

Configuration-independent elastic interactions in metal–hydrogen solutions

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Abstract. We demonstrate quantitative methods for estimating that part of the elastic interaction energy between defects in solids which does not depend on the precise spatial arrangement of the defects. This energy involves both the total volume change per defect in the finite solid and the purely shear part of the volume change. Several different continuum and atomistic modelling methods are used to calculate these volume changes for H in Pd, V, Nb and Ta. An estimate of the configuration-independent elastic interaction energy is made for the Pd–H system as a function of the H concentration, and is given in a form suitable for comparison with statistical models.

1. Introduction

The early statistical-mechanical calculation on the Pd:H system by Lacher (1937) was based on a lattice-gas model in which pairwise attractive interactions were assumed between nearest-neighbour hydrogens. Subsequently Brodowsky (1966) suggested that a direct elastic interaction was responsible for these empirical attractive interactions. Alefeld (1972) noted, however, that there were also indirect effects in a deformable lattice with a stress-free surface. These indirect attractive terms are configuration independent, i.e., they do not depend on the precise arrangement of the hydrogens relative to one another, and they make no contribution to solute correlations. Nevertheless, these configuration-independent interactions can be a substantial fraction of the total elastic energy, and they should be subtracted from experimental data before comparisons are made with results from model calculations of the configuration-dependent terms. When comparing model calculations with experiment one should not ignore the corresponding purely electronic term which would exist even in a rigid lattice. This comes from the hydrogen-induced shift in the Fermi level which will itself lead to both a volume change and a modification of the defect forces giving the elastic interaction (Stoneham 1983a, b).

The origin of these indirect configuration-independent elastic interaction terms can be seen readily. When a hydrogen enters a lattice with a stress-free surface, it causes a volume change ΔV . This ΔV is the sum of a contribution ΔV_D dilating the crystal as a whole and a contribution ΔV_S from shear alone (Eshelby 1955, 1956). The dilation works against the defect forces of other hydrogens already present, so an indirect interaction energy E_I per

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pair of hydrogens results. Simple arguments (e.g., that ΔV is the result of a defect 'pressure' $p_D \equiv -B\Delta V/\Omega_T$, where B is the isothermal bulk modulus and Ω_T is the crystal volume, so that the work done is $p_D\Delta V_D$) show that $E_1 = -B\Delta V\Delta V_D/\Omega_T$. The negative sign for E_1 implies an attractive interaction between like defects.

Two main descriptions have been used to divide ΔV into ΔV_S and ΔV_D . The first is continuum elasticity theory; in this continuum limit $\Delta V_S/\Delta V$ and $\Delta V_D/\Delta V$ are simply functions of the elastic constants. The second approach uses an atomistic description of the host lattice, with pairwise (or possibly more complex) interatomic forces (Horner and Wagner 1974, Wagner 1978, Dietrich and Wagner 1979, Futran *et al* 1982). In the linear approximation the ratios of the sums over interactions ($\sum_{ab} W_{ab}^\infty$ and $\sum_{ab} W_{ab}$ of Horner and Wagner (1974)) define $\Delta V_S/\Delta V$ and $\Delta V_D/\Delta V$. Both approaches have advantages. The continuum method models correctly all the long-range interactions, and (with numerical evaluation of certain integrals) models correctly the changes with temperature or degree of hydrogenation. The lattice methods have the advantage that the configuration-dependent and configuration-independent terms are calculated in a consistent and equivalent way. In the present paper we shall estimate the elastic interactions which depend on the hydrogen concentration but not on its disposition.

2. Calculations of ΔV , ΔV_D and ΔV_S

In discussing the different volume changes it is convenient (Eshelby 1956) to introduce the coefficients γ and γ' where

$$\gamma = \Delta V/\Delta V_S \quad (1)$$

$$\gamma' = \Delta V_D/\Delta V = 1 - (1/\gamma). \quad (2)$$

Several approaches for calculating the volume change ΔV , the uniform dilatation component ΔV_D and the pure shear component ΔV_S are possible. In most of the examples given below we shall refer to Pd:H, using a nearest-neighbour model potential due to von Heugten (published by Stoneham and Taylor (1981)) which was also adopted by Oates and Stoneham (1983). These provide a convenient reference case, although, for reasons discussed by Oates and Stoneham, one should be cautious of expecting detailed agreement with experiment because of the limitations of the potentials. In other cases we have used the experimental elastic constants of Hsu and Leisure (1979) which are given in table 1. There is clear anisotropy, shown by the deviation from unity of the ratio $2c_{44}/(c_{11} - c_{12})$,

Table 1. Elastic constants and their ratios. Experimental values are from Hsu and Leisure (1979), 'model' values are from Oates and Stoneham (1983). All elastic constants are in 10^{12} dyn cm^{-2} .

