

ELASTIC INTERACTIONS BETWEEN SURFACE ADATOMS AND BETWEEN SURFACE CLUSTERS

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One major term is omitted in most conventional treatments of interactions between surface adatoms or groups of adatoms. This is the elastic interaction, in which adatoms interact through mutual distortion of the substrate. The indirect elastic interaction explains a range of observed surface phenomena in a consistent quantitative way. These phenomena include static and dynamic effects ranging from ordered structures to correlated motions of adatom clusters. It is likely also that substrate distortion is important in clean surface reconstruction. The elastic interaction is typically comparable with or larger than the indirect electronic interactions usually presumed. It follows that detailed calculations which ignore the substrate distortions produced will be of limited value only.

1. Introduction

Most treatments of interactions between adatoms on surfaces consider just two terms: direct adatom-adatom interactions, and indirect interactions via the perturbation of the electronic structure of the rigid substrate. These omit a major term which comes from the elastic distortion of the substrate by the adatoms, a contribution which is estimated in the present paper. The results indicate that the indirect elastic interactions play a central part in a variety of surface phenomena. These elastic interactions also exist between surface defects or between large clusters of adatoms, and they can be important for metal, semiconductor or insulator substrates. Examples of phenomena strongly influenced by elastic interactions fall into three broad categories. There are those which directly reflect interactions, like the pair-distribution functions, site occupancies and coverage-dependent heats of adsorption. There are the various orderings observed on surfaces including superstructures and possibly surface reconstruction. Finally, there are the remarkable correlated motions of adatom clusters, which are at least partly determined by elastic interactions.

2. Elastic Interactions

When a perfect substrate is distorted, the atomic displacements \underline{r} define the energy change in the harmonic approximation as $\frac{1}{2} \underline{v} \cdot \underline{G}^{-1} \cdot \underline{v}$. The lattice Greens' function \underline{G} is a function of the interatomic forces (or of the elastic constants for a continuum) and embodies the boundary conditions at the surface. When a defect or adatom is added to the surface, there is an

energy change $E_D(\underline{v}) = E_{D0} - \underline{F} \cdot \underline{v}$, where \underline{F} denotes the "defect forces". Several useful results hold for equilibrium under these forces:

- (i) The equilibrium displacements are \underline{v}_0 where

$$\underline{v}_0 = \underline{G} \cdot \underline{F} \quad (1)$$

- (ii) There is an enthalpy change $E_{D0} - E_R$ on adding the defect, where E_R represents the increase in strain energy and the work done by the defect forces:

$$E_R = \frac{1}{2} \underline{F} \cdot \underline{G} \cdot \underline{F} \quad (2)$$

- (iii) If $\underline{F} \equiv \underline{F}_1 + \underline{F}_2$ is the sum of terms from two distinct defects then the indirect elastic interaction between them is $(E_{R1} + E_{R2} - E_R)$ or

$$E_{INT} = - \underline{F}_1 \cdot \underline{G} \cdot \underline{F}_2 \quad (3)$$

i.e. the work done against the force \underline{F}_1 in creating displacements \underline{v}_{02} . It should be stressed that these interactions do not involve any changes in local force constants, surface softening or similar modifications; such changes only appear with higher order terms in $E_D(\underline{v})$.

The Greens function can be obtained in several ways. It can be approximated by the elastic continuum result for a half-space. This has been done by Mindlin [1] whose result for an elastically-isotropic continuum is especially useful for tungsten, a common substrate. For more complicated systems, computer methods are

needed, e.g. using programs like HADES [2]. There is one important common feature: at large distances $G(\underline{r})$ falls off as $|\underline{r}|^{-1}$. This is completely general for an infinite or semi-infinite harmonic system (see e.g. pps 181-3 of [3]). If, in addition, the forces \underline{F}_1 and \underline{F}_2 have a finite range much less than $|\underline{r}|$, then the interaction energy falls off as $|\underline{r}|^{-3}$ at large separations.

One factor which appears repeatedly is the virial of the defect forces, $\Lambda_{\alpha\beta}$. If the defect forces \underline{F}_i act at sites \underline{R}_i measured from the centre of force, then the virial is defined by:

$$\Lambda_{\alpha\beta} = \sum_i F_{i\alpha} R_{i\beta} \quad (4)$$

Thus if an adatom bridging two surface atoms at $(\pm a, 0, 0)$ relative to it applies outward forces F to each, $\Lambda_{xx} = 2Fa$ is the only finite term. This system will be used in later examples.

