Strain-induced interaction energies between hydrogen atoms in palladium

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Abstract. We have made quantitative calculations of the elastic interactions between interstitial hydrogen atoms in Pd metal. These calculations use the Harwell HADES code, and hence go beyond the usual harmonic models. Results have been obtained for several potentials and, where appropriate, agree well with those of previous workers. We find (i) that the absolute values are sensitive to assumptions for the potentials, suggesting caution in the prediction of thermodynamic properties, and (ii) that there are significant few-body terms not included in the usual approaches. These extra terms will affect the equilibrium structure, for example by removing the symmetry between fractional occupancies θ and $(1 - \theta)$, and may lead to the initial nucleation of metastable structures during hydrogenation. The present results suggest that corner-sharing tetrahedra are favoured.

1. Introduction

It is convenient to begin with a question of vocabulary, since not all workers adopt a consistent convention for the terms 'energy', 'potential' and 'interaction'. The total energy E_{TOT} (not calculated in this paper) is not just the sum of one-electron eigenvalues, but it includes nuclear–nuclear terms and corrections for double-counted electron–electron interactions. The variation of E_{TOT} as a function of atomic positions is represented by a sum of two-body *potentials*, e.g. Pd–H potentials, often obtained empirically in a convenient analytic form. The total energy, calculated including lattice relaxation to equilibrium, can also be expressed in terms of the site occupancies only (i.e. not involving the precise distorted geometric positions), and this defines the H–H *interactions* which are used in the simulation of phase diagrams. These points are discussed further by Stoneham (1983). Here we shall use *two*-body potentials to show the existence of significant *few*-body interactions.

It is widely recognised that there are important elastic interactions between hydrogen interstitials in metals and metal hydrides. These are a natural consequence of the distortions each hydrogen atom produces and which are directly observed. In dilute solutions, the excess chemical potential of H, μ_H^E, decreases, i.e. it becomes more exothermic, with increasing hydrogen concentration, $r(= H/Pd)$. Brodowsky (1965) attributed this decrease to strain-induced (direct) attractive interactions solely between nearest-neighbour H atoms. Alefeld (1972), on the other hand, discussed the way in which the volume expansion, accompanying H dissolution in metals, gives rise to a substantial

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indirect, image contribution to the elastic interaction energy. Subsequently, Wagner and Horner (1974) and Horner and Wagner (1974) showed how the lattice theory of defects could be used to calculate the direct and indirect elastic interactions, and Dietrich and Wagner (1979) have calculated both for the Pd–H system. They also note that the elastic interactions by themselves are insufficient to account for the whole of the observed decrease in μ_H^E in this particular system. Electronic interactions must also be considered, and both they and Khan *et al* (1981) have attempted to calculate these.

In the Horner–Wagner calculation of the direct elastic interaction the host lattice is assumed to be harmonic, the metal–hydrogen interaction is assumed to be linear, and only pairwise interactions between H atoms are considered. One assumption is especially important, namely that the interactions are pairwise: the interaction between any two hydrogen atoms is assumed to be independent of any other nearby hydrogen atoms. Wagner (1978) has attempted to justify the neglect of any many-body interactions and changes in force constants.

In the present work, a computer simulation model has been used to calculate the strain-induced interaction energies. These simulations have the advantages over analytical methods for central pairwise calculations that assumptions regarding the force constants are unrestricted and that defect clusters may be considered just as readily as pairs so that the presence of any many-body effects is readily discernible. A primary aim was to test the accuracy of the assumptions made by Horner and Wagner. A secondary aim is to note the role of pairwise and non-pairwise interactions in phase structure and phase transitions. Pair interaction energies were used by Dietrich and Wagner (1979) in a Monte Carlo calculation of the configurational partition function for Pd–H alloys. This determines the equilibrium structure. However, non-pairwise interactions are particularly important when a new phase is nucleating or when order is developing. The structures which are favoured for small nucleation clusters may differ from the final ordered equilibrium forms.

