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STRUCTURE AND DYNAMICS OF LOW-DIMENSIONAL SYSTEMS

By

WEIQING ZHONG

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the Degree of

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ABSTRACT

STRUCTURE AND DYNAMICS OF LOW-DIMENSIONAL SYSTEMS

by

Weiqing Zhong

I studied structural and dynamical properties of low dimensional systems using numerical approaches at different levels of sophistication. I focused my interest on the physical phenomena associated with the interaction of atoms with surfaces. I studied two topics which are intimately connected with this interaction. One of them is a procedure to quantitatively interpret atomic force microscopy (AFM) images of solid surfaces. The other topic is the effect of adsorbate on structural, electronic and dynamical properties of the substrate.

When studying theory for the AFM, I considered a model system consisting of a Pd metal tip probing the graphite surface. Using *ab initio* density functional theory (DFT), I calculated the interaction between this Pd AFM tip and graphite and mapped it onto a parameterized energy functional. The calculation of AFM tip trajectories at different loads revealed that atomic resolution is only achievable for loads exceeding 5×10^{-9} N. Larger loads, on the other hand, are likely to lead to surface destruction. Calculated variation of potential energy along a trajectory has been used subsequently to determine atomic scale friction. Assuming no wear and a complete dissipation of the energy gained by the Pd tip atoms, I found a very small friction coefficient $\mu \approx 10^{-2}$ for loads near 10^{-8} N and an increase in μ with increasing load in agreement with experiments.

I selected H/Pd as the model system to study the effect of adsorbate on the structural and dynamical properties of the substrate. I based the description of the H-Pd system on density functional calculations, which were subsequently mapped onto a parametrized many-body alloy Hamiltonian. Using this Hamiltonian, I calculated the equilibrium structure of the clean and hydrogen covered Pd (001) and Pd (110) surfaces, as well as the corresponding surface phonon spectra. The most pronounced effect of hydrogen is a strong softening of the Rayleigh wave on Pd(001), which is indirectly related to "hydrogen embrittlement" observed in the bulk. I addressed this latter problem using molecular dynamics. I studied the equilibrium structure, elastic properties, and in particular the mechanical breakdown of bulk Pd under tensile stress, as a function of temperature and hydrogen concentration. My results indicate that the microscopic origin of "hydrogen embrittlement" is an increased *ductility* and *plasticity* in regions saturated by hydrogen, in agreement with the postulated Hydrogen Enhanced Local Plasticity mechanism.

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PUBLICATIONS

- W. Zhong and D. Tománek, First-Principles Theory of Atomic-Scale Friction, Phys. Rev. Lett. 64, 3054 (1990).
- W. Zhong, G. Overney, and D. Tománek, Theory of Atomic Force Microscopy on Elastic Surfaces, The Structure of Surfaces III, edited by S.Y. Tong, M.A. Van Hove, X. Xide and K. Takayanagi, Springer-Verlag, Berlin (1991), p243.
- W. Zhong, G. Overney, and D. Tománek, Limits of Resolution in Atomic Force Microscopy Images of Graphite, Europhys. Lett. 15, 49 (1991).
- 4. G. Overney, W. Zhong, and D. Tománek, Theory of Elastic Tip-Surface Interactions in Atomic Force Microscopy, J. Vac. Sci. Technol. B9, 479 (1991).
- D. Tománek, W. Zhong, and H. Thomas, Calculation of an Atomically Modulated Friction Force in Atomic Force Microscopy, Europhys. Lett. 15, 887 (1991).
- 6. D. Tománek and W. Zhong, Palladium-Graphite Interaction Potentials Based on First-Principles Calculations, Phys. Rev. B43, 12623 (1991).
- W. Zhong, Y. S. Li, and D. Tománek, Effect of Adsorbates on Surface Phonon Modes: H on Pd(001) and Pd(110), Phys. Rev. B44, 13053 (1991).
- G. Overney, D. Tománek, W. Zhong, Z. Sun, H. Miyazaki, S. D. Mahanti, and H.-J. Güntherodt, Theory for the Atomic Force Microscopy of Layered Elastic Surfaces, J. Phys. : Cond. Mat. 4, 4233 (1992).
- W. Zhong, Y. Cai, and D. Tománek, Mechanical Stability of Pd-H Systems: A Molecular Dynamics Study, Phys. Rev. B 46 8099 (1992).

- W. Zhong, G. Overney, and D. Tománek, Structural Properties of Fe Crystals, Phys. Rev. B 47 95 (1993).
- G. Overney, W. Zhong, and D. Tománek, Structural Rigidity and Low Frequency Vibrational Modes of Long Carbon Tubules, Z. Phys. D 27 93 (1993).
- W. Zhong, D. Tománek, and George F. Bertsch Total Energy Calculation for Extremely Large Clusters: The Recursive Approach, Solid State Comm. 86 607 (1993).
- W. Zhong, Y. Cai, and D. Tománek, Computer Simulation of Hydrogen Embrittlement in Metals, Nature 362 435 (1993).
- 14. G. Overney, W. Zhong, and D. Tománek, Structural Optimization of Stage-1 Alkali-Metal-Graphite Intercalation Compounds Using Density Functional Theory, in preparation.
- 15. D. Tománek, W. Zhong and E. Krastev Stability of Multi-Shell Fullerenes, submitted for publication.

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Chapter 1 Introduction

The major task of theoretical physics is to understand the laws which govern nature, use them to explain observed phenomena, and predict the properties of new physical systems. The subject of interest for theoretical condensed matter physics are electronic, magnetic, structural, and dynamical properties of solids and liquids. The most popular technique to address these properties from first principles is the Density functional theory [Lun 83] in the Local Density Approximation (LDA), which has been shown to describe ground state properties of solids with a high accuracy. Since this theory is free of adjustable parameters, I will use it as a basis for all the calculations in this Thesis.

The large computational requirement associated with *ab initio* methods such as the LDA limits the range of its applicability to relatively small systems with a high symmetry. In order to describe the dynamical behavior of large systems with low symmetry, I calculate the interatomic forces using a parametrized Many-Body Alloy Hamiltonian [Zho 91a], which I developed as an efficient interpolation scheme between *ab initio* results. In spite of its simplicity, this Hamiltonian describes the interatomic interactions in simple metals and late transition metals with sufficient accuracy. The total energy calculations in this Thesis are performed using the combination of the LDA and MBA formalisms. The dynamical behavior is then calculated using the interatomic forces in the equations of motion. For a canonical ensemble, this procedure yields lattice dynamics at zero and finite temperatures, and the elastic response to externally applied loads.

In this thesis, I have applied these calculation tools to study structural and dynamical properties of low dimensional systems. I focused my interest on the physical phenomena associated with the interaction of atoms with surfaces. One important application of this interaction is the quantitative interpretation of atomic force microscopy (AFM) images of solid surfaces. For the model system consisting of a Pd metal tip and graphite. I calculated the AFM images, the limits of nondestructive imaging, and the origin of atomic-scale friction. The second important topic is the effect of adsorption on the properties of the substrate. I considered Pd as a model system, and studied the effect of adsorbed hydrogen on the surface structure and phonon spectra. I found these results to be of significance when interpreting bulk phenomena associated with adsorbed hydrogen, such as the "hydrogen embrittlement. In the following Section 1.1 and 1.2, I will introduce these two topics, emphasizing the open questions and the general importance of these calculations. The structure of my Thesis will be addressed in Section 1.3.

1.1 Theory for the Atomic Force Microscopy

Following its invention by Binnig et al in 1986, the Atomic Force Microscope (AFM) [Bin 86, Bin 87] has been rapidly evolving into a powerful tool to examine the morphology and local rigidity of conducting and insulating surfaces alike [Tom 89]. The AFM uses an "atomically" sharp tip to scan the sample surface at a sample-to-tip separation of a few angstroms. Unlike the more established Scanning Tunneling Microscope (STM) [Bin 82], which is sensitive to the electronic density of states near the Fermi energy [Ter 83], the AFM probes the force field F_{ext} between an "atomically sharp" tip and the substrate (Figure 1.1). This force F_{ext} is detected by the deflection of a soft cantilever which supports the tip. During a horizontal scan of the surface, the AFM measures and records the equilibrium vertical tip position, while F_{ext} is been kept constant by regulating the deflection of the cantilever. The resolution of atomic-scale features at the surface is possible if the equilibrium tip height z is detectably different at inequivalent (e.g. on-top, hollow) surface sites. This is the case if the corresponding corrugation $\Delta z \gtrsim 0.05$ Å, which is the sensitivity of the AFM under ideal conditions.

Since the AFM provides real-space image, same as the STM, the ambiguity and complexity of interpreting diffraction patterns is avoided. The power of the AFM lies in its ability to detect local structure rather than periodic patterns. These can be point defects, steps, grain boundaries, and similar on conducting or non-conducting surfaces. The AFM has been used successfully to image a variety of systems with atomic resolution. Very good results have been achieved in ionic system such as NaCl [Mey 90], and layered materials such as graphite [Bin 87]. While the experiments have primarily focused on achieving atomic resolution, two questions have remained unanswered so far. The first is, under which conditions atomic-scale features can be observed by a microscopic tip, and how these features relate to the surface topography. The second open question, which will be addressed in this Thesis, relates to the conditions, under which nondestructive imaging can be achieved.

The major challenge for the theory is to determine whether it is possible to achieve atomic resolution using the AFM on a specific material, under well controlled and idealized conditions. The potential for atomic resolution is limited in two ways.



Figure 1.1: Schematic picture of the Atomic Force Microscope (AFM)

First, if the load applied to the tip, F_{ext} , is very small, the tip-substrate separation is large, and the corrugation Δz is too small to be observed. For "dull" tips with multiple apex atoms, the corrugation is further decreased due to the tip/substrate incommensurability. At large values of F_{ext} , where the tip is capable of probing the corrugation of the charge density, the tip-surface distance is very small. Under these conditions, a destruction of the surface or the tip is likely. The objective of my calculations is to determine if there is an optimum force, which yields detectable corrugations on the atomic scale, but which is still non-destructive to the surface.

The AFM has been used to investigate the friction on the atomic scale [Mat 87]. This experiment investigated the friction force experienced by the tip during a scan with no wear across a perfect surface. In general, friction forces are observed in nature whenever two bodies in contact are in relative motion [Lan 60]. The force F_f is related to the applied load F_{ext} between the two bodies by

$$F_f = \mu F_{\text{ext}}.\tag{1.1}$$

The friction coefficient μ has been found to range typically between 10^{-2} for very smooth interfaces and 1 for rough interfaces. Friction forces have dissipative character: they couple the macroscopic mechanical degrees of freedom to microscopic degrees of freedom. In this way, macroscopic mechanical energy is dissipated. At rough interfaces, dislocation motion and plastic deformations are mainly responsible for the dissipation of macroscopic energy. This fact makes the friction process with wear one of the most complex and least understood process in nature. Friction without wear, on the other hand, occurs between perfect and weakly interacting surfaces and is much easier to understand. Since in this case, no atomic rearrangement occurs, it is phonons and electronic excitations which serve as the only source for energy dissipation. Atomic-scale friction, which can be quantitatively studied using the AFM operating in a nondestructive manner, falls in this second category. [Sla 93]

The idealized conditions for this atomic-scale friction open the problem to an independent fist-principles theoretical study [Zho 90]. In absence of plastic deformations, friction originates in an atomic-scale corrugation of the interaction potential which is probed by the tip when scanning the surface under an external force F_{ext} . The two contributions to this potential are the variation of tip-substrate bond strength and the work against F_{ext} if the tip-substrate distance varies along the trajectory. The maximum friction force can be estimated using the variations of the total potential energy of the tip-substrate system during the scan.

