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Elastic interaction of hydrogen in palladium studied by molecular-dynamics simulation

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A simulation model for the palladium-hydrogen system is studied by Andersen's scheme of molecular dynamics in the isothermal-isobaric ensemble. Widom's particle-insertion method is used to determine the chemical potential of the hydrogen lattice gas. It is shown that Andersen's Lagrangian corresponds to a lattice with a free surface (although periodic boundary conditions are used), and in agreement with this the α-α' ("gas-liquid") phase transition of metal-hydrogen systems is reproduced by the simulation model. A value of 3.0 Å^3 is found for the partial volume V_H of hydrogen in palladium, in almost exact agreement with experiment. Further, the thermodynamic Maxwell relation $(\partial\mu/\partial p)=V_H$ is confirmed by the simulations (i.e., classical mechanics). Finally, the effective elastic interaction of the hydrogen lattice gas is determined, and compared with the Wagner and Horner theory, which expresses this interaction in terms of phonon modes in the first Brillouin zone.

I. INTRODUCTION

Lattice gas models are used for the statistical mechanics of hydrogen in metals,[1,2] and recently for oxygen in high-temperature superconductors.[3] A realistic lattice gas model takes into account effective pair interactions between the particles (hydrogen or oxygen atoms). Effective pair interactions, which are mediated by the lattice, can be electronic or elastic in nature. For oxygen in the high-temperature superconductor $YBa_2Cu_3O_z$ electronic effective pair interactions have been calculated from total-energy band-structure calculations.[4] The thermodynamic behavior of hydrogen in metals, in particular the α-α' phase transition, has been explained by effective elastic interactions.[5] Wagner and Horner[6] have developed a theory to calculate elastic interactions, which was applied by Horner and Wagner[7] to the niobium-hydrogen system, with reasonable success. The theory has also been applied to the niobium-vanadium-hydrogen ternary system.[8]

Recent developments in the technique of molecular-dynamics simulation of statistical-mechanical systems have made it possible to study a lattice gas with elastic interaction by direct integration of the classical equations of motion, as will be shown in this paper. These developments are now discussed briefly.

Conventional molecular-dynamics simulation is done in the microcanonical ensemble, which means that the total energy of the system is constant. Simulation in the canonical ensemble can be done by keeping the kinetic energy (i.e., the temperature) constant instead of the total energy. This can be achieved either by scaling the velocities after each integration step,[9] or by introducing stochastic collisions.[10,11] Simulation in the isothermal-isobaric ensemble requires both the temperature and the pressure (instead of the volume) to be kept constant. Andersen[10] has proposed a Lagrangian which allows for volume fluctuations of a system with periodic boundary conditions. Andersen's scheme has been generalized by Parinello and Rahman[12] to allow also for shape fluctuations. Since the elastic interaction of a lattice gas is intimately related to lattice expansion, the simulations described in this paper are done in the isothermal-isobaric ensemble.

Of great importance for the Monte Carlo and molecular-dynamics technique has been the development of a method to determine free energies from simulations. A direct determination of the free energy is not possible, since the free energy is not an ensemble average of an observable (as opposed to, e.g., the internal energy). An indirect determination can be obtained by the particle insertion method of Widom (see Frenkel[13]). This method consists of probing the interaction energy of a test particle added to the system. The method was first used for the determination of the chemical potential of a Lennard-Jones fluid.[14-16] The method works well at low densities, becomes less accurate at higher densities, and fails completely for crystalline solids.[13] It will be shown in this paper that the method does work for a lattice gas, even up to concentrations of the order of $c=1$ (c is the average number of particles per site).

The system chosen for the present study is the palladium-hydrogen system, which is perhaps the oldest physical example of a lattice gas.[17] Recently, Gillan[18] proposed a simulation model for the palladium-hydrogen system, and studied the diffusion of hydrogen in the lattice by microcanonical molecular-dynamics simulation. This simulation model was also used by Culvahouse and Richards[19] and Salomons.[20]

This paper is organized as follows. In Sec. II the simulation method is described in detail. In this section also the lattice gas model is described, which is used for the interpretation of the simulation results. In Sec. III the results are presented, and in Sec. IV the results are compared with the theory of Wagner and Horner. Section V contains the conclusions.