2. Model and potentials

2.1. Techniques for lattice relaxation

The calculations were made with the HADES computer program, which was designed to calculate the energies of defects and defect aggregates in ionic materials by using the shell model. Detailed descriptions of the model and program are available elsewhere (Lidiard and Norgett 1972, Catlow and Norgett 1976). The essential nature of the calculation is that lattice displacements and energies are evaluated explicitly in the region immediately surrounding the defect (region I) where most of the distortion occurs. The harmonic approximation is not assumed. The energy of this region is minimised by an extremely efficient method in order to find the optimum configuration. Far from the defect (region II) the crystal is treated in the harmonic approximation, its relaxation energy being obtained from the product of the forces due to the distortion of the inner region and the displacements of the atoms in region II. In order to ensure a smooth transition of the calculated displacements by the two different methods of calculation in the two regions, the displacements for the inner part of region II are evaluated explicitly, the remaining outer part being treated as a continuum. For the results reported in the present work the 'crystal' contained approximately 1500 atoms with approximately 450 atoms in the explicit region. These choices were found to give a satisfactory compromise between the increasing insensitivity of the calculated relaxation energies to the increasing size of region I and the

concomitant increase in computing time. As is desirable in this type of calculation the sizes of the regions were kept constant for the different defect aggregates considered.

The difference between the total potential energy of the crystal in the unrelaxed and relaxed states gives the total relaxation energy. The total interaction energy is given by the difference between the relaxation energy of the defect cluster of size N atoms and N times the single-defect relaxation energy.

The HADES program can be used for 'metals' if a very large harmonic coupling constant between core and shell is used so that no ionic polarisation due to the relative displacement of core and shell is permitted to take place.

2.2. Interatomic potentials

The ideal metal–metal interatomic potential should reproduce all those properties of the perfect crystal which are determined by the total energy function of atomic positions. In practice, empirical potentials are usually derived by fitting to a selection of experimental results, e.g. cohesive energy, elastic constants, vacancy and stacking fault energies, etc (Johnson 1973, Stoneham and Taylor 1981). A 'total' potential which holds the metal in equilibrium at the correct lattice parameter may be derived or, alternatively, a 'core' potential may be obtained which describes only energies at constant volume. The 'core' potential by itself does not give the correct equilibrium condition; a volume-dependent energy term must also be incorporated. Clearly the metallic nature of a solid is partly associated with the electron-gas terms and their volume dependence. When one uses a 'total' potential the metallic nature is only implicit.

A simple central two-body 'total' potential implies the validity of Cauchy's relation, $C_{12} = C_{44}$, between the elastic moduli, whereas this is known to be invalid for Pd. This problem may be overcome by using a 'core' potential, if the complementary Cauchy pressure is used in the volume-dependent term. One such 'core' potential has been derived for Pd by Baskes and Melius (1979). However, its use in the present work would have entailed giving similar attention to the volume-dependent term in the Pd–H interaction and this, in turn, would have meant evaluating only the structural contribution to the forces exerted by the H impurity. It seemed more straightforward, therefore, to retain a 'total' Pd–H potential and this then necessitated a 'total' Pd–Pd potential. Subsequently, it was found that the interaction energies between H atoms were to a large extent independent of the Pd–Pd interatomic potential chosen, so long as the potential describes the elastic properties approximately. Thus the choice of a 'total' potential is not considered to be a serious limitation of the present calculations, and such a choice also enabled a direct comparison of the computer simulation results with those of Dietrich and Wagner (1979) and of Johnston and Sholl (1980) for the relaxation energies in this system. Their harmonic lattice calculations are equivalent to using a restricted form of a 'total' potential.