A microscopic description of friction without wear must address the fact that friction is a non-conservative process. In other words, the friction force depends on the direction of motion between the two bodies in contact. A closed-loop integral over such a force yields a nonzero value which corresponds to the dissipated energy. In other words, the friction force cannot be obtained from a gradient of a potential. A quantitative study of friction requires the investigation of the microscopic mechanisms for energy dissipation and of the effectiveness with which macroscopic degrees of freedom are coupled to microscopic degrees of freedom.

In order to study these process quantitatively, a Friction Force Microscope (FFM) has been constructed and used to measure the atomic-scale friction [Ove 92]. A very precise FFM can determine the horizontal and vertical force on the tip simultaneously Since different portions of otherwise flat surface may have different friction coefficients, the FFM may provide the most detailed information and enhanced contrast as compared to the AFM image of such a surface. Hence, friction imaging may prove to be a very useful application of the FFM [Ove 92].

1.2 Structure and dynamics of H–Pd systems

The interaction of hydrogen with transition metals is a fundamentally interesting topic with wide ranging technological applications [Ale 78]. The dissociative adsorption of molecular hydrogen at a metal surface and the subsequent surface and bulk diffusion of atomic hydrogen is a prototypical surface process. This is a well-suited model system for the study of the hydrogen-metal bond at different stages of the reaction. At least of equal importance is the microscopic understanding of the effect of hydrogen on the structural and dynamical properties of the substrate or host metal. This effect, which has received less attention in the literature, manifests itself on the surface as H-induced surface relaxation, surface reconstruction, as well as a change of the surface phonon spectra. Hydrogen atoms are known to diffuse into many metals easily. In the bulk, hydrogen can change the equilibrium structure and elastic properties of the host metal. Technologically, hydrogen atoms in the bulk of transition metals can also reduce the mechanical stability of the system significantly, which is known as hydrogen embrittlement. The particular interest in Pd is motivated to a large degree by the ability of this metal to form hydrides and thereby to act as a medium for hydrogen storage.

In this Thesis, I will concentrate on studying the effect of adsorbed hydrogen on the surface phonon modes of Pd, and the microscopic origin of hydrogen embrittlement in Pd. I will show that both phenomena are intimately related.

1.2.1 Effect of hydrogen on surface phonon modes of Pd

Extensive studies of interaction between adsorbed H and the Pd surface include the characterization of the H-metal bond, hydrogen induced surface relaxation and reconstruction, and the effect of hydrogen on the the electronic structure of the metal substrate [Tom 86b, Sun 89, Tom 91a, Cat 83, He 88, Beh 80, Rie 83, Rie 84, Tar 86, Nyb 83, Bes 87]. So far, most research effort has been focussed on the adsorption geometry and on the electronic and structural properties of the adsorption system. Surface phonons have received far less attention in the recent literature, in spite of the wealth of information they contain about the nature of bonding at surfaces. This is caused mainly by the difficulty to measure and calculate reliable surface phonon dispersion curves throughout the whole surface Brillouin zone.

Only recently, He time-of-flight spectroscopy [Toe 87, Lah 87, Doa 83, Har 85] and electron-energy-loss spectroscopy(EELS)[Leh 83, Roc 84, Wut 86, Iba 87, Yos 88] have been used to measure the dispersion curves of surface phonons on a variety of metal substrates. The quantitative interpretation of these data is lacking in most cases, since predictive *ab initio* calculations (such as "frozen-phonon" calculations) are computationally very involved. Only in selected cases, Local Density Approximation (LDA) [Koh 65] calculations have been performed for the high-symmetry modes [Ho 86].

The majority of published phonon calculations use lattice dynamics based on simple two- and three-body potentials [Joh 72, Bor 84, Bor 85, Hal 88]. These types of calculations use bulk and surface interatomic force constants and distances as independent parameters which are chosen to fit experimental results [Lah 87]. In general, these calculations show a good agreement with the observed data. The predictive power is limited by the generally large number of force constant parameters which depend on the model, the system and the surface studied. While these calculations can provide a rough guidance in the interpretation of experimental results, direct comparisons between different models are of limited use.

More recently, the Embedded-Atom Method (EAM) [Daw 84, Foi 85, Foi 87,

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Daw 89, Foi 89] has been used to calculate phonon dispersion relations on surfaces such as Cu(100), Cu(111) and Ag(111) [Nel 77, Nel 89, Luo 88]. The major difference with respect to the calculations quoted above is that all parameters have been obtained by fitting the measured bulk properties. The EAM has proven to be quite successful in the prediction of surface phonon spectra and the corresponding changes of interatomic force constants and distances at surfaces. The major weakness of these calculations is the limitation to single-component systems, since charge transfers between different sites are assumed to be zero. Of less importance is the fact that the success of the EAM technique depends on the type and quality experimental data and that the fit is based mainly on such observed bulk properties.

To avoid these weak points, I developed a model Many-Body Alloy (MBA) Hamiltonian for the Pd-H system, based on *ab initio* calculations of bulk materials (both single component systems and alloys). This Hamiltonian can be easily applied to many alloy systems, and the parametrization can be uniquely determined from a set of *ab initio* calculations. This mapping does not leave any adjustable parameters. The MBA technique is a very useful tool to determine the total energy and forces acting on individual atoms at the surface and in the bulk. In particular, using lattice dynamics, the surface phonon modes of clean and hydrogen adsorbed Pd surface can be calculated. This allows for a detailed analysis of the effect of hydrogen on the surface phonon spectra of Pd.

1.2.2 Mechanical stability of Pd-H systems

Fundamental understanding of the mechanical stability of transition metals under various conditions is of great technological importance. Very little is known about the atomic-level response of bulk metals to applied tensile stress, at varying temperature and hydrogen concentration. The study of these effects is expected to answer some key questions related to macroscopic materials properties, especially the so-called "hydrogen embrittlement". This hydrogen-induced reduction of the mechanical strength of metals causes great concerns when considering hydrogen storage in metals, stability of fusion reactors and underwater structures, and space technology.

In spite of a significant effort to resolve this important problem, there is still substantial controversy regarding the microscopic origin of "hydrogen embrittlement" in a given system [Bir 79]. One of the oldest and most commonly referred to mechanisms of hydrogen embrittlement is the "decohesion mechanism" which associates this effect with a decreased metal bond strength in the presence of hydrogen [Ste 60, Foi 86]. The "hydrogen related phase change mechanism" has been suggested as the origin of "hydrogen embrittlement" in systems where a brittle hydride phase is stabilized by the presence of hydrogen and the crack tip stress field [Wes 69]. The "Hydrogen Enhanced Local Plasticity" (HELP) mechanism postulates a hydrogen-induced local plasticity enhancement at crack tips which facilitates fracture formation [Bea 72].

The most straight-forward way to address the above questions is to use a molecular dynamics (MD) technique. Such a calculation describes the evolution of the system with time, based on a direct numerical solution of the equations of motion for individual atoms. This procedure goes beyond lattice dynamics [Mar 63] which is limited to small atomic displacements and can not address problems such as the melting transition or fracture. The appropriate MD technique for these questions will describe the evolution of the system at constant nonzero temperatures using Nosé dynamics. It can also model the response of a system to an externally applied tensile stress [All 90, Car 90]. Such a simulation provides microscopic information about the dynamics of the system, including structural changes during phase transitions (such as melting or crack formation due to tensile stress under different conditions).

1.3 Structure of the Thesis

In this Thesis, I will address primarily two subjects related to interaction between adsorbed atoms and surfaces. They are the Atomic Force Microscopy and atomicscale friction at graphite surface, and the structure and dynamics of Pd-H systems.

In Chapter 2, I will review the computational tools I used. I will start with the Density Functional Theory, in particular its implementation in the Local Density Approximation (LDA) technique. I will briefly discuss the computational details, such as the basis and use of *ab initio* pseudopotentials. Then, I will derive the Many-Body Alloy Hamiltonian for metal and alloy systems. At the end, I will present the formalism for Nosé and Rahman-Parrinello Molecular Dynamics simulations, which allows for the description of the dynamics of a canonical ensemble exposed to an external anisotropic stress field.

In Chapter 3, I will develop the theory of Atomic Force Microscopy. I will first present the *ab initio* results for the Pd-graphite interaction. Next, I will present a parametrization of the Pd-graphite interaction potential, which is inspired by Embedded Atom Method and which is not restricted to high symmetry sites. Combined with continuum elasticity theory, these results will be used to determine whether atomic resolution can be achieved nondestructively in AFM experiments on the graphite surface. Then, I calculate the atomic scale friction of a sharp Pd tip on graphite and determine the friction coefficient. I propose two idealized friction machines to explain the possible microscopic mechanisms of energy dissipation in the friction process.

In Chapter 4, I calculate the equilibrium structure and dynamics of Pd-H systems. This chapter is divided into two parts. In the first part, I construct and test the manybody alloy Hamiltonian for the Pd-H system. I calculate the equilibrium structure and surface phonon spectra of clean and hydrogen covered Pd surfaces, in order to determine the effect of hydrogen on the equilibrium structure and dynamics of Pd. In the second part, I use molecular dynamics to study the dynamical properties of Pd-H systems at finite-temperature. I will study the melting transition of pure Pd in the bulk bulk and the mechanical stability of bulk Pd at different temperatures and hydrogen concentrations. I will show that the mechanisms of hydrogen embrittlement can be understood by carefully analyzing the MD simulation results.

Chapter 2

Theory

2.1 Ab initio Density Functional Formalism

The basic theory governing the electronic and structural properties of solids is quantum mechanics. In systems with many particles (such as $\sim 10^{23}$ in solids), the exact solution of quantum mechanical equation is essentially impossible to obtain, due to the complex many-body interactions which couple many degrees of freedom. Even though the ground state energy can be expressed in terms of one- and two-particle Green's functions, the computation of these quantities involves a set of differential equations which couple all *n*-particle Green's functions. The basic difficulty to describe even ground-state properties of solids is significantly reduced in the Density Functional Theory.

2.1.1 Density Functional Theory

In this Thesis, I will derive the Density Functional Theory (DFT) formalism very briefly, and refer the reader to other excellent reviews for more details [Lun 83, Cal 84, Jon 89, Mah 90, Dre 90]. The DFT is based on two theorems proposed by Hohenberg and Kohn in 1964 [Hoh 64], which state that:

- 1. The electron density $n(\vec{r})$ in the ground state is a functional of the potential $V(\vec{r})$.
- 2. The potential $V(\vec{r})$ is a unique functional (to within a constant) of the electron density $n(\vec{r})$.

This is equivalent to saying that the exact ground state properties of a system can be calculated using a variational approach involving only the electron density, rather than an antisymmetric wave function.