II. METHOD OF SIMULATION AND ANALYSIS

A. *N-p-T* molecular dynamics

Molecular-dynamics simulation in the isothermal-isobaric ensemble, or shortly *N-p-T* molecular dynamics, is done by keeping the temperature and the pressure constant.

The temperature is kept constant by the momentum scaling procedure. It has been demonstrated by Haile and Gupta[9] that this procedure yields the correct static properties of an isothermal system.

The pressure is kept constant by a method devised by Andersen.[10] Andersen replaces the coordinates $\mathbf{r}_i$ of the atoms ($i=1,2,\ldots$) by scaled coordinates $\rho_i=\mathbf{r}_i/V^{1/3}$, where V is the volume of the system. The equations of motion are then obtained from the following Lagrangian:

$$L(\rho,\dot\rho,V,\dot V)=\tfrac{1}{2}V^{2/3}\sum_i m_i\dot\rho_i^2-\sum_{i,j}u_{ij}(V^{1/3}\rho_{ij})+\tfrac{1}{2}M\dot V^2-pV\ , \qquad (1)$$

where m_i is the mass of particle i, u_{ij} is the interaction between particles i and j, M is a parameter that could be called "volume mass," and p is the external pressure acting on the system. In addition to the equations of motion for the particles, the Lagrangian also yields an equation of motion for the volume. It should be noted that the Lagrangian has not been derived from first principles.

B. Chemical potential from *N-p-T* molecular dynamics

A general method to determine chemical potentials from simulations is the particle insertion method of Widom (see Frenkel[13]). This technique has been used in canonical (i.e., *N-V-T*) Monte Carlo simulations[14,15] and in microcanonical molecular-dynamics simulations.[16] Frenkel[13] has indicated how the method should be implemented in microcanonical simulations (this was not done correctly in Ref. 16). The implementation in isothermal-isobaric simulations is straightforward, and will be described now.

The chemical potential μ is determined by the following expression:

$$\mu=kT\ln(N\Lambda^3)-kT\ln\left[\left\langle\int d\mathbf{r}\exp(-u^t/kT)\right\rangle\right]\ , \qquad (2)$$

where N is the number of particles, $\Lambda=(h^2/2\pi mkT)^{1/2}$, u^t is the interaction energy of a test particle inserted at position $\mathbf{r}$ in the system (the test particle does not affect the trajectories of the other particles), and the angular brackets indicate an ensemble average. The integral in Eq. (2) is determined as follows. Test particles are placed at all sites of a simple cubic lattice which fills the entire system, and the interaction energies u_i^t ($i=1,2,\ldots,N_t$) are evaluated. The integral is then approximated by

$$(V/N_t)\sum_{i=1}^{N_t}\exp(-u_i^t/kT)\ . \qquad (3)$$

In the isothermal-isobaric ensemble the volume is fluctuating, so the volume V in (3) cannot be taken out of the angular brackets in (2) (as opposed to the canonical ensemble).

C. Simulation model

The simulation model of Gillan[18] for the palladium-hydrogen system is used, with a small modification.

The potential between the palladium atoms is given by a polynomial which reproduces the phonon dispersion relations of palladium:

$$V_{\mathrm{PdPd}}(r)=\sum_{s=0}^{6}A_s r^s \qquad (4)$$

with cutoff radius $r_0=3.305$ Å. The values of the coefficients A_s are given in Table I. The palladium-hydrogen interaction, which reproduces the local mode frequency of hydrogen in palladium, is given by