	Model	Pd (0 K)	Pd (300 K)	PdH _{0.66} (0 K)	PdH _{0.66} (300 K)
c_{11}	2.05	2.34	2.24	2.27	2.11
$\frac{1}{2}(c_{11} - c_{12})$	0.31	0.29	0.25	0.33	0.27
c_{44}	0.89	0.71	0.71	0.69	0.63
Bulk modulus	1.64	1.95	1.90	1.83	1.75
$\frac{1}{3}(c_{11} + c_{12})$					
Anisotropy ratio	2.87	2.45	2.81	2.11	2.34
$2c_{44}/(c_{11} - c_{12})$					

and there is a distinct Cauchy violation for $c_{12} \neq c_{44}$. The model potential for Pd gives a similar elastic anisotropy to that observed.

In the presence of significant anisotropy we must go beyond the classic analysis of Eshelby (1956). The critical fact is that if we write the displacements due to a defect in a harmonic crystal of any symmetry in the form

$$\mathbf{u}(\mathbf{r}) = \mathbf{u}_D(\mathbf{r}) + A_S \mathbf{r}/r^3 \quad (3)$$

where the average over angles of \mathbf{u}_D only contains forms falling off faster than r^{-2} , then the second term leads to a volume change $4\pi A_S$ but no dilatation. It is the second term, and only this term, which contributes to ΔV_S . This is a mathematical result, unconnected with elasticity theory or any specific assumptions about the elastic constants. Only the term $\mathbf{u}_S(\mathbf{r})$, proportional to \mathbf{r}/r^3 , has the properties of a finite value of $r^2(\mathbf{r}/r) \cdot \mathbf{u}_S(\mathbf{r})$ and zero dilatation ($u_{xx} + u_{yy} + u_{zz}$). In practical terms, we should want to estimate A_S at distances not too close to the defect (where parts of \mathbf{u}_D may be hard to separate from \mathbf{u}_S) and not too close to any real surface (where the precise topography may matter).

We now consider several different methods for obtaining ΔV_D , ΔV_S , ΔV , and their ratios.

2.1. ΔV as the pressure derivative of the formation energy

It is a general result that in a finite crystal the volume of formation is given (Finnis and Sachdev 1976) by

$$\begin{aligned} \Delta V &= -(\partial U_F / \partial \ln \Omega)_T / B \\ &= -(\partial U_F / \partial \ln a)_T / 3B \end{aligned} \quad (4)$$

where U_F is the formation energy, $B \equiv (c_{11} + 2c_{12})/3$ is the bulk modulus and a is the lattice parameter. U_F is found readily using the Harwell HADES or DEVIL codes (see Oates and Stoneham (1983) for details) and the derivative is obtained simply by numerical differentiation. A comment on the potentials is made in the appendix. Values are given in § 2.4.

2.2. ΔV from the virial of the defect forces

Oates and Stoneham (1983) fitted the defect forces \mathbf{F} to the experimental result of Peisl (1978), $\Delta V = 2.8 \text{ \AA}^3$, using the well known virial form

$$\Delta V = \sum_{i,j} \sum_k s_{ijkk} G_{ij} \quad (5)$$

$$G_{ij} = \sum_{\text{atoms } l} R_{li} f_j(R_l) \quad (6)$$

(Eshelby 1956, Kanzaki 1957, Hardy 1968, Temkin 1970, Stoneham 1975 p 185). One problem results, for equation (5) omits important terms. This has been noted previously for ionic crystals (Flynn 1971, Lidiard 1981, Gillan 1983, Stoneham 1983b) and for metals (Schober 1977, Schober and Ingle 1980, Gillan 1983, Stoneham 1983b). The correction is ΔV_{rel} in § 2.4. In the present case ΔV_{rel} is only a small correction (0.28 \AA^3 out of 3.05 \AA^3).