3. Isolated Adatoms and Their Interactions

Isolated Adatoms: The distortion of the substrate affects a number of observed properties. The vibrational frequencies of local modes will be altered, though this effect requires terms beyond those used in §2. Activation energies for adatom diffusion are also affected. Indeed, in some cases an adatom activation energy may be entirely caused by the associated distortion rather than some energy barrier. This is probably the case for hydrogen diffusion (for a discussion of the analogous bulk diffusion see [4]), as it is for electron transport by surface small polarons. The distortion also modifies any electronic transition energies associated with an adatom or surface defect.

This has been discussed in ref. [5] for the F_s^+ centre in MgO, an electron trapped at a surface vacancy.

The enthalpy of adsorption contains the term E_R of eq. (2). As the coverage increases the enthalpy of adsorption will change as the interaction terms E_{INT} become important. However the surface tension change $\Delta\sigma$ remains an additive property within the approximations of §2. If there are N adatoms per unit area of an x - y surface, and if the virial $\underline{\Lambda}$ of each defect and the surface Greens function do not change with N , then $d(\Delta\sigma)/dN$ is simply $\frac{1}{2}(\Lambda_{xx} + \Lambda_{yy})$.

Interactions between Isolated Adatoms.

Adatom-Adatom interactions are usually deduced from observed pair distribution functions. The three important factors for the interactions are their magnitude, their dependence on spacing r , and their anisotropy. Here the main features alone will be summarised, reserving detailed calculations for a separate paper.

First, the interactions can be substantial. For two bridging adatoms of the sort described at the end of §2, for example,

$$E_{INT} = \frac{F^2 a^2}{2\pi \mu r^3} \Phi(\nu, \underline{\Omega}) \equiv E_0 \Phi \quad (5)$$

where ν is Poisson's ratio, μ the shear modulus, and $\underline{\Omega}$ handles the anisotropy of the interaction.

If one combines the elastic constants for W with values for the virial for H in bcc metals [6], E_0 is around 0.1 eV. This is fully of the order indicated experimentally [7].

The second point is that the elastic interactions fall off relatively slowly with separation. As argued in §2, E_{INT} varies as r^{-3} when the defect forces have a finite range much less than r . The important feature is that the elastic interaction has longer range than the indirect electronic interaction. The purely-electronic part falls off rapidly, roughly as $\exp(-Br)$ or r^{-5} ([8], esp. p.3644), though an oscillatory form $\cos(Ar+\phi)/r^3$ is sometimes proposed. At large separations the elastic interaction will always dominate.

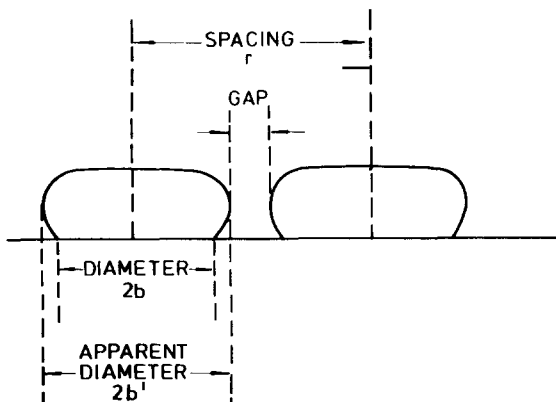
Thirdly, the interactions between adatoms can be strongly anisotropic. This is easily shown, e.g. for the interactions between two bridging impurities, from the precise form of Φ in eq. [5], though the expressions are complex and will not be reproduced here. However, the origin of the anisotropy can be seen from eq.(3). Basically, any anisotropic forces \underline{F}_2 will create anisotropic displacements $\underline{v}_{02} \equiv G \cdot \underline{F}_2$. Clearly the work done in creating these displacements against another set of anisotropic forces \underline{F}_1 will depend on the position of one defect relative to the other, even at constant r . An attractive interaction is expected if \underline{F}_1 dilates the regions compressed by \underline{F}_2 , or a repulsive interaction if both compress or dilate the same regions.

The anisotropy results from the anisotropy of the defect forces or from any substrate anisotropy reflected in \underline{G} . It should thus be quite a common feature. Most experiments are analysed in terms of purely radial interactions, often with a complex dependence on r . The same results may well be consistent with an anisotropic interaction with a simpler r -dependence.

Ordering of Adatoms: Many systems show ordered structures of adatoms, especially at high coverages. But others are seen at modest coverage, and result from longer-range interactions between the adatoms [9]. In at least three other cases similar ordering has been shown to arise from elastic interactions: the void lattice in radiation-damaged metals [10,13,14], the ordering of shear planes in non-stoichiometric oxides [11] and in interstitial alloys like V:N [12]. Thus it is natural to see if elastic energies give a significant contribution to the ordering here. There are two main questions, namely the energy gain from ordering, and the particular structures favoured. Both will be discussed in detail elsewhere, though two comments are appropriate. First, the elastic energy gains from ordering are a few kcal/mole, and are comparable with those reported experi-

mentally. Secondly, there is a choice of methods for the theory of these structures. In bulk crystals a reciprocal lattice method is favoured [13] over the direct-space form [14] because of convergence problems. For surfaces, both approaches are satisfactory.

