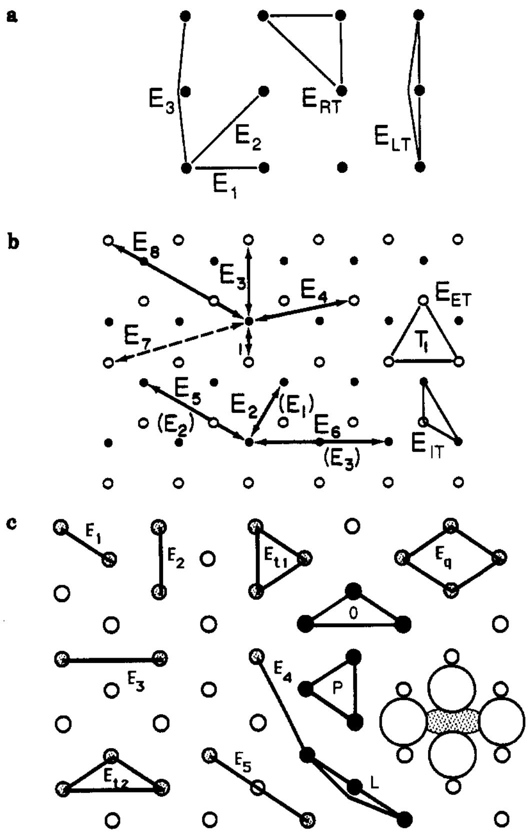

Figure 1. Schematics to illustrate some important pair and trio configurations on high-symmetry adsorption grids. The configurations are labeled by the corresponding energy: (a) square lattice, e.g., atop or center sites on (100) faces of fcc and bcc substrates; (b) honeycomb lattice, indicating the two kinds of 3-fold (center) sites (both forming triangular lattices) on (111) faces of facc substrates or (0001) faces of hcp substrates. The energies in parentheses are for a triangular lattice (in this case the filled circles) (adapted from ref 25, with addition of the trimers of ref 59; (c) centered rectangular lattice, showing the long-bridge sites usually used for simulations. The large circles at the lower right show the sites of the top-layer substrate atoms. In many cases, the adsorption takes place in the quasi 3-fold sites, which are connected by a shallow barrier and so might allow rapid movement back and forth (shaded region). The trimers L, O, and P are considered in ref 32.

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showed that allowing direct interactions at this range made an overwhelming difference in the interactions. (I explicitly neglected these direct efforts in my tight-binding calculations.) (4) The local density of states increases with coordination number (as one would expect from TB theory) and is taken to be constant over an energy range (as for a 2-d band). (5) The Coulomb integral U is independent of coordination and of adsorbate species. After exploring the range of input parameters producing the observed minimum, Bourdin et al. took some account of substrate bandlike contributions, adjusted U on species to reproduce the experimental dimer pair attraction, and then computed trimer—no substraction of pairs—energies (finding the minimum at Re). Since there is no estimate of the pair interaction between the two end atoms in the linear trimer, the only way to gauge the trio energy is simply to subtract twice the dimer energy from the trimer energy. This estimate of the trio strength actually peaks at Re, with a value of −0.19 eV and nearly vanishes for Ta (but curiously jumps back down to −0.17 eV for Ir). The estimated trio energies are attractive (except for a tiny repulsion for Ta) and range from the same magnitude as the pair energy down to below 1 order of magnitude smaller.