2.3. Values of γ and γ' from elasticity theory

Isotropic elasticity theory gives directly (see, e.g., Stoneham 1975 p 185) the ratios

$$\gamma = 3c_{11}/(c_{11} + 2c_{12}) \quad (7)$$

$$\gamma' = 2(c_{11} - c_{12})/3c_{11} \quad (8)$$

and these expressions lead to the 'isotropic' values of table 2. Liebfried and Breuer (1978) give a list of these for many metals. They also quote expressions appropriate for weak anisotropy. These results have been extended to anisotropic cases by other workers (see, e.g., Dederichs and Pollmann 1972, Liebfried and Breuer 1978). ΔV_S can be expressed as an integral which is evaluated analytically for small cubic anisotropy ($c_a = c_{11} - c_{12} - 2c_{44}$ is small). By a variational procedure it has been shown that γ can be expressed to first order of the anisotropy factor c_a/c_{44} by a formula of the form of equation (7) using the effective isotropic elastic constants (Voigt averages) $\bar{c}_{11} = c_{11} - 2c_a/5$, $\bar{c}_{12} = c_{12} + c_a/5$, $\bar{c}_{44} = c_{44} + c_a/5$. For most metals the difference between the exact value of γ and the effective isotropic one is less than 5%.

Following Dederichs and Pollmann (1972), the shear component of the volume change of a point defect in a cubic crystal may be calculated from

$$\begin{aligned} \Delta V_S &= \int d^3r \operatorname{div} \mathbf{u}(\mathbf{r}) \\ &= \int_{|\mathbf{K}|=1} \frac{d\Omega}{4\pi} \mathbf{K} \cdot \mathbf{u}(\mathbf{K}) \\ &= G \int_{|\mathbf{K}|=1} \frac{d\Omega}{4\pi} \frac{t(\mathbf{K})}{1 + (c_{44} + c_{12})t(\mathbf{K})} \end{aligned} \quad (9)$$

where $G\delta_{\alpha\beta}$ is the double force tensor and the function t is defined by

$$t(\mathbf{K}) = \sum_{\alpha=1}^3 \frac{K_\alpha^2}{c_{44} + (c_{11} - c_{12} - 2c_{44})K_\alpha^2}. \quad (10)$$

Bansil's (1975) 'special directions' method may be used to evaluate this integral, since the integrand has full cubic symmetry. Thirteen directions within the irreducible $\frac{1}{48}$ of the

Table 2. Elasticity theory for γ , γ' . Other estimates of γ' for Nb are 0.26 (Wagner and Horner 1974) and 0.425 (Zabel and Peisl 1979).

FCC	Model	Pd (0 K)	Pd (300 K)	PdH _{0.66} (0 K)	PdH _{0.66} (300 K)
$\gamma(\Delta V/\Delta V_S)$ isotropic	1.25	1.20	1.18	1.08	1.21
Anisotropic		1.34	1.33	1.37	1.34
Effective isotropic	1.52	1.43	1.43	1.47	1.43
$\gamma'(\Delta V_D/\Delta V)$ isotropic	0.20	0.17	0.15	0.07	0.17
Anisotropic		0.25	0.25	0.27	0.25
Effective isotropic	0.34	0.30	0.30	0.32	0.30

BCC	V	Nb	Ta
γ	1.403	1.290	1.468
γ'	0.287	0.225	0.319

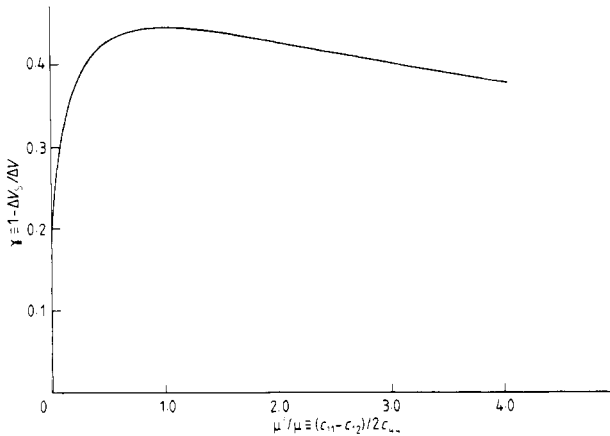


Figure 1. Eshelby's (1956) coefficient γ for a cubic crystal obeying the Cauchy relation $c_{12} = c_{44}$. The value of γ is given as a function of the ratio μ'/μ of the two shear moduli $\mu' \equiv \frac{1}{2}(c_{11} - c_{12})$ and $\mu \equiv c_{44}$.