The Pd–Pd potentials calculated by van Heugten (1979) from fitting the phonon dispersion curve were used. The three potentials given by him, which are tabulated in the compilation of Stoneham and Taylor (1981), differ in the number of neighbours considered in the fitting process. Most of the present calculations were carried out using the potential based on nearest neighbours only and all the results reported here refer to this potential. It gives elastic constants which differ by no more than a few per cent from the experimental values for Pd. We shall ignore any dependence of the Pd–Pd potentials on hydrogen concentration.

In the same spirit, we have chosen total potentials for the Pd–H interaction, even though there are some indirect (Wagner 1978) and delocalised (Stoneham 1983) terms

whose magnitude is hard to estimate. Three different Pd–H potentials were used. All were based on the harmonic result (Hardy 1960, 1968; see also Eshelby 1956, Temkin 1970, Stoneham 1975) relating defect formation volume to defect forces:

$$\Delta V = \frac{1}{3B} \sum_i F_i^* R_i \tag{1}$$

where the defect forces F_i^* are evaluated at the *relaxed* configuration of metal atoms initially at the perfect lattice sites R_i. Schober and Ingle (1980) have discussed the consequences of breakdown of the harmonic approximation. In our case, where we have to postulate suitable forces, any difficulties of this sort will simply affect the extent to which the predictions agree from model to model.

Potential 1 was based on a model where constant forces are assumed to act on nearest-neighbour Pd atoms only, this being the model adopted in the calculations of both Dietrich and Wagner (1979) and Johnston and Sholl (1980). From available data for the Pd–H system, the dipole strength, P, was calculated to be 3.15 eV, which is equivalent to a force F_1 of 0.809 eV Å^{-1} at the metal atom sites. These values come from the values $\Delta V = 2.80$ Å^3 atom^{-1} (Peisl 1978) and $B = 18.053 \times 10^{10}$ Pa (Salama and Ko 1980).

Potential 2 was also a constant force model but the forces were assumed to act on both the first and second nearest Pd neighbours. The forces on the second nearest neighbours were assumed, quite arbitrarily, to be one quarter of that acting on the nearest neighbours. With the same dipole strength the forces at the unrelaxed sites were calculated as $F_1 = 0.513$ and $F_2 = 0.128$ eV Å^{-1}.

Potential 3 was of the Born–Mayer form, $\psi = A \exp(-R/\beta)$. With this potential there is the opportunity to use the optical mode frequency as a parameter in giving further information about the Pd–H potential. The chosen potential was assumed to give forces acting on nearest-neighbour Pd atoms only. It is readily shown that a classical harmonic oscillator vibrating in a 'breathing' octahedral cage will do so with a frequency given by

$$w^2 = \frac{2}{m} \left(\psi'' + \frac{2\psi'}{r} \right) \tag{2}$$

where the first and second derivatives of U are evaluated at the unrelaxed positions. Using the optical mode frequency obtained by Drexel *et al* (1976) and by matching the single-defect relaxation energy with that obtained from potential 1, the following potential was obtained (in eV for R in Å):

$$\psi = 12.36 \exp(-R/0.6068). \tag{3}$$

This potential gives slightly different displacements, and hence different forces, at the relaxed positions from those calculated using potential 1. It follows, therefore, that the defect volume is also slightly different from that which was used in calculating potential 1.

All three potentials were cut off at a distance which exceeded the appropriate neighbour distance.

3. Results and discussion

3.1. Single H atom

The three potentials gave the following relaxation energies for a single H atom at an

octahedral site:

potential 1 (meV)	133.6
potential 2 (meV)	60.4
potential 3 (meV)	133.8.

The way in which potential 3 was chosen ensures a value close to that for potential 1. The result for potential 1 may be compared with the value of 161 meV obtained by Johnston and Sholl (1980) from a harmonic lattice calculation. The differences are due mainly to the slightly lower dipole strength used here. Our relaxation energy, 133.6 meV, scaled by the square of the ratio of their value of P to ours, $(3.5 \text{ eV}/3.15 \text{ eV})^2$, gives 164.9 meV, close to the value of Johnston and Sholl.