I follow the derivation by Levy [Lev 79]. The Hamiltonian describing the motion of N electrons in an external potential $V_{ext}(\vec{r})$ is

$$H = T + V_{ee} + V_{ext}, \tag{2.1}$$

where T and V_{ee} are the kinetic and electron-electron interaction operators, respectively. For all densities $n(\vec{r})$ which can be obtained from an antisymmetric wave function $\psi(\vec{r_1}, \vec{r_2}, \ldots, \vec{r_N})$, Levy defined the functional

$$F[n] = min\langle\psi|T + V_{ee}|\psi\rangle = \langle\psi_{min}^{n}|T + V_{ee}|\psi_{min}^{n}\rangle, \qquad (2.2)$$

where the minimum is taken over all ψ that give the density *n*, and ψ_{min} minimize F[n].

Let us denote E_{GS} , ψ_{GS} , and $n_{GS}(\vec{r})$ to be ground state energy, wave function, and electron density of the system under external field V_{ext} . Then,

$$E[n] \equiv \int d\vec{r} V_{ext}(\vec{r}) n(\vec{r}) + F[n]$$

$$= \langle \psi^n_{min} | T + V_{ee} + V_{ext} | \psi^n_{min} \rangle$$

$$\geq E_{GS},$$
(2.4)

which follows from the variation principle applied to the ground state. This relation applies in particular to the ground state wave function $\psi_{min}^{n_{GS}}$, which gives

$$\langle \psi_{GS} | T + V_{ee} + V_{ext} | \psi_{GS} \rangle \le \langle \psi_{min}^{n_{GS}} | T + V_{ee} + V_{ext} | \psi_{min}^{n_{GS}} \rangle.$$

$$(2.5)$$

The charge density corresponding to ψ_{GS} and $\psi_{min}^{n_{GS}}$ are the same, so the interaction with the external potential can be subtracted on both sides of the inequality,

$$\langle \psi_{GS} | T + V_{ee} | \psi_{GS} \rangle \le \langle \psi_{min}^{n_{GS}} | T + V_{ee} | \psi_{min}^{n_{GS}} \rangle.$$

$$(2.6)$$

Combined with Eq. (2.4), we find

$$\langle \psi_{GS} | T + V_{ee} | \psi_{GS} \rangle = \langle \psi_{min}^{n_{GS}} | T + V_{ee} | \psi_{min}^{n_{GS}} \rangle = F[n_{GS}]$$
(2.7)

So, the ground state energy

$$E_{GS} = \int d\vec{r} V_{ext}(\vec{r}) n_{GS}(\vec{r}) + F[n_{GS}]$$
(2.8)

is a functional of ground state charge density. This equation, combined with Eq. (2.4) completes the proof of the basic theorems. These theorems provide a general method for calculating ground state properties. However, theses theorems do not suggest any particular form of the functional F[n]. To solve this problem, Kohn and Sham introduced the Local Density Approximation (LDA) in 1965 [Koh 65].

2.1.2 Local Density Approximation

In their famous paper [Koh 65], Kohn and Sham decomposed the energy functional as

$$E[n] = T_0[n] + F + E_{xc}, (2.9)$$

where

$$F = \int d\vec{r} V_{ext}(\vec{r}) n(\vec{r}) + \int \int d\vec{r_1} d\vec{r_2} \frac{n(\vec{r_1})n(\vec{r_2})}{|\vec{r_1} - \vec{r_2}|}.$$
 (2.10)

Here, T_0 is the kinetic energy of a system of non-interacting quasi-electrons with the density $n(\vec{r})$. F is the Coulomb energy of the system of quasi-electrons. E_{xc} is the exchange-correlation energy, which gives the contributions to the total energy except for the kinetic and Coulomb terms.

Variational theory, applied on this energy functional, gives

$$\frac{\delta T_0[n]}{\delta n} + V_{ext} + V_H + V_{xc} - \mu = 0.$$
(2.11)

Here, V_H is Hartree potential derived from the second term of F, $V_{xc} = \delta E_{xc}[n]/\delta n$, and μ is the Lagrange multiplier which constrains the total number of particles to be constant. On the other hand, the variational equation for a system of non-interacting quasielectrons reads

$$\frac{\delta T_0[n]}{\delta n} + V - \mu = 0. \tag{2.12}$$

Inspection of Eqs. (2.11) and (2.12) shows that they are the same if $V = V_{ext} + V_H + V_{xc}$. The solution of Eq. (2.12) can be obtained using a Schrödinger equation. For a system of quasi-electrons, this leads to a set of Kohn-Sham equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{ext} + V_H(\vec{r}) + V_{xc}(\vec{r})\right]\psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r})$$
(2.13)

and

$$n(\vec{r}) = \sum_{i=1}^{\infty} |\psi_i(\vec{r})|^2.$$
(2.14)

Note that ϵ_i and ψ_i are not necessarily the eigenvalues and eigenfunctions of the system; only the electron density $n(\vec{r})$ is the correct physical quantity.

Kohn-Sham equations involve a universal functional, the exchange-correlation energy $E_{xc}[n]$, and its functional derivative $V_{xc}(\vec{r})$, which are only known exactly for a homogeneous electron gas. As a manageable simplification which has been introduced in the Local Density Approximation (LDA), the functional $E_{xc}[n]$ is replaced by a local function $E_{xc}(n)$. Hence,

$$E_{xc} = \int d\vec{r} n \epsilon_{xc}^0(n(\vec{r})), \qquad (2.15)$$

where ϵ_{xc}^{0} is the exchange-correlation energy density for the homogeneous electron gas. Many parametrizations of ϵ_{xc}^{0} have been proposed, such as that of Wigner[Wig 38], Kohn and Sham[Koh 65], Hedin and Lundqvist[Hed 71], Ceperly and Alder[Cep 80] etc.. In our calculation, we usually use Hedin-Lundqvist parametrization, which have been proven to give good results.

The LDA is a accurate in systems with a slowly varying charge density. It is also accurate in systems with a large charge density, where the kinetic and Hartree terms dominate E_{xc} , and in systems with small charge densities, where gradient of $n(\vec{r})$ are small. This formalism has been successfully applied to many systems, including atoms, molecules, clusters, surfaces and bulk of solids.

2.1.3 Computational details

In the real calculations based on the DFT, the initial guess of the charge density is obtained using a superposition of atomic charge densities. Using this charge density as input, V_{xc} can be obtained using the LDA. This provides all of the information needed to set up the Kohn-Sham equations, which are usually solved as matrix equations in a given basis. The solution of the Kohn-Sham equations gives ϵ_i and ψ_i . Then the Fermi energy can be determined and the charge density obtained as output. In the next iteration, this charge density is used as input, and the procedure is repeated until self-consistency is achieved. In the self-consistent field method, the input and output potential is required to be the same.

One practical consideration in a realistic calculation is the selection of a basis. The plane wave basis is the simplest and easiest to implement, since all basis functions are orthogonal to each other. Plane waves give a complete set of basis functions; a finite basis is typically limited by the cutoff energy E_c . This basis is ideal for nearly free electron systems like simple metals, where the effective potential does not vary too much. The number of basis functions needed is proportional to $E_c^{d/2}$, where d is the dimensionality of the system. The computational load increases as $E_c^{3d/2}$, since solution of Kohn-Sham equations involves matrix diagonalization. This computational effort makes a plane wave basis impractical for materials with localized electrons, i.e. transition metals and semiconductors.

In my Linear Combination of Atomic Orbitals (LCAO) [Laf 71, Cal 72, Che 84] calculation, I use a local Gaussian basis in order to improve efficiency [Har 82]. The form of the basis functions is

$$f_i = \begin{cases} exp(-\alpha_i r^2) & \text{for } s \text{ states} \\ (x, y, z)exp(-\alpha_i r^2) & \text{for } p \text{ states} \\ (xy, yz, zx, x^2 - y^2, r^2 - 3z^2)exp(-\alpha_i r^2) & \text{for } d \text{ states} \end{cases}$$

This basis provides an efficient representation of the atomic wave functions in systems with localized electrons. More than one radial Gaussians are typically used for each orbital to allow for variational freedom. Completeness of the basis is tested by increasing the number and location of Gaussian functions and monitoring the convergence of the calculated total energy. In my calculations, usually three to four Gaussian decays for each atomic orbital $(s, p_x, p_y, ...)$ are found to give a sufficiently complete basis set. The decay constants α for a given atomic type are chosen to minimize the total energy of the bulk system. Since the LCAO basis contains nonorthogonal basis functions, the solution of the Kohn-Sham equations is more involved.

Beside using Gaussian functions for basis functions, it is very useful to fit the screened atomic potentials and charge density to a set of Gaussians as well. This procedure allows for an efficient evaluation of crystal LDA-Bloch functions up to very high Fourier components corresponding to a large value of the energy cutoff E_c .

Most electronic and structural properties of solids are determined by the behavior of valence electrons, while the core electrons are essentially inert. Valence electrons feels a very weak potential outside the core due to the screening by the core electrons. Replacing the true ionic potential by a pseudopotential, which models the nuclear and the nonlocal core potential, simplifies the calculation considerably. I use the *ab initio* pseudopotential form proposed by Hamann, Schlüter, and Chiang [Ham 79, Bac 82], which has following desirable properties:

- 1. Pseudopotentials are continuous non-divergency functions with a continuous first derivative everywhere.
- 2. Real and pseudo eigenvalues for valence states agree for a chosen "prototype" atomic configuration.
- 3. Pseudo wavefunctions are nodeless.
- 4. Real and pseudo wavefunctions agree beyond a chosen "core radius" r_c .
- 5. The integral from 0 to r of the real and pseudo charge densities agree for $r > r_c$ for each valence state (norm conservation).
- 6. The logarithmic derivatives of the real and pseudo wave functions and their first energy derivatives agree for $r > r_c$.

Properties 5 and 6 are important to ensure optimum transferability of the pseudopotential between different chemical environments. Norm conservation enables the use of the pseudo charge density instead of the real charge density in DFT calculations. Property 6 ensures the correct scattering properties of the potential. No adjustable parameters occur in the construction of the Hamann-Schlüter-Chiang pseudopotentials.

The LCAO Gaussian basis and *ab initio* pseudopotentials are very powerful which make precise LDA calculations for transition metals or semiconductors feasible. Nevertheless, the computational load increases rapidly with increasing complexity of the system (reduced symmetry, increased size of the unit cell). For very large systems, parametrized calculation schemes are more appropriate. A very efficient scheme to calculate the total energy of a system is the Many-Body Alloy Hamiltonian to be discussed below.

2.2 Many-Body Alloy Hamiltonian

The Many-Body Alloy (MBA) Hamiltonian is an extension of a total energy scheme, which has been successfully used previously to study the electronic and structural properties of small clusters, surfaces of metals and dilute metal alloys [Tom 83, Tom 86a, Tom 85b, Tom 85a, Spa 84]. Its derivation has been published recently by W. Zhong, Y.S. Li, and D. Tomanek [Zho 91a].