Brillouin zone were used. Figure 1 shows the results for a Cauchy solid ($c_{12} = c_{44}$) for various ratios of the two shear constants ($\mu' \equiv \frac{1}{2}(c_{11} - c_{12})$)/($\mu \equiv c_{44}$). Values for the BCC metals V, Nb, Ta and for Pd are given in table 2, together with the effective isotropic values.

2.4. Calculations of ΔV by computer simulation

The double force tensor G_{ij} (equation (6)) can be calculated easily by computer simulation techniques. Two possible techniques have been discussed by Schober and Ingle (1980) and a third method will be discussed later in this section. In the first method G_{ij} is calculated as the moment of the forces exerted by the movable atoms in region I, because of their relaxation, on the fixed atoms in the surrounding region II. For pair forces this gives

$$G_{ij} = \sum_{\substack{m \in \text{II} \\ n \in \text{I}}} R_i^{0m} F_j (R^m - R^n) \quad (11)$$

where R^{0n} and R^n denote the ideal and displaced positions, respectively, of atom n . The second method uses the displacements calculated in region I to define generalised Kanzaki forces K which contain the contributions of the host lattice anharmonicity:

$$K_i^m = \sum_{ni} \varphi_{ij}^{mn} (R_j^n - R_j^{0n}) \quad (12)$$

where φ is the ideal lattice harmonic-coupling matrix and

$$G_{ij} = \sum_{m \in \text{I}} R_i^{0m} K_j^m. \quad (13)$$

Both methods converge rapidly with increasing number of atoms N_I in region I but require a higher-accuracy energy minimisation than is needed if one is interested in the energies only, in common with all methods for calculating G or ΔV . For the model of H in Pd considered here we have calculated a value of $G_{ij} = 2.85\delta_{ij}$ eV, and hence $\Delta V = 2.77 \text{ \AA}^3$. Using the zeroth-order formula (11) we would have obtained $G_{ij}^0 = 3.13\delta_{ij}$ eV and

$\Delta V^0 = 3.05 \text{ \AA}^3$ instead. The relaxation of the Pd lattice therefore causes an anharmonicity correction $\Delta V_{\text{rel}} = -0.28 \text{ \AA}^3$. With the 'effective' isotropic value of γ we obtain $\Delta V_s = 1.82 \text{ \AA}^3$.

We can also exploit the explicit volume dependence of the model to calculate γ by computer simulation with elastic boundary conditions. The energy of the crystal is given by

$$E = \frac{1}{2} \sum_{RR'} \varphi(R - R') + p_c V \quad (14)$$

where $p_c = \frac{1}{2}(c_{12} - c_{44}) = 0.178 \text{ eV \AA}^{-3}$ is the Cauchy pressure. We now impose continuum theoretical displacements on the atoms in region II. The energy change in region I can be expanded in a power series in $\text{Tr } G$ (note G is isotropic in our case) as

$$\Delta E = \varepsilon_1 (\text{Tr } G) + \varepsilon_2 (\text{Tr } G)^2 + \dots \quad (15)$$