$$V_{\mathrm{PdH}}(r)=A\exp(-r/\rho_1) \qquad (5)$$

with cutoff radius $r_1=3.8$ Å, $A=15.3$ eV, and $\rho_1=0.5$ Å. The hydrogen-hydrogen potential was simply set equal to the palladium-hydrogen potential by Gillan. However, this corresponds to a rather strong repulsion of about 0.05 eV between hydrogen atoms at nearest-neighbor octahedral sites in the palladium lattice. The Monte Carlo study of Bond and Ross[21] has shown that the fact that ordered structures in the palladium-hydrogen system occur only for temperatures below about 50 K implies that the nearest-neighbor hydrogen-hydrogen repulsion can only be of the order of 0.005 eV. In agreement with this, the following hydrogen-hydrogen potential is used:

$$V_{\mathrm{HH}}(r)=A\exp(-r/\rho_2) \qquad (6)$$

with cutoff radius $r_1=3.8$ Å, $A=15.3$ eV, and $\rho_2=0.35$ Å.

D. Lattice gas model

For the interpretation of the simulations of the palladium-hydrogen system in terms of an effective elastic interaction, a lattice gas model is used, which is described in this section.

Consider the palladium-hydrogen model system described in the previous section, with a number N_{H} of hydrogen atoms in the lattice. The equilibrium site of a hydrogen atom is the octahedral site,[18] in agreement with experiment. Using the formalism of Wagner and Horner,[6] the chemical potential $\mu=(\partial G/\partial N_{\mathrm{H}})_{p,T}$, where G is the total Gibbs free energy of the system, can be written as

TABLE I. Coefficients of the palladium-palladium potential (4) (units are eV and Å).

A_0	345.5856	A_4	−129.0614
A_1	−247.5615	A_5	25.39365
A_2	−204.0164	A_6	−1.907044
A_3	292.8391		

$$\mu(c)=\varepsilon+u_{\text{elastic}}(c)+u_{\text{electronic}}(c) -Ts_{\text{conf}}(c)+\mu_{\text{vib}}(c)+pV_{\text{H}} \ . \tag{7}$$

Here, c is the hydrogen concentration (i.e., the average number of hydrogen atoms per site), ε is the site energy of a hydrogen atom, u_{elastic} represents the effective elastic interaction, $u_{\text{electronic}}$ represents the direct electronic interaction through the (screened Coulomb) potential (6), s_{conf} is the partial configurational entropy of the hydrogen atoms at octahedral sites, μ_{vib} is the contribution of the vibrations of the hydrogen atoms, and V_{H} is the partial volume of hydrogen [i.e., $V_{\text{H}}\equiv(\partial V/\partial N_{\text{H}})_{p,T}$].

In calculating the site energy ε, it is important to account for the lattice relaxation around a single hydrogen atom [which is not accounted for by the elastic interaction u_{elastic}, since $u_{\text{elastic}}(0)=0$]. This can be done by the technique of damped molecular dynamics, with the result $\varepsilon=1.605$ eV for a hydrogen atom at an octahedral site.[18,20]

The electronic interaction $u_{\text{electronic}}$ is small, and it is sufficient to take into account only the interaction between hydrogen atoms at nearest-neighbor octahedral sites. In mean-field approximation (which turns out to be an excellent approximation here, as demonstrated in the next section) the electronic interaction is given by

$$u_{\text{electronic}}(c)=qcV_{\text{HH}}(r_{\text{NN}}) \tag{8}$$

with $q=12$ the coordination number and r_{NN} the distance between nearest-neighbor octahedral sites. Note that r_{NN} is not a constant, but depends on the lattice parameter, which in turn depends on the hydrogen concentration.