Surface reconstruction: The principles of adatom ordering just discussed apply equally to any surface imperfection, including local surface rebonding. Clearly there is an elastic distortion energy associated with any reconstructed surface, and it is likely that this plays an important rôle. One of the puzzles of surface reconstruction is the variety of structures seen



(b) The function $f(x)$ for equation (6).

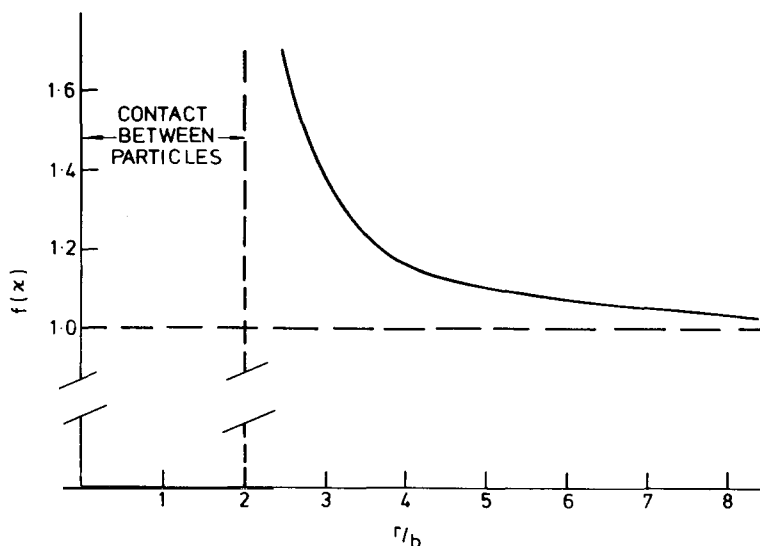
for a single system, those on Si being especially varied [15]. Several explanations have been given, usually based on impurity effects or on exotic features of the host one might not expect to find as often as observation would require. The importance of the elastic strain energy

associated with the various possible reconstructions arises because the distortion can effectively stabilize a metastable configuration by providing an activation barrier against relaxation to a more stable geometry. Suppose some pattern of surface rebonding is set up, with or without impurity cooperation. Then a finite strain energy must be supplied to distort the system to a new structure before the gain in bonding energy can be achieved. This strain energy provides the activation barrier.

4. Microcrystals or Adatom Clusters on Surfaces

When evaporated-metal films are prepared on insulators or semiconductors, small metal clusters are formed in the early stages. The clusters typically contain tens or hundreds of metal atoms and have a diameter of a few nanometres. They can be important catalysts, e.g. in the oxidation of a graphite substrate, and they may move over surfaces at speeds of up to tens of nanometres per second. Evidence for cluster-cluster interactions comes from correlations in these observed motions [16], from the pair distribution function of the clusters [17], and from a noticeably reduced probability of coalescence [18]. Typical forces between clusters are of the order of 10^{-7} to 10^{-6} dynes.

Possible interaction mechanisms have been discussed by previous workers [19] who conclude the elastic interactions dominate. The present work leads to the same conclusion by a different method. The result can be summarised for the system in fig. 1a, where the clusters have a circular area of contact with the substrate. If b is the radius of contact, r the spacing of centres, and if μ is the shear modulus, ν is Poisson's ratio and γ the interfacial tension, then the interaction energy is:



(a) Geometry of interacting metal atom clusters. This illustrates a case where the apparent radius from microscopy (b') is different from the contact radius (b).

$$E_{\text{int}}(r) = \frac{\pi(1-\nu)}{2\mu} \gamma^2 b^2 \left(\frac{b}{r}\right)^3 f(r/b)$$

$$= E_{\text{io}}(b/r)^3 f(r/b) . \quad (6)$$

Here $f(x)$ tends to unity at large x ; its form at small x is shown in fig. 1b. At large distances one finds the r^{-3} dependence expected from §2. Further, the interactions have the right order of magnitude. With $\nu = \frac{1}{4}$, $\mu = 10^{11}$ dynes/cm², $\gamma = 10^3$ ergs/cm² [20] and $b = 10\text{\AA}$ an energy E_{io} of 8.4 kcal/mole is obtained, and a force $(1.8 \cdot 10^{-5} \text{ dynes})(b/r)^4 \times (1 + d \ln f / d \ln(r/b))$. Both values are in satisfactory accord with experiment.