As discussed earlier [Tom 83, Tom 86a, Tom 85b, Tom 85a], the total cohesive energy of a solid can be decomposed into individual atomic binding energies $E_{coh}(i)$, as

$$E_{coh}(tot) = \sum_{i} E_{coh}(i).$$
(2.16)

The binding energy of atom *i* consists of an attractive part due to the hybridization of orbitals, $E^{BS}(i)$, and a term $E^{R}(i)$ describing repulsive interactions. Hence,

$$E_{coh}(i) = E^{BS}(i) + E^{R}(i).$$
(2.17)

Different simplified parametrization forms have been proposed [Bre 89] for the manybody energy $E^{BS}(i)$. The embedded-atom method (EAM) [Daw 84, Foi 85, Foi 87, Daw 89, Foi 89] takes $E^{BS}(i)$ as a unique function of the total charge density of the unperturbed host at the site *i*. Since this parametrization might cause problems in the case of alloys with nonzero charge transfer, I base my expression for $E^{BS}(i)$ on a tight-binding Hamiltonian. In a one-electron picture, the binding energy of atom *i* is given by an integral over the local density of states at *i*, $N_i(E)$, as

$$E^{BS}(i) = -\int_{-\infty}^{E_F} (E - E_0) N_i(E) dE.$$
(2.18)

In the second moment approximation, $E^{BS}(i)$ is proportional to the effective bandwidth, which in turn is proportional to the square root of the second moment $M_2(i)$ of the local density of states. Then,

$$E^{BS}(i) \propto M_2(i)^{1/2} = \left\{ \sum_{j \neq i} t_{ij}^2 \right\}^{1/2} \propto \left\{ \sum_{j \neq i} e^{-2qr_{ij}} \right\}^{1/2}.$$
 (2.19)

In the last part of this equation, I have related M_2 to the hopping integral t_{ij} between neighboring sites *i* and *j* and assumed an exponential distance dependence of the effective (screened) hopping integrals, as $t(r) \propto e^{-qr}$.

The repulsive part is parametrized by a pairwise Born-Mayer potential with an exponential distance dependence, as

$$E^{R}(i) \propto \sum_{j \neq i} e^{-p\tau_{ij}}.$$
(2.20)
Then,

$$E_{coh}(i) = E^{BS}(i) + E^{R}(i)$$

= $-\left\{\sum_{j \neq i} \xi_{0}^{2} \exp\left[-2q\left(\frac{r_{ij}}{r_{0}} - 1\right)\right]\right\}^{1/2} + \epsilon_{0}^{R} \sum_{j \neq i} \exp\left[-p\left(\frac{r_{ij}}{r_{0}} - 1\right)\right].$ (2.21)

Here, r_{ij} is the distance between atoms *i* and *j*. Parameters *p* and *q* describe the distance dependence of the hopping integrals and the Born-Mayer interactions, respectively, and are related to the bulk elastic properties. In the case of a single-component bulk crystal, Eq. (2.21) can be used to reproduce the equilibrium properties, such as the equilibrium nearest neighbor distance r_0 and the bulk cohesive energy E_{coh} (bulk). In this case, assuming isotropic hopping integrals, ξ_0 and ϵ_0^R in Eq. (2.21) are given by

$$\xi_0 = \frac{E_{coh}(\text{bulk})}{(1 - q/p)(Z_{\text{bulk}})^{1/2}}, \qquad (2.22)$$

$$\epsilon_0^R = \frac{\xi_0}{Z_{\text{bulk}}^{1/2}} \frac{q}{p} , \qquad (2.23)$$

where Z_{bulk} is the bulk coordination number.

For systems with more than one component (such as alloys and compounds), Eq. (2.21) can be generalized to

$$E_{coh}(i,\alpha) = -\left\{\sum_{j\neq i} \xi_{0,\alpha\beta}^{2} \exp\left[-2q_{\alpha\beta}\left(\frac{\tau_{ij,\alpha\beta}}{\tau_{0,\alpha\beta}}-1\right)\right]\right\}^{1/2} + \sum_{j\neq i} \epsilon_{0,\alpha\beta}^{R} \exp\left[-p_{\alpha\beta}\left(\frac{\tau_{ij,\alpha\beta}}{\tau_{0,\alpha\beta}}-1\right)\right], \qquad (2.24)$$

where α, β represent the types of atoms *i* and *j*, respectively.

As I discussed above, the Hamiltonian underlying the energy expression in Eq. (2.24) describes the essential physics governing cohesion in many solids. The large flexibility and the microscopic basis for the description of many-body attractive interactions in alloys makes the MBA Hamiltonian superior to embedded-atom like schemes [Daw 84, Bre 89] for two main reasons. First, unlike the EAM, Eq. (2.24) does distinguish the changed binding of atom *i* that is surrounded either by Z_{α} atoms of type α or Z_{β} atoms of type β . This holds even in the case that the charge density at site *i* due to the surrounding atoms is the same. Second, in contrast to the EAM, this approach does not assume local charge neutrality in alloys. For this reason, I feel confident to apply this energy expression as an "intelligent interpolation scheme" to determine the energy of structures with low symmetry, once the corresponding *ab initio* data for high symmetry structures are available. Specifically, I will use this energy expression to study the equilibrium structure and dynamics of selected systems. The calculation of dynamical properties will focus on phonon spectra, to be addressed by lattice dynamics techniques, and large scale deformations during the process of melting and fracture to be addressed in molecular dynamics simulations.

2.3 Lattice dynamics

Lattice dynamics is used to determine phonon dispersion relations of a crystaline solid. The phonon spectra can be compared directly to experimental results for the equilibrium state at very low temperatures. The phonon frequencies of a crystal can be obtained using the dynamical matrix [Mar 63]. This matrix $D(\vec{k})$, corresponding to the wave vector \vec{k} , is given by

$$D_{\alpha\beta,\kappa\nu}(\vec{k}) = (M_{\kappa}M_{\nu})^{-1/2} \sum_{\vec{R}_i - \vec{R}_j} \Phi_{\alpha\beta,i\kappa,j\nu} \exp[-i\vec{k}\cdot(\vec{R}_i - \vec{R}_j)].$$
(2.25)

Here, M_{κ} is the mass of the κ -th atom and M_{ν} is the mass of the ν -th atom. $\Phi_{\alpha\beta,i\kappa,j\nu}$ is the force-constant matrix, which can be expressed as

$$\Phi_{\alpha\beta,i\kappa,j\nu} = \frac{\partial^2 E_{coh}(\text{tot})}{\partial u_{\alpha,i\kappa} \partial u_{\beta,j\nu}},\tag{2.26}$$

where $E_{coh}(tot)$ is the total energy of the system. $u_{\alpha,i\kappa}$ is the α -th Cartesian component of the displacement of κ -th atom in *i*-th unit cell, and $u_{\beta,j\nu}$ is the β -th Cartesian component of the displacement of the ν -th atom in the *j*-th unit cell.

Finally, the phonon frequencies $\omega(\vec{k})$ are the eigenvalues of $D(\vec{k})$, which are calculated by solving

$$det[\omega^2(\vec{k})\mathbf{I} - \mathbf{D}(\vec{k})] = 0.$$
(2.27)

2.4 Molecular dynamics

Unlike lattice dynamics, molecular dynamics (MD) describes the evolution of the system with time, based on a direct numerical solution of the equations of motion for individual atoms. Atomic motion is not restricted to the close vicinity of the equilibrium site. Such a simulation provides microscopic information about the dynamics of the system, including structural changes during phase transitions (such as melting or stability breakdown under tensile stress).

The dynamics of an isolated N-particle system in three-dimensional space is governed by the Lagrangian

$$L = \sum_{i=1}^{N} \frac{1}{2} m_i \dot{\mathbf{q}}_i^2 - V(\{\mathbf{q}_i\}) .$$
(2.28)

Here, q_i is the position vector of atom *i* in the system and $V(\{q_i\})$ is the total potential energy, given by the MBA Hamiltonian. The dynamical evolution of the system is described by Euler-Lagrange equations derived from the above Lagrangian. This procedure yields statistics for a micro-canonical ensemble. Unfortunately, the simulation of realistic micro-canonical systems requires a very large number of particles which imposes unrealistic requirements on the computation. A more natural choice is the canonical ensemble, which considers the temperature (rather than the total energy) to be constant, and which allows for a free energy exchange with the external heat bath. I use an algorithm due to Nosé [Nos 84] to describe a canonical ensemble. In the Nosé scenario, the fixed temperature canonical ensemble can be simulated by considering a single additional variable s. In this extended phase space, the net effect of the heat bath is assumed to be a scaling of the velocities as $v_i = sq_i$. Nosé interpreted the scaled velocity v_i as the true velocity resulting from the heat exchange with the external heat bath. The canonical ensemble can be described in an augmented Lagrangian of the form

$$L = \sum_{i=1}^{N} \frac{1}{2} m_i s^2 \dot{\mathbf{q}}_i^2 - V(\{\mathbf{q}_i\}) + \frac{1}{2} Q \dot{s}^2 - (N_f + 1) T_{eq} \ln s .$$
 (2.29)

Here, $N_f = 3N$ is the number of degrees of freedom of the system. Q is the mass associated with the new variable s which describes the coupling to the external heat bath. T_{eq} is the temperature of the heat bath and consequently the equilibrium temperature of the system. The optimum choice of Q provides an efficient damping of the equilibrium state. Overdamping is avoided by choosing Q in such a way that the oscillation period of s is much smaller than the damping time constant. The Lagrangian in Eq. (2.29) contains a logarithm of s in the potential energy part which makes this extended system equivalent to the canonical ensemble describing the original N-particle system. This new Lagrangian is justified by the correct statistics it yields for the system. In other words, when integrating the partition function over the new dimension in phase space, I regain the partition function for the canonical ensemble. Consequently, the microcanonical ensemble of the augmented Lagrangian, described by Eq. (2.29), generates precisely the canonical ensemble of the original N-particle system.

In order to describe the effect of mechanical coupling between the ensemble and

the outside world, Andersen applied molecular dynamics to systems under constant hydrostatic pressure [And 80]. In this technique, the variable space is extended by an additional quantity which scales all the atomic coordinates in the unit cell, thus allowing the volume to change uniformly. This method can be combined with Nosé's treatment of the canonical (TN) ensemble to describe the behavior of that system at constant tensile stress (or tension) t (TtN ensemble). This method has been further generalized by Parrinello and Rahman [Par 80, Par 81, Par 82, Ray 84, Ray 88] to allow for anisotropic stress and corresponding shape changes of the unit cell.