For the vibrational contribution μ_{vib} the classical expression for independent harmonic oscillations is used:

$$\mu_{\text{vib}}=3kT\ln(\hbar\omega/kT) \ . \tag{9}$$

The local mode frequency ω of hydrogen in palladium is calculated from the potential (5) by the method used by Gillan.[18]

III. RESULTS

In this section the results of the simulations of the palladium-hydrogen system in the isothermal-isobaric ensemble are presented. A palladium lattice of $3\times3\times3$ fcc unit cells is used, with periodic boundary conditions. There are 108 palladium atoms in the lattice, and also 108 octahedral sites, which are the most favorable sites for hydrogen occupation. The simulations are started with the palladium atoms on their regular positions, and the hydrogen atoms randomly distributed over the octahedral sites. For the integration of the equations of motion the velocity form of the Verlet algorithm[22] is used, with an integration time step of 2.6×10^{-15} s. The system is always allowed to reach equilibrium during 5×10^{3} integration steps, followed by 2×10^{4} integration steps for the determination of ensemble averages.

In agreement with experiment, hydrogen is found to cause a sizable volume expansion of the palladium lattice. If the initial value of the volume is chosen close enough to the equilibrium value, the system is stable with a volume oscillating around the equilibrium value. The amplitude of this oscillation is only about 1% of the total volume. At high hydrogen concentrations it is more difficult to reach a stable state, and the volume is often found to "explode." However, by increasing the external pressure acting on the system this problem can be suppressed, and the range of accessible hydrogen concentrations is significantly increased. In the simulations reported here, a reduced pressure of $p^*=0.001$ ($p^*=p\rho_1^3/A$) is used, which corresponds to a real pressure of $p=196$ kbar. Such a high pressure is not uncommon in the field of metal hydrides (see, e.g., Hemmes *et al.*[23]). For the parameter M in the Lagrangian (1) a value of 0.01 is used. Ensemble averages are independent of the value of M.

To determine the chemical potential of hydrogen, the particle insertion method is applied after each 100 integration steps. Test particles are placed at the 13 824 sites of a $24\times24\times24$ simple cubic grid, and the interaction energies are evaluated. Changing to a $12\times12\times12$ grid results in a change in chemical potential of the order of only 0.01 eV, from which it is concluded that the $24\times24\times24$ grid is a sufficiently dense filling of the system.

A. Partial volume of hydrogen

In Fig. 1 the volume V is shown as a function of the number of hydrogen atoms N_{H} in the lattice, for $T=600$, 800, and 1000 K. The partial volume of hydrogen $V_{\text{H}}\equiv(\partial V/\partial N_{\text{H}})_{p,T}$ is obtained from a second-order polynomial fitted to the data in Fig. 1. This gives $V_{\text{H}}=3.0\pm0.1$ Å^3 for $c\leq0.5$, at all three temperatures. This value is in remarkably good agreement with the experimental value of $V_{\text{H}}=2.9$ Å^3 (see Peisl[24]).

The value of $V_{\text{H}}=3.0$ Å^3 has an interesting implication for isobaric molecular-dynamics of solids in general. It is well known that the lattice expansion produced by

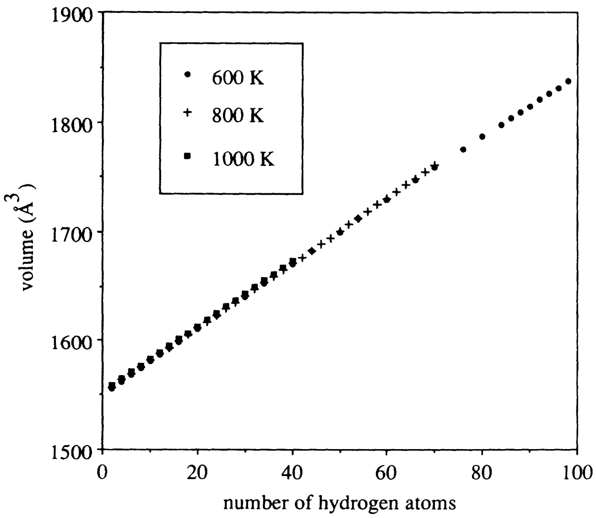

FIG. 1. The volume V of the system as a function of the number of hydrogen atoms N_{H} in the lattice.