The equilibrium condition of the ideal lattice gives

$$\varepsilon_1 (\text{Tr } G) = -p_c \Delta V_s \quad (16)$$

and hence γ and ε_1 are related by the expression

$$\gamma = -\frac{3B}{p_c} \varepsilon_1. \quad (17)$$

We have evaluated this formula for a number of crystal sizes and geometries (see table 3). The anisotropic elastic continuum model displacements of atoms in region II were calculated by a one-dimensional numerical integration routine (Deutz and Schober 1983). Region I was taken either as cubic with the dilatation centre at $(0.5a, 0, 0)$ or as spherical with the dilatation centre at the origin. To estimate the lattice surface effects, ΔE included either the full I-II bonds (ΔE_1) or half the bonds (ΔE_2). The resulting values of γ are compiled in table 2. The difference in the γ values obtained from ΔE_1 and ΔE_2 shows the importance of I-II cross bonding. There is also a pronounced dependence on the shape of region I and a less pronounced dependence on its size. This has to be expected since, due to lattice anharmonicity, a point-dipole force is smeared out over a large area (Schober 1977). The difference between the values of γ including a single H defect and those excluding it is less than 0.01, showing that γ is indeed a host lattice property as predicted by theory.

Another method for calculating ΔV_s has been used by Seeger and Mann (1960) and Johnson (1964). They make an effective isotropic ansatz for the displacement field in region II,

$$\mathbf{u}(\mathbf{r}) = (\Delta V_s / 4\pi)(\mathbf{r}/r^3),$$

Table 3. Values of γ deduced from equation (17).

Model	N_1	From ΔE_1	From ΔE_2
Effective isotropic value		1.52	1.52
Cubic inner region	655	1.46	1.65
	1687	1.41	1.56
Spherical inner region	466	1.31	1.53
	682	1.30	1.50

Table 4. Summary of ΔV estimates for H at octahedral sites of Pd. The forces were fitted by Oates and Stoneham (1983) using $B = 18.05 \times 10^{10}$ Pa, whereas the virial estimate is obtained using $B = 16.40 \times 10^{10}$ Pa consistent with the potential.

	ΔV (\AA^3)
Experiment	2.9
Virial ΔV	3.05
$-(\partial U_{\text{F}}/\partial \ln \Omega)/B$	2.77
ΔV_{S}	1.82
ΔV_{rel}	-0.28

and ΔV_{S} is calculated as a variational parameter in addition to the displacements of the ions in region I. The total energy for this ansatz is given by

$$\Delta E = \frac{1}{2} \sum_{m \in \text{I}} \sum_{n \in \text{I, II}} \varphi(R^m - R^n) + b(\Delta V_{\text{S}})^2 \quad (18)$$

where the last term is the elastic energy stored in the infinite crystal outside region I. For a spherical region I (of volume V_{I}) the constant b can be calculated easily (Johnson 1964) as

$$b = \frac{2}{3} [c_{44} + \frac{1}{3}(c_{11} - c_{12})] / V_{\text{I}}. \quad (19)$$

It should be noted that V_{I} , the volume of the inner region, is not a well defined quantity and the inner region is never completely spherical for a finite N_{I} . Nevertheless Johnson's results minimising equation (18) agree quite well with the results given by Dederichs *et al* (1978), who calculated the dipole force tensor by the surface force and extended Kanzaki force (1957) models. In the present case the situation is much worse since ΔV_{S} is much smaller. This results in the linear term in equation (18) being three orders of magnitude larger than the quadratic dependence on ΔV_{S} in the first and third terms. The linear second term should cancel exactly with the linear ΔV_{S} dependence of the first term. This cancellation can be made simply for energy calculations (Schober 1983) by comparison with ideal crystal calculations with the same boundary conditions. For calculations of ΔV_{S} this is also possible, but very tedious. By very careful minimisation of equation (18) we gained a value of $\gamma = 1.57$. The good agreement with the values in table 4 is perhaps fortuitous since a change in energy of 10^{-5} eV causes a change of 15% in ΔV_{S} and hence in γ . If we count only half the I-II bonds towards the first term we find no minimum at all with respect to ΔV_{S} . We may conclude that the determination of ΔV_{S} by direct energy minimisation is highly unreliable, especially for systems with small ΔV and large p_{c} . Whilst the other methods, based on surface forces or generalised Kanzaki forces, can become inaccurate, they cannot fail catastrophically like the direct energy minimisation.

2.5. Other methods

The most simple atomistic method, though regrettably unreliable, is to look at values of $4\pi r(\mathbf{r} \cdot \mathbf{u})$ from a typical HADES run[†]. Here \mathbf{u} is the outward normal displacement of atoms at distance r from the interstitial. The problems are clear: at small r various small short-range effects confuse the results and at large r the displacements are constrained to fall to zero at a chosen distance. We plot some results in figure 2 for illustrative purposes. Clearly this approach to ΔV_{S} is not too useful.