The mechanical stability of Pd and PdH systems which will be addressed in Chapter 4 is intimately related to the dynamics of these systems under uniaxial tensile stress. I will address this process using the method of Parrinello and Rahman [Par 80]. In the molecular dynamics calculations, I will consider a unit cell which is spanned by the three Bravais lattice vectors \mathbf{a} , \mathbf{b} and \mathbf{c} . These vectors define a shape matrix $\mathbf{h} = (\mathbf{a}, \mathbf{b}, \mathbf{c})$ which is used to describe the response of the system to applied stress. This matrix maps the true atomic coordinates onto reduced coordinates \mathbf{q}_i which lie in a cube of unit length, so that the true coordinates are obtained by the scaling transformation $\mathbf{h}\mathbf{q}_i$. The Lagrangian describing the TtN ensemble is then given by

$$L = \sum_{i=1}^{N} \frac{1}{2} m_i s^2 (\dot{\mathbf{q}}_i^T \underline{\mathbf{G}} \dot{\mathbf{q}}_i) - V(\{\mathbf{q}_i\}) + \frac{1}{2} Q \dot{s}^2 - (N_f + 1) T_{eq} \ln s$$

+
$$\frac{1}{2} W_i Tr(\dot{\mathbf{h}}^T \dot{\mathbf{h}}) - V_0 Tr(\underline{\mathbf{t}} \boldsymbol{\epsilon}). \qquad (2.30)$$

The first term describes the kinetic energy of the system, and the matrix \underline{G} is given by $\underline{\mathbf{G}} = \underline{\mathbf{h}}^T \underline{\mathbf{h}}$. W_t is the mass of the "piston" which exerts the external tension on the system. The equilibrium volume of the MD unit cell at zero tension is denoted by V_0 and the equilibrium shape by $\underline{\mathbf{h}}_0$. In the case of nonzero tension, I define a strain matrix $\underline{\epsilon}$ by

$$\boldsymbol{\epsilon} = \frac{1}{2} [(\mathbf{h_0}^{-1})^T \mathbf{G} \mathbf{h_0}^{-1} - \mathbf{I}] .$$
(2.31)

The quantity \underline{t} in Eq. (2.30) is the thermodynamic tension tensor which gives the work dW due to an infinitesimal distortion of the system as $dW = V_0 Tr(\underline{t\epsilon})$. \underline{t} is related to the stress tensor $\underline{\sigma}$ by [Par 80]

$$\underline{\sigma} = V_0 \mathbf{h} (\mathbf{h_0}^{-1}) \underline{\mathbf{t}} (\mathbf{h_0}^{-1})^T \mathbf{h}^T / V, \qquad (2.32)$$

where **h** is the average value of the shape matrix and $V = det(\mathbf{h})$ is the average volume.

Once the Lagrangian L is established, the equations of motion are given by

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_{i\alpha}} \right) - \left(\frac{\partial L}{\partial q_{i\alpha}} \right) = 0$$

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\underline{h}}_{\alpha\beta}} \right) - \left(\frac{\partial L}{\partial \underline{h}_{\alpha\beta}} \right) = 0$$

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{s}} \right) - \left(\frac{\partial L}{\partial s} \right) = 0.$$
(2.33)

Here, I have used Greek indices to denote the vector and matrix components of q_i and **h**, respectively.

The dynamics of the system is obtained by integrating the equations of motion in real time using a predictor-corrector method of fifth order [Gea]. The typical time step in the MD calculation of bulk Pd is 2×10^{-15} s. For hydrogen loaded Pd, the time step is reduced to 5×10^{-16} s due to the high vibration frequency and large-scale diffusion of the light hydrogen atoms. The generalized energy of the system is a constant of motion. I control the numerical fluctuations of this quantity (due to the

finite time steps) to lie within a small error margin of 10^{-4} , which is indicative of a precise integration. In order to avoid overdamping, I tune the mass Q associated with the temperature and the mass W_t associated with the tensile stress in such a way that the fluctuations of temperature and volume occur over large periods of \approx 50-100 time steps. In a typical MD calculation, I consider a periodic arrangement of unit cells (with originally cubic shape) which contain 500 Pd atoms and a fixed number of hydrogen atoms. When studying the properties of the system at a specific temperature or pressure, I first let the system equilibrate over a period of \approx 30,000 time steps and only then start collecting data for statistics. I find this time period to be sufficient for an excellent statistics with negligible error bars.

In the derivation of the algorithm, Nosé has assumed the system to be ergodic [Nos 84]. Doubts have been raised about the validity of this assumption [Kus 90], especially in the case of small systems. There are two reasons why this criticism should not affect the results presented in Chapter 4.3. First, I consider a very large system with more than 1500 degrees of freedom. Second, the many-body alloy potential contains anharmonic terms which gain importance at interatomic distances substantially different from r_0 . Especially at elevated temperatures, this fact contributes to a fast onset of chaotic behavior.

Chapter 3

Theory for the Atomic Force Microscopy

As discussed in Chapter 1, the Atomic Force Microscope (AFM) is a recently developed instrument which allows a direct imaging of topological structure at insulator, semiconductor, and metal surface alike [Bin 86, Bin 87]. The challenging question is whether the AFM can achieve atomic resolution of a given surface, and what are the theoretical limitations of this capacity. The study of the interaction between an AFM tip and a surface are also of relevance for the fundamental understanding of friction and the related phenomena.

These problem areas which are the subject of this Chapter, have been addressed in the following seven publications:

- W. Zhong and D. Tománek, First-Principles Theory of Atomic-Scale Friction, Phys. Rev. Lett. 64, 3054 (1990).
- W. Zhong, G. Overney, and D. Tománek, Theory of Atomic Force Microscopy on Elastic Surfaces, The Structure of Surfaces III, edited by S.Y. Tong, M.A. Van Hove, X. Xide and K. Takayanagi, Springer-Verlag, Berlin (1991), p243.
- 3. W. Zhong, G. Overney, and D. Tománek, Limits of Resolution in Atomic Force

Microscopy Images of Graphite, Europhys. Lett. 15, 49 (1991).

- 4. G. Overney, W. Zhong, and D. Tománek, Theory of Elastic Tip-Surface Interactions in Atomic Force Microscopy, J. Vac. Sci. Technol. B9, 479 (1991).
- D. Tománek, W. Zhong, and H. Thomas, Calculation of an Atomically Modulated Friction Force in Atomic Force Microscopy, Europhys. Lett. 15, 887 (1991).
- 6. D. Tománek and W. Zhong, Palladium-Graphite Interaction Potentials Based on First-Principles Calculations, Phys. Rev. B43, 12623 (1991).
- G. Overney, D. Tománek, W. Zhong, Z. Sun, H. Miyazaki, S. D. Mahanti, and H.-J. Güntherodt, Theory for the Atomic Force Microscopy of Layered Elastic Surfaces, J. Phys. : Cond. Mat. 4, 4233 (1992).

The description of tip-surface interactions in the AFM is determined quantitatively for Pd/graphite as a prototype system. Pd is a non-magnetic transition metal with near-noble electronic configuration. The valence 4d electrons are less localized than in 3d elements, yet unlike in the 5d elements, no relativistic effects need to be considered. This element is also chosen for its wide spread industry application. Graphite is a very common and important material in the industry and research alike. The inert nature of graphite layers facilitates cleavage and preparation of perfect surfaces. Graphite is also one of the most commonly used systems in AFM and STM studies of surface morphology [Mey 88].

3.1 Calculation of the Pd-graphite interaction

Accurate determination of the interaction energy between Pd and graphite is crucial for predictive calculations of AFM images of graphite, obtained with a Pd AFM tip. I start with an *ab initio* calculation of the interaction between a perfect layer of Pd atoms and the graphite substrate. In this calculation, I determine the adsorption energy of Pd atoms in the on-top (T) and the sixfold hollow (H) site as a function of the Pd-graphite separation. Total energies are calculated from first principles using the Local Density Approximation (LDA) [Koh 65]. I am using the ab initio Pseudopotential Local Orbital Method which has been described in Chapter 2 and successfully applied to short wavelength distortions of graphite [Tom 89]. In this calculation, ionic potentials are replaced by norm-conserving ionic pseudopotentials of Hamann-Schlüter-Chiang type [Ham 79] and the Hedin-Lundqvist [Hed 71] form of the exchange-correlation potential is used. The surface of hexagonal graphite is represented by a 4-layer slab and the adsorbate by a monolayer of Pd atoms in registry with the substrate (1 Pd atom per surface Wigner-Seitz cell of graphite). The basis consists of s, p and d orbitals with four radial Gaussian decays each on Pd sites and of s and p orbitals with three radial decays each on carbon sites, i.e. 40 independent basis functions for Pd and 12 basis functions for C. In order to obtain accurate energy differences between the "T" and "H" geometry, I introduce floating orbitals on sites not occupied by atoms and use the same extended basis [Tom 86c] for both "T" and "H" calculations. To insure high accuracy and complete convergence of total energies, I use an energy cutoff of 49 Ry in the Fourier expansion of the charge density and sample the 2-dimensional Brillouin zone with a mesh of 49 \vec{k} -points, using a specialpoint scheme [Cha 73].

In Fig. 3.1, I show the adsorption energy E_{ad} of a Pd atom (representing the Pd



Figure 3.1: Pd adsorption energy E_{ad} as a function of the adsorption height z above the surface of hexagonal graphite. The solid and dashed lines correspond to the sixfold hollow (H) and the on-top (T) sites, respectively. An enlarged section of the graph near equilibrium adsorption is shown in an inset. A second inset shows the adsorption geometry in top view; a possible trajectory of the Pd layer along x is shown by arrows. (From Ref. [Zho 90]. ©American Physical Society)

monolayer), defined by

$$E_{ad} = E_{total}(Pd/graphite) - E_{total}(Pd) - E_{total}(graphite),$$

for the on-top and hollow site registry. The calculation yields a very weak adsorption bond strength ≤ 0.1 eV at an equilibrium adsorption height $z \approx 3$ Å. At this distance from the substrate, the corrugation of the graphite charge density is negligibly small due to Smoluchowski smoothing and the position-dependence of the adsorption bond strength is << 0.1 eV. This effect is also responsible for the large value of the surface diffusion constant and apparent small sensitivity of surface friction to adsorbed films as discussed in Ref. [Ski 71]. These calculations show that at bond lengths $z \leq 2$ Å, the hollow site is favored with respect to the on-top site. At $z \approx 2$ Å, the adsorption energies are nearly the same, and at larger distances, it is the on-top site which is slightly favored by < 0.05 eV. This is consistent with the dominant interaction changing from closed-shell repulsion (which strongly favors the hollow site at very small adsorption bond lengths) to a weak chemisorption bond (which is stabilized by the hybridization with p_z orbitals in the on-top site). The magnitude and site dependence of van der Waals interactions between AFM tip and the surface is negligible in the weakly repulsive region of the Pd-graphite potential considered here.

The DFT calculations provide us with very accurate results, but only for small systems with high symmetry. When the Pd atoms are located at low symmetry sites, the calculation is computationally much more intensive. In calculations of AFM images and atomic-scale friction, more efficient total energy schemes have to be used. Model potentials for the interaction with graphite, the material of interest in this study, are typically based on interactions with a "generic" carbon solid [Gou 89, Abr 89]. These model potentials clearly cannot distinguish the surface reactivity of diamond with an sp^3 configuration from that of graphite with sp^2 bonding.

Here, I present a simple expression for the metal-graphite interaction potential which is based on a first-principles total energy calculation of Pd on graphite [Zho 90]. While derived specifically for the Pd/graphite system, the form of the interaction potential is more general and is a good prototype for the interaction of any metal adsorbate on graphite. The expression for the metal-graphite interaction, inspired by the Local Density Approximation (LDA) [Koh 65], provides a basically correct picture of many-body interactions in the adsorption system. The simple parametrization is a major advantage which will allow this potential to be used in computationally intensive molecular dynamics simulations.