In a more sophisticated study, Dreyssé et al.[32] found similar results for Re/W(110). They considered the same contributions, treating the one-electron contribution using 5-fold degenerate tight-binding bands, the correlation energy using second-order perturbation theory (but with local atomic densities computed from their Green's functions), and the repulsion using Born–Mayer interactions. They also took some account of self-consistency by shifting atomic levels. (For a critique of this procedure, see ref 33.) They computed interaction energies for the three trimer configurations with two nearest-neighbor pairs (i.e., in the $[1\bar{1}1]$ direction): linear (L), nearly equilateral (P for "pointed"), and H_2O-like (O for "open"), as well as the six shortest-separation pairs. For the pairs, including correlation energy—with intraatomic Coulomb integral U = 1.6 eV—has a considerable effect, in most cases reversing the sign of the interaction; U is just big enough to make the nearest-neighbor pair interaction repulsive, to reproduce experiment. The trimer interactions (lamentably called "trio") for L, O, and P configurations are −0.18, −0.14, and +0.12 eV, respectively, consistent with Fink and Ehrlich's experiments.[34] With their tabulated pair energies, the trio interactions are −0.23, −0.35, and −0.17 eV, respectively, strikingly large values, considerably greater than the pairs. It is not clear how small changes in the many—albeit sensibly estimated—input parameters would alter the results. The paper contains an extensive, informative discussion beyond the scope of this review.

To take advantage of the success of computationally intensive schemes such as FLAPW[35] to compute details of monolayer adsorption, Gollisch[36] constructed an effective potential, a generalization of the Morse form, with several parameters to be fit to the numerical "data". Two global parameters, on which the quality depends sensitively, adjust the exponents of competing terms. Three more parameters adjust the scale and exponent of a separation-dependent interaction function, here a sum of two exponentials, introducing four more parameters. These seven parameters are computed from bulk properties and tabulated for each element of interest. Parameters for interactions between different atomic species are determined by various sorts of means of the elemental form. As discussed below, the numbers produced for Cu, Ag, and Au on W(110) provide a good starting point for simulations.

The semiempirical embedded-atom method (EAM)[37,38] has offered a relatively easy way to contend with the low-symmetry problem we face. In this approach, the cohesive energy is written

$$E_{\mathrm{coh}} = \sum_i F\Big(\sum_j{}' \rho^{\mathrm{a}}(R_{ij})\Big) + {}^1/_2 \sum_{ij} U(R_{ij}) \qquad (1)$$

where the ρ^{a}'s are spherically averaged atomic electron densities, the prime on the summation indicates $j = i$ is excluded, and U is the electrostatic Coulomb repulsion. The effective charge densities Z inserted into U are determined by the formula $Z(R) = Z_0(1 + \beta_z R)\exp(-\alpha_z R)$. The embedding energy can be determined numerically by embedding an atom in a homogeneous background, as in effective medium theory[18] or by using the "universal" binding curve of Rose et al.[39] Typically, the parameters are adjusted to fit the bulk properties such as lattice constant, cohesive energy, and elastic constants. For adsorption of one species on another, one can fit adsorption site and height and vibration frequencies. The fact that fitting functions are not uniquely specified has been criticized by some, especially theorists performing massive self-consistent, total-energy computations. In fact, this flexibility can be a strength in that one can tailor functions for specific applications and gauge uncertainties by use of different sets of functions. On the other hand, it serves as a warning to the uninitiated that the numbers emerging from EAM calculations are most useful in identifying trends and rough magnitudes; for high-symmetry systems more exacting band-structure techniques are most reliable. (However, the flexibility of EAM can often lead the practitioner to unexpected structural relevations. For example, for H/Pd(111) the existence of subsurface sites and their domination of the interactions needed to describe the phase diagram[40] were discovered "by accident" during dynamical simulations!) EAM is quite helpful in assessing the effects of coordination number on bonding. Also, the driving program easily allows for substrate relaxations, or motion of any atom in any direction can be frozen. On the other hand, since there is no Fermi surface in the method, EAM cannot describe any effect involving Friedel oscillations, such as the asymptotic form of lateral interactions.[1,5,6,41]

In recent EAM calculations of H/Ni(111) and H/Pd(100), we[42] assessed the ability of EAM to predict lateral interactions. To lowest order, the positive curvature of $F(\rho)$ leads EAM to predict repulsions, with magnitude proportional to the number of shared substrate nearest neighbors (except at the shortest separations, when direct interactions can overwhelm the physics). For H/Ni(111) only the first-, second-, and third-nearest neighbors are above 1 meV (cf. last sentence of the preceding paragraph). Their magnitudes are comparable to those found by Muscat[21-23] but all of ours are positive, consistent with