The sensitivities of these relaxation energies, and those for pairs and clusters given below, to details of the Pd–H potential are sufficient in themselves to emphasise that, although data relevant to the Pd–H system were used in deriving the interatomic potentials, it would be unrealistic to believe that the present calculations are quantitatively applicable to the actual Pd–H system.

In the calculation of the homogeneous contribution to the elastic free energy the effect of volume changes on the relaxation energy is of interest. Using potential 1, for which the defect forces are the same in each case, the following effects were found:

lattice parameter (Å)	relaxation energy (meV)
3.80	145.3
3.89	133.6
4.00	119.9

Clearly the relaxation energy is lower as the cell volume Ω_{cell} increases. We can express the results approximately as

$$\partial \ln E_{rel}/\partial \ln \Omega_{cell} \simeq -1.24.$$

Since the relaxation energy is inversely proportional to a lattice force constant $K \equiv M_{Pd} \omega^2$, and since one expects $\partial \ln \omega/\partial \ln \Omega_{cell}$ to be given by the Grüneisen constant, $-\gamma$, we might have anticipated

$$\partial \ln E_{rel}/\partial \ln \Omega_{cell} \simeq +2\gamma.$$

The predicted relaxation energy changes correspond to $\gamma \sim -0.62$. This is sensible in magnitude; the unexpected negative sign presumably comes from some feature of van Heutgen's potential.

3.2. Pairs of H atoms

The results for various pair interaction energies, calculated from the three Pd–H potentials, are shown in table 1. The results of Dietrich and Wagner (1979) are also shown for comparison with those obtained from potential 1, both as given originally and scaled to compensate for different choices of dipole strength. The differences between the two sets of results are due principally to the different choices of the dipole strength, but some of the differences result from whether or not the harmonic approximation is used for the Pd–Pd potential.

Table 1. H–H pair interaction energies (in meV) calculated from different Pd–H interatomic potentials. The separation vector for the pairs is expressed in units of $a/2$. The results in parentheses scale values from Dietrich and Wagner (1979) by $(3.1/3.5)^2$ to compensate for a different choice of dipole tensor. Negative values are attractive.

Pair vector	Potential 1	Dietrich and Wagner (1979)	Potential 2	Potential 3
1, 1, 0	− 10.93	− 16.04(− 13.0)	− 24.8	− 37.21
2, 0, 0	+ 21.45	+ 26.31(+ 21.3)	+ 2.51	+ 9.84
2, 1, 1	− 2.83	− 10.37(− 8.4)	+ 3.04	+ 0.15
2, 2, 0	+ 7.03	+ 6.82(+ 5.5)	+ 3.35	+ 6.74
3, 1, 0	+ 4.47	+ 1.84(+ 1.5)		
2, 2, 2	+ 3.23	+ 2.83(+ 2.3)		

The sensitivity of the calculated interaction energies to the Pd–H potential chosen, even to the extent of changing the sign of the interaction energy, is apparent from the results in table 1. This again emphasises the need for caution in taking calculated interaction energies reported in the literature and applying them quantitatively to a specific system.

A direct H–H interaction energy is readily incorporated into the HADES program. Its influence on the strain-induced interaction energies discussed above was examined briefly. The H–H potential was estimated from knowledge of the difference between the observed values for μ_H^E and an estimate of the total elastic energy. It was found that, by using this potential, the *direct* forces between H atoms are so small compared with those in the H–Pd interaction that the influence on the calculated defect energies is negligible. This validates the superposition of strain-induced elastic and chemical interaction energies in the evaluation of pairwise interaction energies to be used in, for example, a Monte Carlo calculation. As discussed above, the main problem lies in the quantitative accuracy and significance of the calculated strain-induced interaction energies. The direct H–H interaction has a distinct and important role in site exclusion, by ensuring that only one hydrogen atom occupies a specific interstitial site and possibly preventing occupation of other near-neighbour sites by hydrogen atoms.