It is convenient to note that the LDA results for E_{ad} can be well approximated by a local function which depends only on the total charge density of the graphite host at the Pd adsorption site,

$$E_{ad}(\vec{r}) = E_{ad}(\rho(\vec{r})). \tag{3.1}$$

This form of the interaction potential is inspired by the the Density Functional formalism [Koh 65] and the Embedded Atom Method [Daw 84, Foi 85, Foi 87, Daw 89, Foi 89]. Then $E_{ad}(\rho(\vec{r}))$ can be conveniently parametrized as

$$E_{ad}(\rho(\vec{r})) = \epsilon_1 \left(\rho/\rho_0\right)^{\alpha_1} - \epsilon_2 \left(\rho/\rho_0\right)^{\alpha_2}.$$
(3.2)

In the case of Pd on graphite, $\epsilon_1 = 343.076 \text{ eV}$, $\epsilon_2 = 2.1554 \text{ eV}$, $\alpha_1 = 1.245$, $\alpha_2 = 0.41806$, and $\rho_0 = 1.0 \text{ e/Å}^3$. The dependence of E_{ad} on ρ , obtained using the parametrized form in Eq. (3.2), is shown in Fig. 3.2.

From an independent LDA calculation of graphite surfaces, I find that the total



Figure 3.2: Relation between the Pd adsorption energy $E_{ad}(\vec{r})$ and the total charge density of graphite $\rho(\vec{r})$ at the adsorption site \vec{r} , given by Eq. (3.2). An enlarged section of the graph near equilibrium adsorption is given in the inset. (From Ref. [Tom 91b]. ©American Physical Society)

charge density can be well approximated by a superposition of atomic charge densities,

$$\rho(\vec{r}) = \sum_{n} \rho_{at}(\vec{r} - \vec{R}_n). \tag{3.3}$$

This parametrization is especially convenient in the case of deformed surfaces where an LDA calculation is difficult due to reduced symmetry. On flat surfaces, the maximum difference between the LDA charge density and the superposition of atomic charge densities is only few percent.

Finally, it is useful to parametrize the charge density of carbon atoms. I find that ρ_{at} , as obtained from an atomic LDA calculation, can be conveniently expressed as

$$\rho_{at}(r) = \rho_C e^{-\beta r},\tag{3.4}$$

where $\rho_C = 6.0735 \text{ e/Å}^3$ and $\beta = 3.459 \text{ Å}^{-1}$. As shown in Fig. 3.3, this expression is a very good approximation to the LDA results especially in the physically interesting range 1.4 Å < r < 3.0 Å.

One of the primary uses of the above potential is to describe the interaction between a metal AFM tip and graphite. In case of a large tip, one can expect a contribution to the interaction potential from Van der Waals forces, which are not described correctly by LDA especially at large tip-substrate distances. As discussed in Chapter 3.2 and in Ref. [Zho 91b], these forces are not very important since they are very small (typically < 10⁻¹⁰ N) at tip-substrate separations $\gtrsim 3$ Å. At smaller separations, they are dominated by the substrate-tip repulsion which is described correctly within LDA. These dispersive forces are also not very important for the interpretation of experimental results, since they do not show atomic resolution [Hor 92] and are easily compensated in the experiment by adjusting the force on the cantilever which supports the tip.



Figure 3.3: Radial plot of the charge density of a carbon atom $\rho_{at}(\vec{r})$, based on an LDA calculation (dashed line). The solid line shows the parametrized form of the charge density, given by Eq. (3.4). (From Ref. [Tom 91b]. ©American Physical Society)

A parametrized form of the potential, given in Eqs. (3.2), (3.3) and (3.4), allows for a very fast and efficient evaluation on a computer and is ideally suited for molecular dynamics calculations. Adsorption energies of Pd on a flat graphite surface, based on this parametrized form, are compared to LDA results in Fig. 3.4. I find a very good agreement between LDA results and parametrized potential over the whole interaction range. The largest discrepancy occurs at z = 2.0Å, where the switching between the preferential on-top and hollow sites is not reproduced by the parametrized potential, corresponding to an error of ≤ 0.1 eV. In the following, I will use the *ab initio* results whenever possible, and the parametrized results in other cases.

Summarizing the results of this section, I calculated the Pd/graphite adsorption energy as a function of the adsorption height, for Pd at the on-top and hollow site. The interaction is characterized by a hard-core repulsion at small distances and very weak chemical bond at larger distance (z > 2.5Å). This interaction can be well parametrized in terms of the charge density of the graphite host.

3.2 Limits of resolution in AFM images of graphite

As pointed out in Chapter 1, the possibility of atomic resolution in the AFM is limited in two ways. Too small forces lead to insufficient corrugations, and too large forces may destroy the surface. So far, these limitations of the atomic resolution have not been addressed in the literature. Present theoretical information is limited to calculations of the interaction between an infinite "periodic" carbon or aluminum tip and a rigid surface [Cir 90, Bat 88], and the interaction between a single AFM tip and an elastic surface represented by a semi-infinite continuum [Tom 89] or by a model system of finite thickness [Abr 89, Lan 90].



Figure 3.4: Adsorption energy E_{ad} of Pd on graphite as a function of the height z of Pd atoms above the graphite surface. First-principles results are given by \diamond and \bullet for the hollow and the on-top site, respectively. These data are compared to the present results, obtained using Eqs. (3.2), (3.3) and (3.4) and given by the solid and the dashed line for the hollow and the on-top site, respectively. Upper inset: Schematic top view of the adsorption geometry. Lower inset: An enlarged section of the graph near equilibrium adsorption. (From Ref. [Tom 91b]. ©American Physical Society)

In this Section, I discuss for the first time the theoretical limits of atomic resolution in AFM. I will use the *ab initio* results of the interaction between a "sharp" monatomic Pd tip and the surface of graphite discussed in Section 3.1, to predict corrugations for a varying load F_{ext} applied on the AFM tip. These calculations also predict tip-induced elastic substrate deformations which limit the range of applicable loads F_{ext} .

Using the adsorption energies E_{ad} given by an *ab initio* calculation, the force on a "sharp" monatomic AFM tip is given by

$$f_{ext} = -\frac{\partial E_{ad}(z)}{\partial z}.$$
(3.5)

Here, microscopic forces per atom are denoted by f and macroscopic forces applied to large objects by F. I also investigated the effect of the long-range Van der Waals forces on the tip-substrate interactions which are not described correctly by the LDA especially at large tip-substrate distances.

The Van der Waals force between an extended conical tip and a flat surface is estimated using the expression $F_{VdW}(z) = A_H \times \tan^2 \alpha/(6z)$, where α is half the opening angle of the cone [And]. In this expression, A_H is the Hamaker constant and z is the distance between the cone tip and the surface. In this calculation, I consider $\alpha = 30^{\circ}$ and $A_H = 3 \times 10^{-19}$ J, which is a typical value for metallic systems. For tip-substrate distances z > 3 Å, the Van der Waals forces are very small, typically $F_{VdW} < 10^{-10}$ N. At smaller distances, these forces can be neglected when compared to the closed-shell and internuclear repulsion which are described correctly within LDA. Since each of these regions is dominated only by one type of interaction, I determine the total tip-substrate force F_{ext} as a superposition of the force described by LDA and the Van der Waals force. In Fig. 3.5(a), I present results for the total force $F = f_{ext}$ between a conical AFM tip with 1 Pd apex atom and a graphite substrate, together with a schematic top view of the geometry.

The LDA calculations yield nearly the same weak Pd-graphite interaction potential ($E_{ad} < 0.1 \text{ eV}$) in the "H" and "T" sites beyond the equilibrium Pd-graphite bond length $z_{eq} \approx 3$ Å and consequently the same weak interaction force. This is plausible since E_{ad} is closely related to the total charge density ρ , shown in Fig. 3.5(b), which has only a very small site-dependence in the attractive region of the potential at $z > z_{eq}$ due to Smoluchowski smoothing [Smo 41]. Consequently, the corrugation Δz in this region is too small to be detected by the AFM. In the weakly repulsive region of the potential, for 2 Å < z < 3 Å, the on-top site is slightly favored with respect to the hollow site due to a weak chemisorption bond with substrate $C2p_z$ orbitals. For atom bond length z < 2 Å, the strongly repulsive Pd-graphite interaction is mainly determined by the closed-shell repulsion which energetically favors the hollow site. Hence, in the repulsive region of the potential, the Pd tip comes closest to the substrate near the "T" site for small loads. For large loads, the tip is closest to the surface near the "H" site.

Fig. 3.6(a) shows the expected AFM corrugation Δz during an xy scan of the graphite surface, for $f_{ext} = 10^{-8}$ N. The equilibrium bond length $z(f_{ext})$ at other than the calculated high-symmetry sites has been determined using a separate model calculation, described in Section 3.1 and Ref. [Tom 91b], which relates E_{ad} to the total charge density of the graphite host at the Pd adsorption site. This energy functional is assumed to be universal and reproduces E_{ad} in high-symmetry sites accurately. In this calculation, I assumed a perfectly rigid substrate and a monatomic Pd tip. A top view of this tip at the graphite hollow site is shown schematically in the inset of Fig. 3.6(b).



Figure 3.5: (a) Calculated force F between a Pd AFM tip with one apex atom and the surface of hexagonal graphite, as a function of the Pd-graphite distance z. The solid and dashed lines correspond to the sixfold hollow (H) and the on-top (T) sites, respectively. An enlarged section of the graph near the equilibrium is shown in the inset. A second inset shows the adsorption geometry in top view. A possible trajectory of an AFM tip along x is shown by arrows. (b) Valence charge density of the Pd/graphite system. The results of the LDA calculation are for the on-top adsorption site near the equilibrium adsorption distance z_{eq} , and are shown in the xz plane perpendicular to the surface. The ratio of two consecutive charge density contours $\rho(n + 1)/\rho(n)$ is 1.2. (From Ref. [Zho 91b]. ©Les Editions Physique)



Figure 3.6: (a) Surface corrugation Δz experienced by a monatomic Pd AFM tip scanning the *xy* surface plane of rigid graphite under the applied AFM load (per atom) $f_{ext} = 10^{-8}$ N. (b) Δz (with respect to the "H" site) along the surface *x* direction for a "sharp" 1-atom tip, for $f_{ext} = 10^{-9}$ N (dotted line), 5×10^{-9} N (dashed line), 10^{-8} N (solid line), and 2×10^{-8} N (dash-dotted line). The inset shows the geometry of the tip-graphite system in top view. The AFM tip is shown above the hollow site, and the shaded area represents the Pd atom. (From Ref. [Zho 91b]. ©Les Editions Physique)

Fig. 3.6(b) shows the AFM corrugation $\Delta z(x)$ for different loads f_{ext} . The tip trajectory along the surface x-direction, shown by arrows in the inset of Fig. 3.6(b), contains the "T" and "H" sites and yields the largest corrugation. As discussed above, the favored surface site changes with changing load. For the sake of simple comparison, I set Δz (hollow site)=0 in Fig. 3.6(b) and obtain a sign change of Δz near $f_{ext} = 2.5 \times 10^{-9}$ N. These calculations show that atomic resolution in the constant force mode in the AFM, corresponding to $\Delta z \gtrsim 0.05$ Å, requires loads $f_{ext} \gtrsim 5 \times 10^{-9}$ N. Since the corrugation Δz along a trajectory connecting adjacent "T" sites is very small (see Fig. 3.6(b)), the observation of individual carbon atoms is unlikely, which has been confirmed by the experiment [Mey 88].