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behavior deduced from Monte Carlo fits of the phase diagram.[25] We found a tiny attractive trio interaction for the smallest equilateral triangle of adatoms in the same kind of 3-fold site, comparable in size to that found by Muscat but of the opposite sign. Overall, the signs of the interactions seem more reliable than Muscat's, there are no anomalous attractions, but the second-neighbor repulsion is less than $^3/_2$ of the third; a p(2×1) overlayer is predicted instead of the observed graphitic (2 × 2) (or (2 × 2) - 2H).[24] A very recent extension of EAM, called EDIM (embedded diatomics in molecules),[43] obtained magnitudes for the lateral interactions more consistent with expectations from experiment, but with the same sign as we found. There were a number of modifications, with no commentary on the effect of each. A likely possibility is the allowance, for Ni's in the top layer, of a different number of s electrons from the bulk value. Unfortunately, EDIM has not yet been applied to trio interactions.

For H/Pd(100) our calculations found the minimum for H atoms to be slightly below the top Ni plane rather than slightly above. The magnitudes of the lateral interactions are most consistent with experiment, viz. 87 [94], 54, and -9 meV for the first-, second-, and third-neighbor interactions, E_1, E_2, and E_3, respectively. (The bracketed value for E_1 was obtained from analysis of ordered overlayers. By symmetry, local distortions that plague the isolated pair are removed.) However, since the second is more than half the first, a p(2×1) ordering rather than the observed[44] c(2×2) is predicted. (This problem as well as the too-low binding site may be due to use of rather primitive EAM functions, which were then available for Pd.) The smallest area right-triangle configuration has a trio energy $E_{RT} = -25$ meV; it plays no role in the balance between these two ordered states but does affect the phase diagram, as we will see shortly. It may not be a coincidence that the placing of H lower into the surface than in reality leads to more realistic binding energies: for H/Pd(111),[40] as noted above, the interactions producing the ordering come from the *subsurface* H's; those on top of the surface have little interaction, as for Ni(111).

For comparison, Stauffer et al.[45] have just used a state of the art tight-binding approach to present a wealth of information on H atoms near Pd(100). The H atoms are only allowed to sit in lattice planes of the substrate lattice, so the results for the center site of the top layer are the ones of most interest. Then E_1, E_2, and E_3 are +14, -182, and +41 meV, respectively. Removing the constituent pair interactions from their tabulated trimer energies, I find that $E_{RT} = -32$ meV and the linear configuration $E_{LT} = -72$ meV. It would be interesting to know how these numbers would change if the H's were moved slightly above the surface; since the dependence on layer index is not monotonic, there is no obvious interpolation. In comparison with our EAM numbers, the TB E_{RT} is quite similar but E_{LT} is much bigger than expected even in crude calculations and certainly in EAM. Moreover, the pair interactions are starkly different. While their pair energies do lead to the observed c(2×2) ordered phase, the enormous size of E_2/E_1 would produce a broad coexistence region of c(2×2) + "gas" that persists to a temperature close to T_c of the pure c(2×2) phase.[25] Such a stable coexistence region would have been observed in experiment.[44] On the other hand, such regions (of more modest size) were conjectured on the basis of Monte Carlo simulations.[46] Hopefully this dilemma will motivate further experimental investigation of the low-T, low-coverage region.