[†] HADES is the Harwell code for defect studies (Norgett 1974).

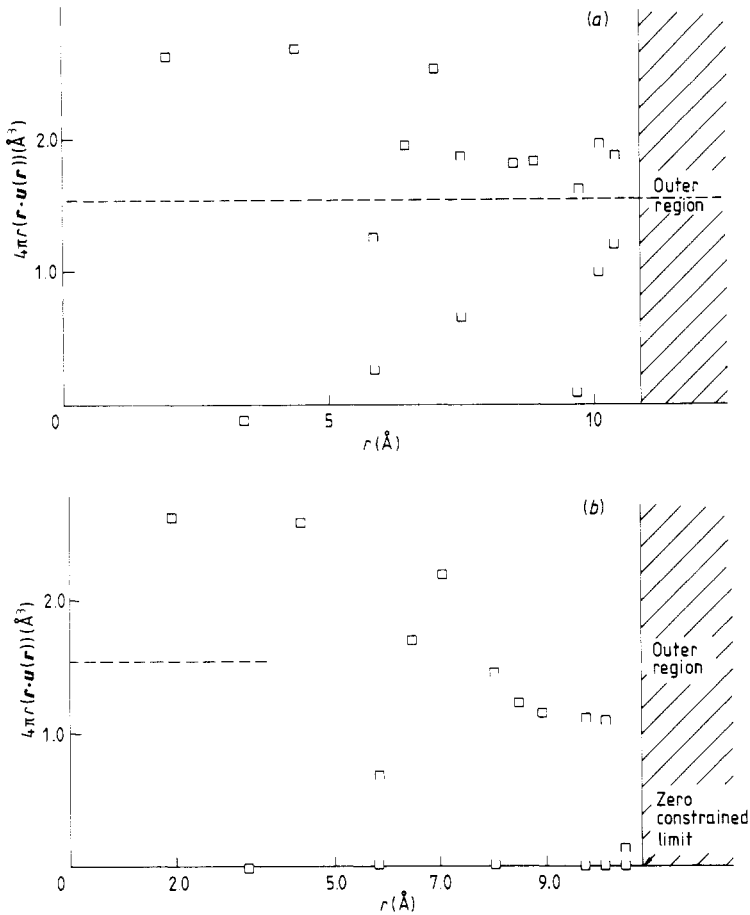


Figure 2. Values of ΔV_S as deduced from the displacements of shells of atoms. The values plotted are $4\pi r(\mathbf{r} \cdot \mathbf{u})$ where \mathbf{u} is the outward normal displacement of the shell initially at r . Note that for some values of r there are two inequivalent shells of atoms, and these are both indicated. (a) The displacements in the outer region have the form $A_S r/r^3$ with chosen A_S ; the value as constrained in the outer region is given (---). (b) A_S is zero; the value for the relaxed outer region is shown (---). The fall-off at large r results from the constraint $u=0$ outside the 267 atoms explicitly relaxed.

3. The configuration-independent interaction energy

In terms of the Eshelby coefficient γ' (equation (2)) the non-configurational interaction energy per pair, E_I , may be written

$$E_I = -\gamma' B(\Delta V)^2 / \Omega. \quad (20)$$

Suppose there are N defects present and that the non-configurational interaction energy is E_I per pair. If E_I is independent of N then the total energy from these interaction is $E_{NC}(N)$ where

$$E_{NC}(N) = \frac{1}{2} N(N-1) E_I \approx \frac{1}{2} N^2 E_I. \quad (21)$$

We can also define an equivalent chemical potential $\mu_{\text{NC}}(N)$ as

$$\mu_{\text{NC}}(N) = \frac{\partial}{\partial N} E_{\text{NC}}(N) \simeq NE_1 \quad (22)$$

$$= -\gamma' B(\Delta V)^2 (\theta/V_S) \quad (23)$$

$$= -\gamma' B(\Delta V)^2 (x/\Omega).$$

Here V_S is the volume per hydrogen site, Ω is the atomic volume of the host and, as measures of concentration, $x \equiv$ hydrogen/metal ratio and $\theta \equiv$ fractional occupancy of the interstitial sites. ΔV is, of course, the partial molar volume of hydrogen.