an interstitial impurity depends on the boundary conditions of the lattice. The average volume change is smaller for a lattice with periodic boundaries (or an infinite lattice) than for a finite lattice with a free surface. For a lattice with a free surface the following relation holds:[25,5,24]

$$V_H = P/B \ , \tag{10}$$

where B is the bulk modulus and $3P$ is the trace of the force-dipole tensor

$$P_{\alpha\beta} = \sum_m \Psi_\alpha^{ma}(R_\beta^m - Q_\beta^a) \ , \tag{11}$$

where Ψ^{ma} is the force between metal atom m at position $\mathbf{R}^m$ and hydrogen atom a at position $\mathbf{Q}^a$ $(\alpha,\beta = x,y,z)$. In a fcc lattice a hydrogen atom is a pure dilation center:

$$P_{\alpha\beta} = P\delta_{\alpha\beta} \ . \tag{12}$$

For the palladium-hydrogen potential (5) and a lattice parameter of 4.0 Å one obtains $P=2.52$ eV. The bulk modulus $B \equiv -(\partial p/\partial \ln V)_T$ is easily determined from isobaric simulations at two slightly different pressures, with the result $B=0.90$ eV/Å^3 (this value is averaged over the entire concentration range; the concentration dependence is small, about 10%). This yields a value of $V_H = 2.8$ Å^3 for the partial volume of hydrogen in a lattice with a free surface, a value which is close to the value of $V_H = 3.0 \pm 0.1$ Å^3 determined directly from the simulations. For hydrogen in a lattice with periodic boundary conditions, the partial volume would be about 3 times smaller (see Eshelby[25]). This implies that the Andersen scheme of isobaric simulation for a solid yields volume changes that correspond to a solid with a free surface.

Another interesting comparison between thermodynamics and classical mechanics can be made as follows. According to thermodynamics, the Maxwell relation

$$(\partial\mu/\partial p)_{T,N_H} = (\partial V/\partial N_H)_{p,T} \equiv V_H \tag{13}$$

should hold. The partial volume V_H has been determined already, and $\partial\mu/\partial p$ is easily determined by simulation at two slightly different pressures. The result is shown in Fig. 2. The agreement is satisfactory, especially if one considers that two derivatives are being compared.

B. α-α' phase transition

In Fig. 3 the chemical potential of hydrogen is shown as a function of the concentration. The shape of the 600-K isotherm indicates the occurrence of the α-α' phase transition (for a large system phase segregation would result in a horizontal plateau). The critical temperature is between 600 and 800 K, which should be compared with the experimental critical temperature of 565 K for the palladium-hydrogen system.[26]

Figure 3 shows that the chemical potential increases with decreasing temperature (at constant concentration). This corresponds to the fact that the system is endotherm, which means that the enthalpy change upon adding a hydrogen atom to the system is positive. The real palladium-hydrogen system, however, is exotherm. This discrepancy is due to electronic band-structure effects,[27] which are absent in the simulation model. For concentrations $c \leq 0.6$ these effects have only a small effect on the shape of the μ-c isotherms, whereas for $c > 0.6$ the electronic d band of palladium is full and the chemical potential increases rapidly with concentration.[26] Obviously the simulation model cannot represent the real system, but rather should be considered as a fictitious metal-hydrogen system with realistic elastic interactions.

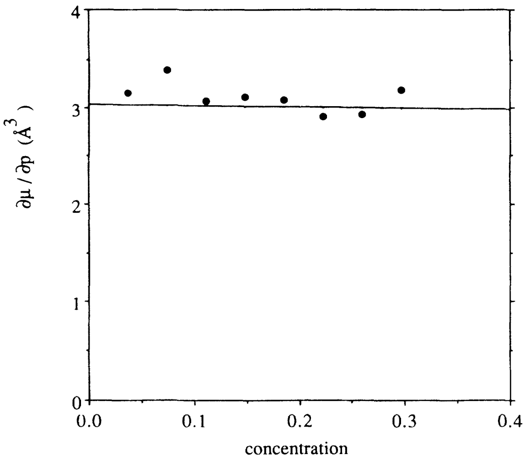

FIG. 2. Comparison of $(\partial\mu/\partial p)_{T,N_H}$ (dots) and the partial volume V_H (line), at $T=800$ K.