For an *n*-atom tip, which is commensurate with the substrate, the average load per AFM tip atom is $f_{ext} = F_{ext}/n$ and the equilibrium tip position z can be estimated from Eq. (3.5). It should be noted that under certain conditions, such a "dull" multiatom tip can still produce atomic corrugation for f_{ext} similar to a monatomic tip. This is the case for an ideally aligned tip with a close-packed (111) surface, since the unit cells of Pd and graphite are nearly identical in this case.

The range of applicable loads F_{ext} is limited by the condition that substrate distortions near the AFM tip should be small and remain in the elastic region. Since fullscale LDA calculations of local AFM-induced distortions of a semi-infinite graphite surface are practically not feasible, I adopt the following approach. First, I use continuum elasticity theory [Lee 89], with elastic constants obtained from *ab initio* calculations [Tom 89], to determine the relaxation of carbon atoms at the graphite surface in response to the AFM load applied through an AFM tip. This continuum approach is applicable in the linear response regime and has been successfully used previously to calculate local rigidity, local distortions and the healing length of graphite near an AFM tip and near intercalant impurities [Tom 89, Lee 89]. In a second step, the atomic structure in the total charge density of the Pd/graphite system is regained from a superposition of atomic charge densities given by LDA-atom calculations.

The semi-infinite system of graphite layers is characterized by the interlayer spacing d, the in-plane C-C bond length d_{C-C} , the flexural rigidity D, the transverse rigidity K (proportional to C_{44}) and c-axis compressibility G (proportional to C_{33})[Tom 89, Lee 89]. The LDA calculations for undistorted graphite yield d = 3.35 Å and $d_{C-C} = 1.42$ Å, in excellent agreement with experiment [Zab 89]. In the continuum calculation, I further use D = 7589 K, K = 932 KÅ⁻² and G = 789 KÅ⁻⁴ which have been obtained from calculated graphite vibration modes [Tom 89] and the experiment [Zab 89].

The total charge density of the graphite surface, distorted by a Pd AFM tip, is shown in Fig. 3.7. A comparison of charge density contours with results of the self-consistent calculation in Fig. 3.5(b) proves a posteriori the applicability of the linear superposition of atomic charge densities. Fig. 3.7(a) shows that the substrate distortion in response to a monatomic AFM tip at a load $F_{ext} = f_{ext} = 10^{-9}$ N is moderate. According to Fig. 3.6(b), the corresponding corrugations during an AFM scan with this load are $\Delta z \approx 0.03$ Å and thus below the limit of detection. A larger load $F_{ext} = f_{ext} = 5.0 \times 10^{-9}$ N leads, according to Fig. 3.6(b), to marginally detectable corrugations $\Delta z \approx 0.06$ Å, but distorts graphite much more, as shown in Fig. 3.7(b).

For larger applied forces $F_{ext} = f_{ext} > 5.0 \times 10^{-9}$ N, which would lead to sizeable corrugations, the local distortions of graphite exceed the elastic limit. A rough estimate of these distortions, based on continuum elasticity theory, indicates that for $f_{ext} \gtrsim 5 \times 10^{-9}$ N, the distance between graphite layers near the AFM tip approaches



Figure 3.7: Total charge density ρ of the monatomic Pd AFM tip interacting with the elastic surface of graphite near the hollow site. Contours of constant ρ are shown in the zz plane perpendicular to the surface, for (a) $F_{ext} = f_{ext} = 1 \times 10^{-9}$ N and for (b) $F_{ext} = f_{ext} = 5 \times 10^{-9}$ N. The ratio of two consecutive charge density contours $\rho(n + 1)/\rho(n)$ is 1.4. The location of the applied load acting on the Pd atom is indicated by a triangle. (From Ref. [Zho 91b]. @Les Editions Physique)

the value of intra-layer C-C distances. This new diamond-like bonding geometry leads to a rehybridization of carbon orbitals and will necessarily result in an irreversible substrate deformation. An independent estimate of the critical AFM force for this plastic deformation can be obtained from a first-principles calculation [Fah 86] of the graphite-diamond transition as a function of external pressure. These results, corresponding to an "infinitely extended tip", indicate a critical force per surface atom of $f_{ext} = 10^{-9}$ N for this transition. Due to the large flexural rigidity of graphite, this force increases by half an order of magnitude for a one-atom tip, in agreement with the above result.

A realistic AFM tip is more complex than the model tip discussed above and could consist of a micro-tip of one or few atoms on top of a larger tip. A substantial portion of this larger tip could, through the "cushion" of a possible contamination layer, distribute the applied load more evenly across a large substrate area, reduce the large curvature near the tip (see Fig. 3.7(b)) and increase the minimum interlayer separation. This effect would increase the upper limit of applicable loads f_{ext} compatible with elastic substrate deformations and would lead to atomic resolution [Mey 88].

Summarizing these results, I used *ab initio* calculations to determine corrugations observable in Atomic Force Microscopy of graphite. I found that in the constantforce mode, atomic resolution is marginally possible for AFM loads (per atom) close to 5×10^{-9} N. For smaller loads, the corrugation Δz is too small to be observed. For loads which are too large, graphite deformations exceed the elastic limit and subsequently result in the destruction of the substrate.

3.3 First-principles theory of atomic-scale friction

In this Section, I present a predictive first-principles theory of atomic-scale friction. I use *ab initio* results of the interaction energy between a perfect layer of atoms and a graphite layer, as a function of their relative distance. I use this information to determine the friction coefficient μ between these systems in contact. My results include quantitative predictions of μ as a function of the external force, a qualitative explanation of the increase of μ with increasing surface roughness, and a qualitative explanation of the decrease of μ with increasing relative velocity between the objects in contact in case of sliding friction.

For a microscopic understanding of the friction process, I first consider the motion of an atomic layer along the surface. This layer is in registry with the substrate and experiences an external force per atom f_{ext} normal to the surface. At each site, the equilibrium adsorption length z is given by the condition

$$f_{ext} = -\frac{\partial}{\partial z} E_{ad}(z). \tag{3.6}$$

I consider a straight trajectory along the x direction in the surface connecting nearest neighbor hollow sites which are separated by Δx (see the inset in Fig. 3.8(a)). The position-dependent part of the potential energy V of the system has two main components. These are variations of the adsorption bond energy and the work against the external force f_{ext} applied to the adsorbate, due to variations of the adsorption length. Hence,

$$V(x, f_{ext}) = E_{ad}(x, z(x, f_{ext})) + f_{ext}z(x, f_{ext}) - V_0(f_{ext}),$$
(3.7)



Figure 3.8: (a) Potential energy V(x) of the Pd-graphite system as a function of the position of the Pd layer along the surface x-direction, for external forces $f_{ext} = 3 \times 10^{-9}$ N (dotted line), 6×10^{-9} N (dashed line) and 9×10^{-9} N (solid line). The inset shows the adsorption geometry and trajectory of the Pd layer in side view. (b) Atomic-scale structure of the force along the surface f_x (dashed line) and the friction force $f_f = |f_x|$ (solid line) for $f_{ext} = 9 \times 10^{-9}$ N. (From Ref. [Zho 90]. ©American Physical Society)

where I arbitrarily set the potential energy to zero at the hollow site by defining

$$V_0(f_{ext}) = E_{ad}(x_H, z(f_{ext})) + f_{ext} \ z(x_H, f_{ext}).$$
(3.8)

In Fig. 3.8(a) I show V(x) for different external forces. I obtain the periodic potential V(x) at other than the calculated high-symmetry sites from a Fourier expansion over the reciprocal lattice. I keep the lowest components of this expansion and determine the expansion coefficients from the calculated values for the "T" and "H" sites. However, the calculated frictional coefficient depends only on extrema of the potential V(x), which is assumed to be at "T" and "H" sites.

From my calculation, In I find that the mechanical component dominates and is only partly compensated by adsorption energy differences. As a result of variations of V along x, there is a position-dependent force f_x along the x direction, shown in Fig. 3.8(b), which is given by

$$f_x(x, f_{ext}) = \frac{\partial}{\partial x} V(x, f_{ext}).$$
(3.9)

The maximum value of f_x describes the static friction governing the onset of stickslip motion. The sliding friction on the other hand must be obtained as a weighted average over this force from the energy dissipated in friction along x. I first consider a conservative part of this process, corresponding to potential energy increase $\Delta V_{max}(f_{ext}) = V_{max}(f_{ext}) - V_{min}(f_{ext})$ along Δx , which yields a positive value of f_x . The non-conservative part corresponds to a decrease of V(x) along x and a negative value of f_x . Friction losses ΔE_f along Δx must not exceed the maximum increase in the potential energy, hence

$$\Delta E_f \le \Delta V_{max}.\tag{3.10}$$

For very slow tracking velocities, any gain in potential energy during the dissipative part of the friction process is efficiently transferred into surface phonons and electronhole pairs. Then, I can consider both sides of Eq. (3.10) to be equal, which corresponds to $f_f = |f_x|$, shown in Fig. 3.8(b). This is the first quantitative prediction of atomicscale structure in the friction force which has been observed recently [Mat 87].

The energy dissipated in friction along Δx can also be related to the average friction force $\langle f_f \rangle$ along the trajectory, as

$$\Delta E_f = \langle f_f \rangle \Delta x. \tag{3.11}$$

Using Eq. (3.10) for ΔE_f , I obtain

$$\langle f_f \rangle = \frac{1}{\Delta x} \Delta V_{max}.$$
 (3.12)

Applying the definition of the friction coefficient $\mu = f_f/f_{ext}$, I find

$$\mu = \frac{\langle f_f \rangle}{f_{ext}} = \frac{\Delta V_{max}}{f_{ext} \Delta x}.$$
(3.13)

In Fig. 3.9 I show μ as a function of f_{ext} . I find a general increase of μ with increasing external force. The minimum in $\mu(f_{ext})$ near $f_{ext} = 5 \times 10^{-9}$ N is caused by the switching of the minima in V(x) from H to B, shown in Fig. 3.8(a). Near $f_{ext} = 5 \times 10^{-9}$ N, the lowest order Fourier components of the potential V vanish. According to the interpolation scheme discussed above, this leads to $\mu = 0$ (shown in Fig. 3.9). In reality, a small nonzero value of μ is expected due to higher-order Fourier components of V (which are usually much smaller than those considered). From former results presented in Section 3.2 and and Ref. [Tom 89], I conclude that if the external force (per atom) exceeds 10^{-8} N, the graphite surface is very strongly deformed [Mam 86] and likely to be ruptured [Ski 71]. Since no plastic deformations have been observed



Figure 3.9: Microscopic friction coefficient μ between a Pd AFM tip and graphite as a function of load per tip atom f_{ext} . (From Ref. [Zho 90]. ©American Physical Society)

in the AFM studies [Mat 87]. the applied forces were probably in the region $f_{ext} < 10^{-8}$ N. For these values of f_{ext} , the calculated friction coefficient of the order $\mu \approx 10^{-2}$ agrees with the experiment [Ski 71, Mat 87].

In order to obtain a meaningful comparison with observable friction forces, I have to make further assumptions about the macroscopic interface and the elastic response of the substrate to external forces. In the simplest case, I consider an atomically flat interface, where N atoms are in contact with the substrate, and neglect elastic deformations. Then, the external force per atom f_{ext} is related to the total external force F_{ext} by

$$f_{ext} = \frac{1}{N} F_{ext}.$$
(3.14)

In Fig. 3.10 I use the calculated $\mu(f_{ext})$ to plot the total friction force F_f for such a perfectly flat interface consisting of 1500 Pd atoms. Since μ increases with increasing value of f_{ext} , the F_f versus F_{ext} relationship is nonlinear, which has also been observed in the AFM experiment [Mat 87].