If we assume that E_1 varies slowly with N , i.e.

$$E_1(N) = E_1(0) + (dE_1/dN)N, \quad (24)$$

then we find that

$$\begin{aligned} E_{\text{NC}}(N) &\sim \frac{1}{2}N^2 E_1(0) + \frac{1}{3}N^3 (dE_1/dN) \\ &\sim \frac{1}{2}N^2 \bar{E} \end{aligned} \quad (25)$$

where we introduce $\bar{E} = \frac{1}{3}(E_1(0) + 2E_1(N))$ as the appropriate average energy. For the chemical potential, if we ignore terms in $d^2 E_1/dN^2$, we have

$$\begin{aligned} \mu_{\text{NC}}(N) &\sim NE_1(0) + N^2 (dE_1/dN) \\ &\sim NE_1(N). \end{aligned} \quad (26)$$

In principle, this equation could be used in conjunction with equation (20), but there remains the problem of knowing γ' as a function of H concentration. Of the methods outlined in § 2, only the isotropic continuum calculations can be used (see table 2 for PdH_{0.66}).

An alternative approach to obtaining the non-configurational contribution at high H concentration is to consider the difference between the total and configuration-dependent interaction energies.

The total elastic interaction energy, E_T , is known exactly for an arbitrary lattice of any shape (see Wagner and Horner 1974, equation 4.44):

$$E_T = -\frac{1}{2}B(\Delta V)^2 \theta^2/V_S. \quad (27)$$

Oates and Stoneham (1983) have demonstrated that the configurational-dependent interaction energy, E_C , depends on both the arrangement and number of H atoms but, to first order, we might expect a simple analytical form for the composition dependence if the H-atom distribution is random. In the case of random substitutional solid solutions, the local relaxation energy varies roughly as $\theta(1-\theta)$ (Flynn 1972, Froyen and Herring 1981). Since the relaxation energy must also be zero at $\theta=0$ and $\theta=1$ for interstitial solid solutions, we may write

$$E_C = -\tilde{A}\theta(1-\theta) \quad (28)$$

where \tilde{A} is a parameter to be determined.

From the difference $E_T - E_C$ we obtain the non-configurational energy and, on comparing this result with that obtained from a combination of equations (20) and (21) for

the dilute solution, the value of \tilde{A} is obtained as

$$\tilde{A} = \frac{1}{2} B \Delta V_2 \theta (1 - \gamma'_0) / V_S \quad (29)$$

where γ'_0 is the value of γ' in the very dilute solution. Hence for this special case of a random distribution of H atoms

$$E_{NC} = [\gamma'_0 + (1 - \gamma'_0)\theta] E_T \quad (30)$$

$$E_C = (1 - \gamma'_0)(1 - \theta) E_T \quad (31)$$

so that $\gamma' = [\gamma'_0 + (1 - \gamma'_0)\theta]$ becomes unity when all the sites are occupied, i.e., all the elastic energy is non-configurational.

Taking $V_S = 8.87 \text{ cm}^3 \text{ mol}^{-1}$ (Pearson 1958), $\Delta V/\Omega = 0.19$ (Peisl 1978), $B = 1.90 \times 10^{11} \text{ Pa}$, $dB/d\theta = -0.232 \times 10^{11} \text{ Pa}$ (Hsu and Leisure 1979) and $\gamma'_0 = 0.25$ for Pd-H alloys at 300 K, equations (27)–(31) may be differentiated, as in (22), to give the total (μ_T), configurational (μ_C), and non-configurational (μ_{NC}) elastic energy contributions