The isotherms shown in Fig. 3 will now be interpreted in terms of the lattice gas model described in Sec. II D. As the partial entropy of hydrogen is determined by the isotherms through the relation $s = (\partial\mu/\partial T)_{p,N_H}$, the configurational entropy s_{conf} in Eq. (7) can be determined from $s = s_{\text{conf}} + s_{\text{vib}}$, where s_{vib} is the vibrational partial entropy. This results in the values shown in Fig. 4. The curve in this figure corresponds to the random mixing or

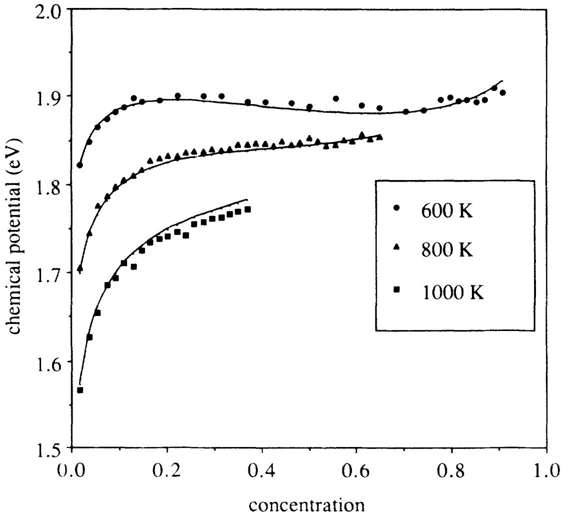

FIG. 3. The chemical potential μ of hydrogen as a function of the hydrogen concentration c. The curve corresponds to Eq. (7) with $s_{\text{conf}} = -k \ln[c/(1-c)]$ (see Fig. 4) and the fit shown in Fig. 5 for $\varepsilon + u_{\text{elastic}}$.

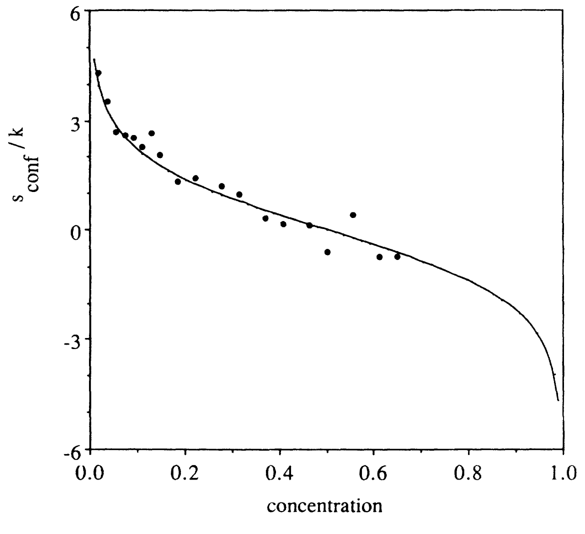

FIG. 4. The configurational partial entropy of hydrogen at 700 K, as determined from the simulations (dots). The curve corresponds to the ideal mixing function $s_{\rm conf}=-k\ln[c/(1-c)]$.

mean-field function $s_{\rm conf}=-k\ln[c/(1-c)]$. The values obtained from the simulations follow this curve rather closely, implying that the mean-field approximation can be used for the configurational entropy. Now the term $\varepsilon+u_{\rm elastic}$ in Eq. (7) can be determined, since all the other terms in this equation have been determined. The result is shown in Fig. 5. Extrapolation to $c=0$ yields a site energy of $\varepsilon=1.600$ eV [since $u_{\rm elastic}(0)=0$], which is close to the value $\varepsilon=1.605$ eV determined by the damped molecular-dynamics technique (see Sec. II; the value of $\varepsilon=1.605$ eV corresponds to $T=0$ K, and the discrepancy of 0.005 eV should be a temperature effect; indeed, the data in Fig. 1 yield a value for the thermal expansion that corresponds to an effect on the unrelaxed site energy of the order of 0.005 eV). The curve in Fig. 5 is a fit, which will be compared to the theory of Wagner and Horner in the next section.