Since EAM successfully treated alloying at surfaces and phase transitions of one noble metal on another,[47] we expected[42] that late-transition metals on each other would be more accurately described in EAM. Recent studies[48] of Pt, Pd, and Ni on Pt(100) bear out this belief. As described in the following contribution by Kellogg, small clusters of these adsorbates may form in lines (Ni), compact clusters (Pd for more than three adatoms), or an alteration between them (Pt for fewer than seven), depending on the relation of the trio interactions to the pairs. For Pt, Pd, and Ni adsorbates, with the Pt(100) rigid, the (E_1, E_2, E_{RT}) energies in are -299, +59, -76; -263, +4, -12; and -64, +97, -40 meV, respectively. [Somewhat relatedly, Ir trimers form chains on Ir(100) but clusters on Ir(111).[49] It is not clear what part of the difference in trimer energies (0.33 ± 0.02 and 0.098 ± 0.004 eV, respectively) is due to pairs vs trios.] Another issue of concern for adsorbates is the large charge gradient near surfaces. For the reconstruction of Au(110), EAM predicts[52] a (1 × 3) pattern rather than the observed (1 × 2). To rectify this problem, Roelofs et al.[53] included the leading correction from such gradients, using a modification of EAM formalism.[54] Moreover, to treat this system with Monte Carlo simulations, they decomposed the interactions of Au atoms in the top layer, finding that not only are trios significant, but so are "quartos" (i.e., the interaction energy of four surface atoms minus the constituent pairs and trios). Specifically, they found linear (along the row) and right-triangle trio energies of +22.0 and -1.9 meV, respectively, and a quarto rectangle energy of +13.7 meV; even the close-packed "hexto" interaction has a strength -3.4 meV. To assess the role of the gradient contribution, I quote the comparable numbers I computed for the trios in an early stage of this project before the corrections were implemented: +25 and -4.6 meV, respectively. [For pair interactions for adatoms on neighboring rows, at the same position along the row or shifted by one unit (so somewhat diagonal), are -10 and +17.6 meV, respectively, without the gradient term vs -2.6 and +12.3 meV with corrections.] In short, the gradient corrections do not change the qualitative results but are important for quantitative assessments.

III. Effects of Trio Interactions on Statistical Mechanics

Having explored the state of the art in computing multisite interactions, it is now time to discuss the role they play. We have already seen that they can determine the geometry of small clusters. As a first item, we show how these trio interactions relate to three-spin terms in the Ising analogue of lattice–gas Hamiltonians. Assuming a square lattice with nearest (E_1) and next nearest (E_2) interactions, as well as a right-triangle trio (E_{RT}), we have

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for the lattice–gas, with $n_i = 1$ or 0

$$\mathcal{H} = E_1 \sum_{\langle ij \rangle}{}_1 n_i n_j + E_2 \sum_{\langle ij \rangle}{}_2 n_i n_j + E_{\mathrm{RT}} \sum_{\langle ikj \rangle}{}_T n_i n_j n_k \quad (2)$$

The mapping to spin language, with $s_i = \pm 1$, is $n_i = (1 + s_i)/2$. We see

$$\mathcal{H} = \left(\frac{E_1}{4} + \frac{4}{8}E_{\mathrm{RT}}\right) \sum_{\langle ij \rangle}{}_1 s_i s_j + \left(\frac{E_2}{4} + \frac{2}{8}E_{\mathrm{RT}}\right) \sum_{\langle ij \rangle}{}_2 s_i s_j + \frac{E_{\mathrm{RT}}}{8} \sum_{\langle ijk \rangle}{}_T s_i s_j s_k \quad (3)$$

In spin language, the three coefficients are called $-J_1$, $-J_2$, and $-J_{\mathrm{RT}}$, respectively. We easily see that

$$\frac{J_{\mathrm{RT}}}{J_1} = \frac{E_{\mathrm{RT}}/E_1}{2 + 4E_{\mathrm{RT}}/E_1} \quad \text{or} \quad \frac{E_{\mathrm{RT}}}{E_1} = \frac{2J_{\mathrm{RT}}/J_1}{1 - 4J_{\mathrm{RT}}/J_1} \quad (4)$$

This highly nonlinear relation leads to some surprising results. For E_{RT}/E_1 anywhere above 1, even far above, J_{RT}/J_1 is close to $^1/_4$. For E_{RT}/E_1 below $-^1/_2$, J_{RT}/J_1 is positive. J_{RT}/J_1 is only negative for E_{RT}/E_1 between $-^1/_2$ and 0. As a result, a simulation using spin variables can deduce a value of J_{RT}/J_1 that seems quite sensible until translated into E_{RT}/E_1. In this case, any positive value of J_{RT}/J_1 around $^1/_4$ will lead to enormous E_{RT}/E_1. On the other hand, in an early Monte Carlo simulation of the phase diagram of H/Pd(100), Binder and Landau[46] concluded that J_{RT}/J_1 probably lies between −0.2 and −0.3, corresponding to E_{RT}/E_1 between −0.22 and −0.27.