3.3. H atom clusters

Small clusters are of interest both because they control nucleation of ordered phases during hydrogenation and because of their role in hydride thermodynamics. The cluster variation method (CVM) appears to be a most satisfactory approximation for calculating the thermodynamic properties of alloys (Kikuchi 1978). An approximate combinatorial formula is used for calculating the entropy which is based on larger basic figures (clusters) than used in pairwise schemes. The cluster energies can be calculated on the basis of pairs or, alternatively, distinct clusters may be given distinct energies, thereby enabling many-body interactions to be introduced into the internal energy. The tetrahedron approximation has been used for FCC solutions (Kikuchi and Sato 1974) and this would be an appropriate choice for the Pd–H system where the interstitial sites form a FCC sublattice. Accordingly, some calculations were carried out in order to see whether many-body effects in the elastic interactions are apparent in the basic tetrahedron, built up of nearest-neighbour pairs, and whether such effects also show up if the tetrahedron is taken as the basic unit. The results are shown in table 2.

We can see immediately that there are significant non-pairwise interactions. In quite a few cases these excess terms are larger than the interaction between two hydrogen atoms at

Table 2. Actual calculated and sum of calculated pairwise interaction energies from potential 1 (in meV) of clusters related to tetrahedra. Geometries are chosen to give neighbours at (110) or equivalent spacings where possible. Negative values are attractive. Case A: actual interactions attractive, with attraction enhanced over pairwise value. Case B: actual interactions attractive, but with attraction reduced relative to the pairwise value. Case C: actual interactions repulsive, but less repulsive than with pairwise interactions.

Defect	Number of atoms	Pairwise interaction energy (meV)	Actual interaction energy (meV)	Actual interaction energy per H atom (meV)	Approximate excess of actual over pairwise per H atom (meV)
1, 1, 0 pair	2	− 10.93	− 10.93	− 5.46	—
Case A					
Equilateral triangle ⟨110⟩ edges	3	− 32.67	− 34.84	− 11.61	− 1
Isosceles triangle (two ⟨110⟩ and one ⟨200⟩ edges)	3	− 0.41	− 1.6	− 0.53	− 0.4
Tetrahedron with ⟨110⟩ edges	4	− 65.34	− 71.8	− 17.95	− 1.6
Octahedron (⟨110⟩ edges)	6	− 66.81	− 102.77	− 17.13	− 6
Two tetrahedra with shared edges	6	− 82.39	− 114.78	− 19.13	− 5
Two tetrahedra with shared corners	7	− 115.17	− 172.68	− 24.67	− 8
Four tetrahedra, tetrahedrally arranged, sharing one corner	13	− 161.82	− 324.64	− 24.97	− 12.5
Corners and face centres of ⟨200⟩ edged cube	14	− 42.37	− 241.46	− 17.2	− 14.2
Case B					
Linear ⟨200⟩ triad	3	− 21.86	− 17.12	− 5.70	+ 1.6
Case C					
Square (⟨200⟩ edges + central atom)	5	56.41	50.41	10.1	− 1.2
Cross (⟨200⟩ axes)	5	113.92	100.37	20.1	− 2.7
Cube (⟨200⟩ edges)	8	354.68	303.48	37.9	− 6.4
Inscribed squares (⟨200⟩ inner edges, ⟨220⟩ outer edges)	8	40.54	20.76	2.6	− 2.5
Inscribed square + central atom	9	82.62	50.78	5.6	− 3.5

their closest separation. Further, the non-pairwise terms are usually attractive. In all but one case the binding energy is increased or the repulsion diminished. In no case is the sign of the interaction changed and in no case is a repulsion enhanced. The few-body terms become rather more important as the cluster size N increases. Initially this occurs for purely combinational reasons: for N particles there are $N(N-1)/2$ pairwise interactions and $N(N-1)(N-2)/6$ three-particle terms. Once the cluster size exceeds the range of the interaction, the ratio will level off, of course.