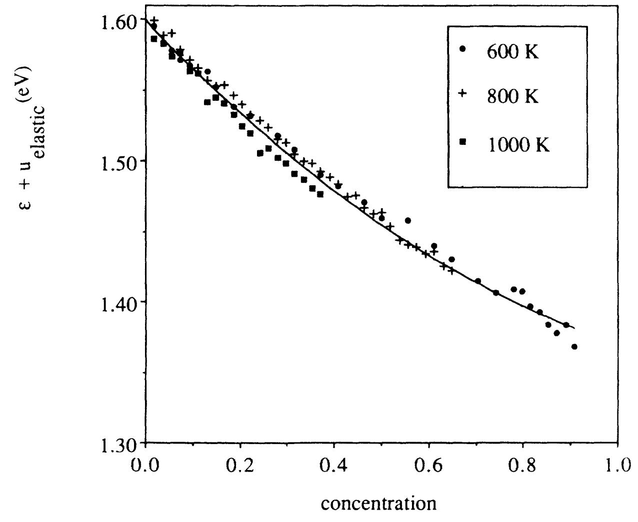

FIG. 5. The term $\varepsilon+u_{\rm elastic}$ as determined from the simulations, using Eq. (7) with $s_{\rm conf}=-k\ln[c/(1-c)]$.

IV. COMPARISON WITH THE THEORY OF WAGNER AND HORNER

In the preceding section it was concluded that the simulations correspond to a crystal with a free surface and a homogeneous hydrogen distribution. The theory of Wagner and Horner was explicitly applied to this case by Wagner.[28] The relevant results are given below.

The elastic energy stored in a crystal loaded with hydrogen is given by a sum of effective hydrogen-hydrogen pair interactions W_{ab}:

$$H=\frac{1}{2}\sum_{a,b}\tau_a W_{ab}\tau_b \ , \tag{14}$$

where $\tau_a=1$ if site a is occupied by a hydrogen atom, and $\tau_a=0$ otherwise. For a homogeneous hydrogen distribution in a fcc crystal with a free surface, this can be written as

$$H=\frac{1}{2}N_{\rm H}(1-c)W_{aa}-\frac{1}{2}N_{\rm H}cBV_{\rm H}^2/V_c \ , \tag{15}$$

in which V_c is the atomic volume of the crystal. The second term can be considered as the average elastic energy (this term can be derived from the thermodynamic Maxwell relation discussed in Sec. III A), and the first term is a correction for the self-energy. According to Wagner, the interaction W_{aa} can be approximated by the expression for an infinite crystal:

$$W_{aa}^{\infty}=-\frac{1}{N_L}\sum_{\mathbf{q},s}\sum_{m,n}\sum_{\alpha,\beta}\Psi_\alpha^{ma}\rho_\alpha(\mathbf{q},s)\Psi_\beta^{na}\rho_\beta(\mathbf{q},s) \times\frac{\exp[i\mathbf{q}\cdot(\mathbf{R}^m-\mathbf{R}^n)]}{M_L\omega^2(\mathbf{q},s)} \ , \tag{16}$$

where N_L and M_L are the number and the mass of the atoms of the crystal, respectively, $\omega(\mathbf{q},s)$ and $\rho(\mathbf{q},s)$ are the frequency and the polarization vector of the phonon with wave vector q and index s, respectively, and the summation is over the wave vectors in the first Brillouin zone. Since there are only 108 wave vectors in the first Brillouin zone of the crystal used for the simulations, the summation in Eq. (16) can be performed exactly. This yields the values of W_{aa}^{∞} given in Table II as a function of