A. Asymmetries in Phase Boundaries of Pure Phases. A rather surprising finding of numerical (Monte Carlo) calculations is that a single type of trio interaction need not necessarily lead to a large asymmetry in the phase boundary about half-coverage.[55] This result, illustrated in Figure 2 for the case of a c(2×2) overlayer described in eq 2, is in sharp contrast to the observation in 2-d calculations that treat fluctuations approximately—mean field and quasi-chemical approximation—that trios must produce such asymmetries.[56] We also see that a linear trio E_{LT} alone does not produce an asymmetry, but when it and E_{RT} are present, the expected notable asymmetry does appear. To make some sense of this effect of trios on the phase boundary, we need some way to assess the *difference* in the way the trio interactions affect the low-temperature ordered phase compared to the high-temperature disordered phase. The fact that trios break the particle–hole symmetry of the pair-interaction lattice–gas Hamiltonian, and so introduce an asymmetry into the ground-state energy, is not the issue.

In the remainder of this subsection, we describe a crude approximation scheme for assessing the change in the disordering temperature T_c of an ordered phase from a known value $T_c(0)$ for some Hamiltonian to $T_c(E_{\mathrm{new}})$ for a more complicated Hamiltonian with a new interaction energy E_{new}. While we have applied our procedure[57] to a wide range of problems,[55] we have as yet no formal derivation. In essence, the idea is that T_c *scales with the lowest-energy excitation from the ground state*. In ref 57 we show, for example, that for a c(2×2) overlayer with 1/2 monolayer coverage, described by a nearest-neighbor repulsion E_1 and a smaller second-neighbor interaction E_2

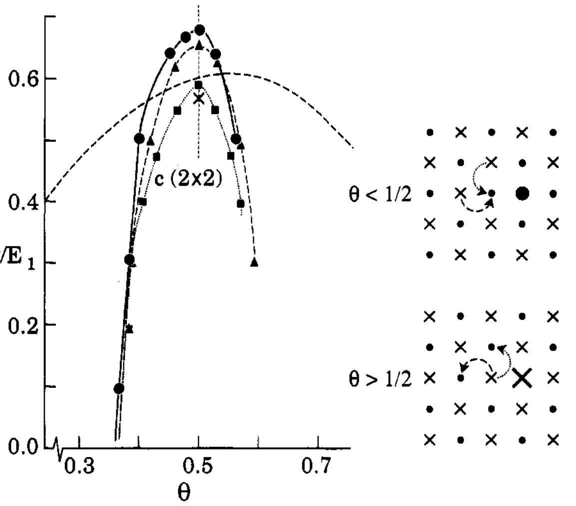

Figure 2. Illustration, for a c(2 × 2) overlayer on a square lattice, of the crude guideline of scaling the elementary excitation used to predict which trios produce sizeable asymmetries in phase boundaries. For the simplest case of a single nearest-neighbor repulsion, E_1 (the disordering temperature is known exactly from the Onsager solution to the Ising model) is indicated by an × on the temperature-coverage phase diagram. The effect of adding a right-triangle trio repulsion, E_{RT}, a linear trio repulsion, E_{LT}, or both was studied by using Monte Carlo[55,57c] for the case $E_{\mathrm{RT}} = E_{\mathrm{LT}} = E_1/4$; the results for the three cases are plotted with filled triangles, squares, and circles, respectively, with dashed, dotted, and solid curves added to guide the eye. The behavior at $\theta = 0.5$ is anticipated by eqs 6 and 7. The dashed and dotted curves appear symmetric about $\theta = 0.5$ (short-dotted line); only with both trios present does the (solid) phase boundary become noticeably asymmetric. In the plots at the right, the ×'s and dots indicate occupied and vacant sites, respectively, in a perfectly ordered configuration, with the large symbols denoting a vacancy ($\theta < {}^1/_2$) or extra adatom ($\theta > {}^1/_2$), respectively. The arrows on the plots depict the lowest-energy excitations, with the line type of the shaft corresponding to the line type of the phase boundary on the phase diagram; for each line type, this excitation energy is the same for $\theta < {}^1/_2$ and $\theta > {}^1/_2$. In the simple argument, these energies scale the disordering temperature. When both trios are present, there is "frustration" over which excitation to use; the simple argument is not viable, and asymmetries occur. In the phase diagram, the broad dashed curve is the result of a mean field calculation, plotted at half its magnitude [i.e., $T_c(0.5) \approx 1.2\, E_1$]; not only is this curve far too large and broad, it also erroneously predicts substantial asymmetry.