Dynamic behaviour: Remarkable cluster behaviour has been observed [16a], including rapid correlated motions of Fe particles over a graphite substrate. Many of the features can be understood with two assumptions. First, the iron particles move by driven diffusion, i.e. with a velocity $(D_p/kT)F$ where F is the driving force. Here D_p is the cluster diffusion constant, related to the atomic diffusion constant D_A within the particle by $D_p/D_A \sim (a/R)^{-4}$ [21] with R/a the

particle radius in units of the atomic radius. It is probable that the moving particles are liquid. Secondly, the repulsive interactions giving the forces F are elastic in origin. Whilst many aspects are still uncertain, two quantitative predictions support this model: the magnitudes of the observed velocities and expected forces are consistent, and the activation energy for the observed motion (15.2 kcal/mole) is close to that expected for liquid Fe (15.7 kcal/mole [22]).

Conclusions - The analysis outlined in this article has shown (1) that surface defects or adatoms distort the substrate and hence have an important mutual interactions, (2) that this interaction explains a range of observed surface phenomena in a consistent quantitative way, and (3) that the elastic interaction is usually comparable with or larger than the indirect electronic interaction usually considered. As a corollary, the results of the many detailed calculations which ignore the distortions produced are likely to be of very limited value.

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REFERENCES

1. R.D. MINDLIN, Phys. 7 195 (1936).
2. A.B. LIDIARD and M.J. NORGETT, in "Computational Solid State Physics" (Plenum 1972 p385). For an application to surfaces see W.C. Mackrodt and R.F. Stewart, J.Phys. C10 1431 (1977).
3. A.M. STONEHAM, "Theory of Defects in Solids" (Oxford University Press 1975).
4. C.P. FLYNN and A.M. STONEHAM, Phys.Rev. B1 3403 (1970).
5. R.R. SHARMA and A.M. STONEHAM, J.Chem.Soc., Faraday Trans. II 72 913 (1976).
6. H. WIPF, J.Less Common Met. 49 291 (1976).
7. T.T. TSONG, Phys.Rev.Lett. 31 1207 (1973) G.ERTL and D. SCHILLINGER, J.Chem.Phys. 66 2569 (1977).
8. T.L. EINSTEIN and J.R. SCHRIEFFER, Phys.Rev. B7 3629 (1973).
9. L.D. SCHMIDT, Springer Topics in Applied Physics 4 64 (1975).
P.J. ESTRUP and J. ANDERSON, J.Chem.Phys. 45 2254 (1966).
P.W. TAMM and L.D. SCHMIDT, J.Chem.Phys. 51 5352 (1969), 54 4775 (1971).
H. FROITZHEIM, H. IBACH and S. LEHWALD, Phys.Rev. B14 1363 (1977).
10. A.M. STONEHAM, p319 of AERE-R7934 (HMSO, London 1974).
11. A.M. STONEHAM and P.J. DURHAM, J.Phys.Chem.Sol. 34 2127 (1973).
12. V. TEWARY, J.Phys. F3 1275 (1973).
13. A.M. STONEHAM J.Phys. F1 778 (1971).
14. K. MALEN and R. BULLOUGH, Proc.Brit.Nucl.Eng.Soc. Reading Conference 1971 (ed. Pugh, Loretto and Norris) p.109.
15. See e.g. G.A. SOMORJAI and L.L. KESMODEL, Int.Rev.Sci., Phys.Chem.Ser. 2, 7 1 (Butterworths 1975).
- 16(a) R.T.K. BAKER, P.S. HARRIS and R.B. THOMAS, Surf.Sci. 46 311 (1974).
- (b) J.J. METOIS, K. HEINEMANN and H. POPPA, Appl.Phys.Lett. 29 134 (1976).
17. J.C. ZANGHI, J.J. METOIS and R. KERN, Phil.Mag. 31 743 (1975).
V.I. TROFIMOV, Sov.Phys.Sol.St. 17 1649 (1976).
18. D. ROBERTSON, J.Appl.Phys. 44 3924 (1973).
19. J.C. ZANGHI, J.J. METOIS and R. KERN, Surf.Sci. 52 556 (1975).
This formulation is distinct from that in §2, but broadly equivalent in physical content.
20. Convenient sources of interfacial energies are:
L.E. MURR "Interfacial Phenomena in Metals and Alloys" (Addison Wesley 1976).
T.M. VALENTINE, AERE Report R8377 (1976).
21. e.g. Y.E. GEGUZIN and M.A. KRIVOGLAZ, "Motion of Macroscopic Inclusions in Solids" (Consultants Bureau 1973).
22. L. YANG, M.T. SIMRAD and G. DERGE, Trans.Met.Soc. AIME 206 1577 (1956).