TABLE II. The pair interaction W_{aa}^{∞} as a function of the lattice parameter (units are eV and Å).

a	W_{aa}^{∞}
3.84	−0.630
3.88	−0.572
3.92	−0.496
3.96	−0.418
4.00	−0.347
4.04	−0.288
4.08	−0.240
4.12	−0.204

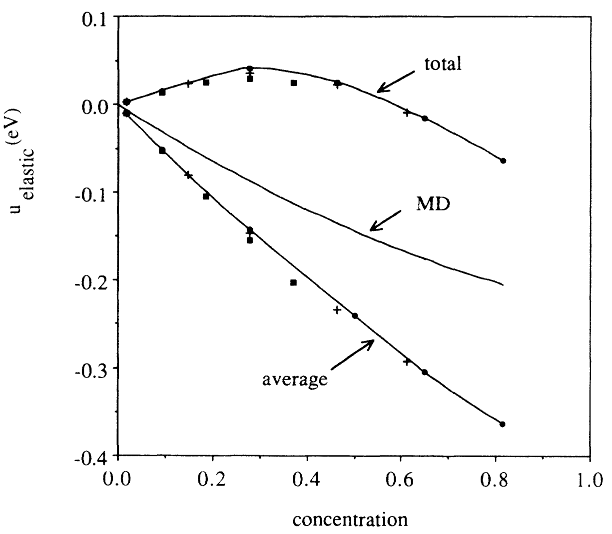

FIG. 6. The function u_{elastic} according to the Wagner and Horner theory (indicated by "total"), and according to the simulations (indicated by "MD"). The data indicated by "average" correspond to the theoretical contribution of the second term in Eq. (15).

the lattice parameter. The rather strong dependence on the lattice parameter originates mainly from the exponential form of the metal-hydrogen force Ψ^{ma}.

With these results it is possible to calculate the function $u_{\text{elastic}}(c)$ in Eq. (7). Since the hydrogen distribution is homogeneous, the Hamiltonian (15) is equal to the internal elastic energy U. The partial elastic energy of hydrogen is $u(c)=\partial U/\partial N_{\text{H}}$, and $u_{\text{elastic}}(c)=u(c)-u(0)$. For the numerical evaluation, values of the bulk modulus B are required, which are determined by simulation at several hydrogen concentrations for $T=600$, 800, and 1000 K. Also the volume as a function of the hydrogen concentration is taken from the simulations, for simplicity. This results in the values for u_{elastic}, which are indicated in Fig. 6 by "total." Also the separate contribution of the average elastic energy [i.e., the second term in Eq. (15)] is shown. The curve labeled "MD" corresponds to the elastic interaction as determined directly from the simulations. Obviously, there is a large discrepancy between the prediction of the theory and the result of the simulations.

Although the theory of Wagner and Horner was developed for macroscopic metal-hydrogen systems, the large discrepancy with the result of the simulations for the small system considered here is rather surprising. The question arises whether the discrepancy originates from a failure of one of the assumptions made in the theory. However, it is outside the scope of this paper to find an answer to this question.

V. CONCLUSIONS

A simulation model of an elastic lattice gas has been presented. Andersen's scheme of molecular-dynamics simulation in the isothermal-isobaric ensemble turns out to be a convenient way of studying the model. It is found that Andersen's Lagrangian yields volume changes which correspond to a lattice with a free surface (although periodic boundary conditions are used).

The particle insertion method to determine free energies is easily implemented in isothermal-isobaric simulations. It is found that the method works well for a lattice gas, even up to the highest concentrations.

The experimental value of the partial volume of hydrogen in palladium is almost exactly reproduced by the simulation model. Also the Maxwell relation $(\partial\mu/\partial p)=(\partial V/\partial N_{\text{H}})$ is confirmed by the simulations. Finally, the well-known α-α' phase transition in metal-hydrogen systems is reproduced by the simulation model.

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