$$T_c(E_2) = T_c(0)[1 - 4E_2/3E_1] \quad (5)$$

For this simple problem, Barber showed[58] that the exact coefficient is $\sqrt{2} \cong 1.41$ rather than $^4/_3 \cong 1.33$; on the other hand, our value is much better than the mean field prediction of 1. For this same problem, the effect of a right-triangle trio interaction E_{RT} (with $E_2 = 0$) is given by

$$(3E_1 + 2E_{\mathrm{RT}})/T_c(E_{\mathrm{RT}}) = 3E_1/T_c(0) \quad \text{or} \quad T_c(E_{\mathrm{RT}}) = T_c(0)[1 + 2E_{\mathrm{RT}}/3E_1] \quad (6)$$

Similarly, for a linear trio E_{LT}

$$T_c(E_{\mathrm{LT}}) = T_c(0)[1 + E_{\mathrm{LT}}/3E_1] \quad (7)$$

We caution that this procedure is applicable only if the new interaction does not alter the symmetry of the ordered state and works well only if the nearby elementary excitation from the fully ordered state is uniquely defined.

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Thus, it works well for a $\sqrt{3} \times \sqrt{3}$ overlayer on a triangular net but not for a p(2×2).[55] It is also curious that this procedure requires a lattice-gas picture in which the number of atoms is conserved (i.e., a canonical ensemble); if the atom instead hopped to a "bath" (i.e., a grand canonical ensemble, or fixed chemical potential, or a single-spin flip in a spin analogue), the predictions are quite poor.

To assess the effect of trios on the symmetry of the temperature-coverage phase boundary of a c(2×2) overlayer, we look at the elementary excitation near a defect, either an extra adatom or a missing one. (See Figure 2.) For just a right-triangle (RT) trio, there are no such trios (no $2E_{RT}$) in the excited state when there is a vacancy; when there is an extra, there are two RT trios in the ordered state, which are lost in hopping to the nearest neighbor (where another two RT trios occur). So in both cases, there is no change in the number of RT trios, i.e., no change proportional to E_{RT} is involved. A similar effect occurs with a linear trio, but with a different elementary excitation. (See Figure 2.) In either case, we saw that the phase boundary computed by using Monte Carlo appears symmetric. Only when *both* trios are present does a marked asymmetry occur. (M. E. Fisher pointed out, however, that a noteworthy inadequacy of this simple picture is its inability to give any idea of the coverage dependence of T_c.)

B. Asymmetries in Boundaries of Coexistence Regions. In the alternative case of a square lattice with $E_1 < 0$, there is a broad, symmetric coexistence region of low-density gas and high-density liquid centered (and peaked) at $\theta = {}^1/_2$. In this case, the presence of trio interactions should produce a shift in T_c and θ_c: For a honeycomb lattice with nearest-neighbor attraction E_1 and two trio interactions E_{IT} and E_{ET} for trimers forming an obtuse isosceles triangle (with 2 E_1 sides and an E_2 side, i.e., sequential sites) and an equilateral triangle (with E_2 sides), Goldstein and Parola[59] found, using perturbation theory

$$T_c(E_{IT},E_{ET})/T_c(0,0) = 1 - 3.732E_{IT}/(-E_1) - 1.732E_{ET}/(-E_1) \quad \text{and } \theta_c(E_{IT},E_{ET})/\theta_c(0,0) = 1 - 0.439E_{IT}/(-E_1) - 0.380E_{ET}/(-E_1) \qquad (8)$$