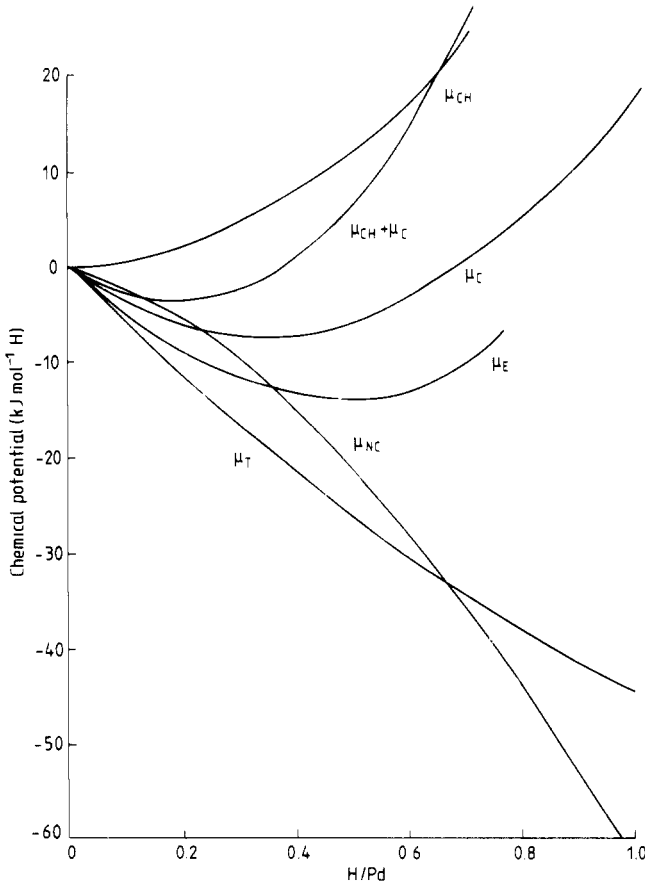


Figure 3. Contributions to the chemical potential for hydrogen in Pd over a range of hydrogen concentrations. The total chemical potential in elasticity theory is μ_T with configurational part μ_C (equations (27) and (31)) and non-configurational part μ_{NC} (equations (27) and (30)). The experimental excess chemical potential, μ_E , is the sum of the total elastic part, μ_T , and a chemical part, μ_{CH} . The combination of terms appropriate for statistical calculations is $\mu_{CH} + \mu_C$ which is also shown.

to the chemical potential. The difference $\mu_E - \mu_T$, where μ_E is the experimental excess chemical potential (Kuji *et al* 1983), is the chemical contribution μ_{CH} to the chemical potential. All these quantities are shown in figure 3 for the Pd–H system at 300 K. It is of interest to note that the effect of H concentration on μ_{CH} is quite different from that expected from simple arguments based on d- and s-band filling. Rather, a strong repulsive interaction between H atoms is indicated. Statistical models should be concerned with the sum $\mu_{CH} + \mu_C$ of the contributions resulting from the direct interactions which is also shown in figure 3. It has been noted previously (Oates and Stoneham 1983) that for μ_C , at least, a pairwise interpretation is inadequate.

Appendix. Interatomic potentials

The Pol potential we use is almost exactly that of Van Heughten (listed as his potential I by Stoneham and Taylor (1981)). The small changes we make ensure a smooth cut-off at $r_c = 3.305 \text{ \AA}$. The coefficient A_1 in $V(R) = \sum_{n=1}^6 A_n R^n$ changes from -396.6696 to -396.6861 , with a similar small change in A_0 to give $V(r_c) = 0$. As can be seen from table 5, there is no significant change in the elastic constants, and we believe the situation will be essentially the same for all but special quantities. Our experience has emphasised how sensitive one must be in making approximations to these potentials, so the agreement indicated is important.

The total energy of the crystal can be written as

$$E = \frac{1}{2} \sum_{R, R'} V(R - R') + p_c V$$

where V is the crystal volume and p_c is the Cauchy pressure

$$p_c = \frac{1}{2}(c_{12} - c_{44}) = 0.178 \text{ eV \AA}^{-3} = 10.33 \text{ eV } a^{-3}$$

where the lattice constant $a = 3.872 \text{ \AA}$.

Table 5. Elastic constants of Pd (in $10^{12} \text{ dyn cm}^{-2}$).

	Original A_0, A_1	Modified A_0, A_1	Experiment
c_{11}	2.05	2.04	2.26
c_{12}	1.43	1.45	1.76
c_{44}	0.89	0.88	0.72
$\frac{1}{2}(c_{11} - c_{12})$	0.31	0.30	0.25

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