One striking result, which needs further investigation, has implications for the

nucleation of a new phase. We can see that the clusters comprising tetrahedra with shared corners are especially stable. For both the seven cluster (two tetrahedra) and the thirteen cluster (four tetrahedra), bindings of almost 25 meV per H atom are predicted. This stability will come as no surprise to those familiar with oxide defect structures (for a summary, see Catlow and Stoneham 1981). The basic tetrahedral unit has more modest binding (around 18 meV per H atom), close to the corresponding energies for quite different clusters like octahedra. Because of possible competition between simple clusters, there may be a nucleation barrier to growth of a corner-sharing tetrahedra phase because the isolated tetrahedral unit is less strongly stabilised.

3.4. Concentrated solutions

The elastic interaction energies presented for pairs and clusters refer to what is essentially the infinitely dilute solution. In the calculation of the partition function for concentrated solutions it is desirable to know how these interaction energies vary with concentration. It is clear from the cluster results given above that the presence of many other H atoms influences the ability of the metal atoms to relax. When all the interstitial sites are occupied the local relaxations, and hence the 'direct' elastic interactions, must be zero, there being only a homogeneous contribution to the elastic energy. Thus elastic interaction energies, whether based on pairs, tetrahedra, etc, will be expected to decrease as the defect concentration is increased.

   As the hydrogen concentration changes, there are two distinct effects. One, from the volume change, is independent of the precise arrangement of the hydrogen atoms. For PdH_x, one could consider every interstitial site as being filled with a 'fractional' hydrogen atom giving a homogeneous system of the right volume. The second term is the configuration-dependent elastic term obtained by redistributing 'fractional' hydrogen atoms to give an 'alloy' with empty and full sites as components. The configuration-dependent term is obtained from our HADES calculations. Limiting forms of the configuration-dependent term, simpler in some respects, are also given by Froyen and Herring (1982), Eshelby (1955) and Hardy (1960). The configuration-dependent elastic energy has the form $N\theta(1-\theta)E_0$ for N sites with fractional occupancy θ. This has the limit discussed already as $\theta \to 1$; it is also symmetrical, in the occupancies of the two species, i.e. θ for hydrogen atoms or $(1-\theta)$ for vacancies. This symmetry will be lacking in more general models.

4. Conclusions

A computer simulation of the short-range, strain-induced interactions between H atoms in Pd has been carried out. The interatomic potentials used in this simulation are 'total' potentials, similar to that used in an analytical treatment by Horner and Wagner and applied by Dietrich and Wagner to the Pd–H system. The computer simulation does not have the same restrictions imposed as are present in the analytical approach.

   It has been found that the elastic interaction energies are very sensitive to the chosen form of the Pd–H interatomic potential, even when the different potentials have been derived from the same experimental input data. Since there is no way of knowing which is the best potential, little reliance can be placed on the *quantitative* significance of such interaction energies. There is a great need to have accurate information about the metal–hydrogen interactions. There is some evidence (Browne 1982, Browne and

Stoneham 1983) that metal–hydrogen potentials have reasonable transferability, so that new types of experimental data can be used in modelling potentials.

One important result is that the interaction energies of clusters of H atoms cannot be regarded as the sum of the pairwise interactions, i.e. many-body effects are present. This is also true when the tetrahedron is taken as the basic unit, as favoured by our calculations. Likewise, the interaction energies derived for isolated defect aggregates in the pure metal lattice cannot be expected to be appropriate for use in concentrated solutions. The presence of other H atoms and clusters will have a marked effect on the total strain-induced interaction energy.

These conclusions raise serious doubts about the use of concentration-independent interaction energies, whether based on pairs or larger units, in configurational models of Pd–H and other interstitial alloys.

Acknowledgments

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