Similar results could presumably be generated, with more algebra, for the square lattice (with coordination number z of 4 rather than 3). By producing some "mixing" of the thermodynamic fields, the trios add nonanalytic terms to some observables, but since they do not favor any one ordered state over the others, these terms have the relatively mild energy-like form, with exponent $1 - \alpha$; the specific heat exponent α is small in 3-d, but in 2-d is substantial for non-Ising universality classes (e.g., ${}^1/_3$ for three-state Potts). In particular, in the T dependence of the "diameter" θ_d of the coexistence curve, i.e., the average of the coverages at the high- and low-density boundaries, normalized by θ_c, Goldstein and Parola argued[59] that the venerable law of rectilinear diameters is altered by the addition of the second term:

$$\theta_d = 1 + A_{new}(T_c - T)^{1-\alpha} + A_1(T_c - T) + \ldots \qquad (9)$$

For the honeycomb case, this result can be proved exactly.[60]

Some Monte Carlo (as well as mean field) results have been obtained for this square-lattice problem, with $E_1 < 0$. Milchev and Binder[61] supposed that at nearest-neighbor distances, there would be strong multiadatom ("nonadditivity") effects; such effects are particularly likely if the adatomic radius is comparable to (half) this distance, as for transition-metal adatoms. More generally, this supposition expresses the general trend for the strength of a chemical bond to decrease as the number of neighbors of the bonding atoms increases.[62] In the first case, they supposed that the interaction strength decreases linearly with the number m of nearest neighbors, from $|E_1(1)|$ to $|E_1(m)|$; the weakest bound is $|E_1(z)| = -W$, where z is coordination number and $P \equiv |E_1(1)|/W$. Explicitly, $|E_1(m)|/W = (Pz - 1)/(z - 1) - m(P - 1)/(z - 1)$. After some algebra, one can show[63] that this picture is equivalent to $E_1 = -PW$ an $E_T = (P - 1)W/2(z - 1)$. Simulations illustrate the shift of the critical point discussed above. In the second case, $E_1(1) = -PW$ while all other $E_1(m) = -W$. To produce this scenario on a square lattice requires strongly repulsive trios: $E_{RT} = E_{LT} = 2(P - 1)W$. There must also be a more attractive longer-range trio and a very repulsive quarto, with strength $4(P - 1)W$. For this seemingly arbitrary ansatz, they found a low-coverage region dominated by dimer aggregates, as casual inspection of the interactions would suggest. (However, their conclusion that this region constitutes a new *phase* seems ill-founded, as there need not be a phase transition from a dimerized phase to an undimerized phase.)

C. Other Examples. Chin and Landau[64] generated with Monte Carlo a global set of phase diagrams for a triangular lattice-gas with nearest-neighbor interaction E_1 and a trio E_T for the smallest equilateral triangle. We focus on the results for $E_1 > 0$, which produces $\sqrt{3} \times \sqrt{3}$ ordering. With no trio, there is particle-hole symmetry, with ordered phases peaking at $\theta = {}^1/_3$ and at $\theta = {}^2/_3$, with a minimum or zero at $\theta = {}^1/_2$. As $R_T \equiv E_T/2(E_1 + E_T)$ increases from 0, it first enhances the higher-θ phase (with two adatoms per triangle) relative to the lower-θ phase, then destroys the low-θ phase, and finally produces a coexistence region between "gas" and the higher-θ phase at the low-θ side of the ordered region, with a tricritical point where the boundaries join, with the opposite effect for $R_T < 0$. While the authors are careful to quote values in terms of the lattice-gas energies, it is noteworthy, when thinking about experimental ramifications, that the figures for $R_T = 0.2$, 0.5, and 1.0 correspond (analogously to eq 4) to $E_T/E_1 = {}^2/_3$, ∞, and -2, respectively, so that only the first case is likely to be observable. The special case $E_T = -E_1$ corresponds to vanishing nearest-neighbor coupling in the spin analogue; known as the Baxter-Wu model, it has been solved exactly in zero field ($\mu = -3E_1/2$).[65]

Trio effects have been considered in the simulations of phase diagrams of various adsorbates on a centered rectangular net: H/Fe(110),[66] O/W(110),[67-69] and Ag/

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W(110).[70] Unlike W or Re/W(110),[32] the long-bridge binding site chosen for simulations is less stable than the quasi 3-fold site,[28,36,71] but does reduce the number of close-separation configurations for which interactions should be considered.[72] For H/Fe(110) the physical importance of a set of impressive computations[66] was vitiated when subsequent experiments determined that the ordered state associated with some extra LEED spots had a different real-space pattern. For O/W(110) Kaski et al.[67] noted that there should be four trio interactions of comparable magnitude,[10] but that the ordered phases can be obtained with just one (the nearly equilateral triangle configuration) if its energy is appropriately rescaled; in a subsequent transfer-matrix finite-size scaling computation, this group achieved reasonable agreement with the measured phase diagram once they decreased the fifth-neighbor interaction from the previously used value.[11,72] In the most recent paper, Roelofs and Bellon[73] considered, with some caveats, a similar model for Cu and Au on W(110), starting with calculated[36] values for three short-range pair repulsions plus two different attractive trios and in the case of Au a repulsive quarto also. Computing the phase boundary using transfer-matrix finite-size scaling, they found that the calculated interactions qualitatively describe the experimental phase diagram,[69] producing the shifts described by Goldstein and Parola.[59] In an attempt to improve the fit, they described the effects of tuning the calculated interactions. While the effect of replacing the hourglass binding sites by a single site ("phonon renormalization") is unclear, they emphasized that with multisite interactions they could reproduce the essence of the phase diagram.

IV. Conclusions

In assessing current ability to compute trio interactions, we find that there are a variety of schemes that can produce numbers that are useful as a *starting* point for simulation studies, which are semiquantitatively sensible but not as reliable as most of the energies we have come to expect from electronic structure calculation. While far from a panacea, EAM offers a convenient and viable way to gauge relatively short range interactions. It is particularly effective on late-transition and noble metal substrates. (However, work is in progress to extend EAM to earlier bcc transition metals. It would be quite desirable to assess the common replacement of quasi 3-fold sites by long-bridge sites.) The adsorbates most reliably treated by EAM are also those with (nearly) filled d shells, but EAM can also be used for H. From recent successes using effective medium theory to describe oxygen-induced restructuring of Cu(110) and Cu(100),[74] we can hope EAM may also eventually be able to treat this important adsorbate.

Until recently most of the experimental evidence for trio interactions has come from phase diagrams measured with LEED and configuration "snapshots" obtained with FIM. With the recent surge of activity using scanning tunneling microscopy,[51] the latter sort of investigation will likely be significantly enhanced. As a particularly intriguing example, extensive observations of S/Re(0001) have very recently been obtained by Ogletree et al.[75] On the triangular net of adsorption sites, they found in addition to the familiar p(2 × 2), four peculiar higher-coverage, lower-symmetry ordered phases, which can only be explained in terms of *several distinct* trio interactions. Calculations of interactions within small clusters may well involve local relaxations of the substrate and small displacements of adatoms from high-symmetry positions. While such effects can be readily treated with the Sandia's EAM package (and have been assessed in some cases[42,53]), they would require a substantial increase of complexity in tight-binding approaches.[45] Similarly, direct interactions between moderately separated transition-metal adsorbates is included automatically in the EAM formalism without ad hoc assessment of hopping parameters. However, once one starts to worry about gradient corrections, one does face analogous questions of adjustment in EAM.

Another area of current activity is the study of kinetics on surfaces. The barriers to motion between stable adsorption sites often play a key role. To compute such barriers,[76] it will generally be necessary to take into account multisite interactions;[77] a particular complication will be local distortions in the intermediate state.

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