In the case of large external forces and an elastic substrate such as graphite, elastic theory predicts [Lan 86] the substrate deformations to be proportional to $F_{ext}^{1/3}$. In case of a spherical tip [Mat 87], the tip-substrate interface area and the corresponding number of atoms in contact is proportional to $F_{ext}^{2/3}$. Then, the force per atom f_{ext} is proportional to $F_{ext}^{1/3}$. Hence for increasing external forces, variations of the effective force per atom and of μ are strongly reduced due to the increasing interface area. This is illustrated by a dashed line in Fig. 3.10, where I used N = 1500 atoms for $F_{ext} = 10^{-6}$ N. These results are in good agreement with the AFM results for a large nonspecific tungsten tip with a radius R = 1500 Å - 3000 Å on graphite [Mat 87], but show a slightly larger increase of the friction force than observed for the range of



Figure 3.10: (a) Calculated macroscopic friction force F_f as a function of the external force F_{ext} for a large object. The solid line describes a "flat" object, the surface of which consists of 1500 atoms in contact with a rigid substrate. The dashed line describes friction of a large spherical tip and also considers the effect of elastic substrate deformations on the effective contact area. The dotted line corresponds to a constant friction coefficient $\mu = 0.012$. (From Ref. [Zho 90]. ©American Physical Society) (b) Experimental measured average friction force as a function of load on the tip as it slides across the surface. (From Ref. [Mat 87]. ©American Physical Society)

external forces investigated.

This theory can be used also to explain the dependence of μ on the roughness of the interface and on the relative velocities of the two objects in contact. At a rough surface, the number of atoms N in contact with the substrate is smaller than at a flat surface which leads to an increase of f_{ext} and hence of μ . Also, with increasing relative velocity, the coupling between macroscopic and internal microscopic degrees of freedom (phonons, electron-hole pairs) gets less efficient. Then, $\Delta E_f < \Delta V_{max}$ in Eq. (3.10) which causes a decrease of $< f_f >$ and μ .

Summarizing the results in this Section, I determined the atomic-scale friction associated with a layer of Pd atoms moving across a graphite substrate from *ab initio* total energy calculations. I evaluated the friction energy caused by variations of the chemical bond strength and work against an external normal load. The calculated value of the friction coefficient is very small, in the order $\mu \approx 10^{-2}$ for loads near 10^{-8} N. This small value can be explained by the weak dependence of Pd-graphite interaction on the adsorption site. I also found μ to increase with load in agreement with recent Atomic Force Microscopy experiments.

3.4 Ideal friction machines

In this last Section, I determine the upper limit of the average friction force $\langle F_f \rangle$, originating from the potential energy barriers $\Delta V(F_{ext})$ during the "surface diffusion" of Pd on graphite. There, I assumed that the energy gained by the tip atom is completely dissipated into microscopic degrees of freedom. In the following, I will address the mechanism which leads to the excitation of microscopic degrees of freedom and hence to energy dissipation. I will make use of the first-principles Pd-graphite interaction potential. Based on these data, I will determine atomic-scale modulations of the friction force F_f along the horizontal trajectory of the Pd tip on graphite in the quasistatic limit of relative velocity $v \rightarrow 0$. I will show that F_f depends sensitively not only on the corrugation and shape of the Pd-graphite interaction potential, but also on the specific construction parameters of the FFM. The latter point is of utmost importance if friction forces obtained with different microscopes are to be compared to one another.

Two models of a Friction Force Microscope are shown in Fig. 3.11. In both models, the suspension of the tip moves quasistatically along the surface x-direction, with its position x_M as the externally controlled parameter. The tip is assumed to be stiff with respect to excursions in the surface y-direction. I restrict the discussion to the case of tip-induced friction and assume a rigid substrate, which applies for friction measurements on graphite [Mat 87, Zho 90]. In the "maximum friction microscope" [Zho 90], the full amount of energy needed to cross the potential energy barrier ΔV along Δx is dissipated into heat. This process and the corresponding friction force can be observed in an imperfect Atomic Force Microscope which is shown in Fig. 3.11(a). A vertical spring connects the tip and the external microscope suspension M. The horizontal positions of the tip and the suspension are *rigidly* coupled, $x_t = x_M = x$. For $0 < x < \Delta x/2$, a constant load F_{ext} on the tip is adjusted by moving the suspension up or down. For $\Delta x/2 < x < \Delta x$, however, the tip gets stuck at the maximum value of z_t . At Δx , the energy ΔV stored in the spring is abruptly and completely released into internal degrees of freedom which appear as heat.

The calculated potential energy V(x) during this process is shown in Fig. 3.12(a). I considered a monatomic Pd tip sliding along a trajectory connecting adjacent hollow and bridge sites on graphite, for a load $F_{ext} = 10^{-8}$ N. In order to predict F_f , I have used the results of my previous *ab initio* calculation for Pd on graphite presented in



Figure 3.11: Two models for the Friction Force Microscope (FFM). In both models, the external suspension **M** is guided along the horizontal surface x direction at a constant velocity $v = dx_M/dt \to 0$. The load F_{ext} on the "sharp" tip (indicated by \bigtriangledown) is kept constant along the trajectory $z_t(x_t)$ (shown by arrows). (a) A "maximum friction microscope", where the tip is free to move up, but gets stuck at the maximum z_t between $\Delta x/2$ and Δx . (b) A "realistic friction microscope", where the position of the tip x_t and the suspension x_M may differ. In this case, the friction force F_f is related to the elongation $x_t - x_M$ of the horizontal spring from its equilibrium value. (From Ref. [Tom 91c]. (ELes Editions Physique)
Section 3.1 and Ref. [Zho 90], which have been conveniently parametrized [Tom 91b]. The force on the tip in the negative x-direction, as defined in Fig. 3.11(a), is given by

$$F_f(x_M) = \begin{cases} \frac{\partial V(x_M)}{\partial x_M} & \text{if } 0 < x_M < \Delta x/2\\ 0 & \text{if } \Delta x/2 < x_M < \Delta x \end{cases}$$
(3.15)

and shown in Fig. 3.12(b). The nonzero value of the average friction force $\langle F_f \rangle$, indicated by the dash-dotted line in Fig. 3.12(b), is a clear consequence of the mechanism which allows the tip to get stuck. $F_f(x_M)$ is a non-conservative force since it depends strongly on the scan direction. In absence of the "sticking" mechanism, F_f is given by the gradient of the potential everywhere, as indicated by the dashed line in Fig. 3.12(b). It is independent of the scan direction and hence conservative. In this case, F_f inhibits sliding for $0 < x_M < \Delta x/2$ and promotes sliding for $\Delta x/2 < x_M < \Delta x$, so that the friction force averages to zero.

A more realistic construction of Friction Force Microscope is shown in Fig. 3.11(b). In this microscope, the AFM-like tip-spring assembly is *elastically* coupled to the suspension in the horizontal direction, so that x_t may differ from x_M . For a given x_t , the tip experiences a potential $V(x_t, z_t) = V_{int}(x_t, z_t) + F_{ext} z_t$ consisting of the tip-surface interaction V_{int} and the work against F_{ext} . The tip trajectory $z_{t,min}(x_t)$ during the surface scan is given by the minimum of $V(x_t, z_t)$ with respect to z_t . For this trajectory, $V(x_t) = V(x_t, z_{t,min})$ represents an effective tip-substrate potential.

This potential $V(x_t)$ depends strongly on F_{ext} and is corrugated with the periodicity of the substrate due to variations of the chemical bond strength and of $z_{t,min}$. It is reproduced in Fig. 3.13(a) in the case of a monatomic Pd tip on graphite and $F_{ext} = 10^{-8}$ N. The corrugation of the potential $V(x_t)$ will elongate or compress the horizontal spring from its equilibrium length which corresponds to $x_t = x_M$. The



Figure 3.12: Potential energy of the tip V(x) (a), the friction force $F_f(x)$ and the average friction force $\langle F_f \rangle$ (b) in the "maximum friction" microscope with a monatomic Pd tip on graphite. The arrows indicate the tip trajectory corresponding to a relaxed vertical position z_t for a constant load on the tip $F_{ext} = 10^{-8}$ N. (From Ref. [Tom 91c]. ©Les Editions Physique)



Figure 3.13: Microscopic friction mechanism in the "realistic friction microscope". The calculations are for a monatomic Pd tip on graphite and $F_{ext} = 10^{-8}$ N. Results for a soft spring, giving nonzero friction, are compared to a zero-friction microscope with a hard spring. (a) Potential energy of the tip $V(x_t)$. (b) A graphical solution of Eq. (3.19) yielding the equilibrium tip position at the intersection of the derivative of the potential $\partial V(x_t)/\partial x_t$ (dashed line) and the force due to the horizontal spring F_f . Solid lines, for different values of x_M , correspond to a soft spring with c = 10.0 N/m, and dashed lines correspond to a hard spring with c = 40.0 N/m. (c) The calculated equilibrium tip position $x_t(x_M)$. (d) The friction force F_f as a function of the FFM position x_M and the average friction force $< F_f >$ for the soft spring (dash-dotted line). (From Ref. [Tom 91c]. ©Les Editions Physique)

friction force is given by

$$F_f(x_M) = -c(x_t - x_M), (3.16)$$

where c is the horizontal spring constant. The total potential energy V_{tot} of the system consists of $V(x_t)$ and the energy stored in the horizontal spring,

$$V_{tot}(x_t, x_M) = V(x_t) + \frac{1}{2}c(x_t - x_M)^2.$$
(3.17)

For a given horizontal position x_M of the FFM suspension, the equilibrium position of the tip x_t is obtained by minimizing V_{tot} with respect to x_t . This gives

$$\frac{\partial V_{tot}}{\partial x_t} = \frac{\partial V(x_t)}{\partial x_t} + c(x_t - x_M) = 0$$
(3.18)

or, with Eq. (3.16),

$$F_f = -cx_t + cx_M = \frac{\partial V(x_t)}{\partial x_t}.$$
(3.19)

A graphical solution of Eq. (3.19) is shown in Fig. 3.13(b) and the resulting relation $x_t(x_M)$ is shown in Fig. 3.13(c). If the force constant c exceeds the critical value $c_{crit} = -[\partial^2 V(x_t)/\partial x_t^2]_{min}$, which for Pd on graphite and $F_{ext} = 10^{-8}$ N is $c_{crit} = 23.2$ N/m, I obtain a single solution x_t for all x_M . This situation is indicated by the dotted line in Figs. 3.13(b) and 3.13(c) for a hard spring with c = 40.0 N/m. The friction force F_f is given by Eq. (3.16) and shown by the dotted line in Fig. 3.13(d). F_f is independent of the scan direction and hence conservative, resulting in $\langle F_f \rangle = 0$. Hence no friction should occur in the AFM, which is the limiting case of an FFM for $c \to \infty$.

A more interesting case arises if the horizontal spring is soft, $c < c_{crit}$. This situation is shown by the solid line in Figs. 3.13(b) and 3.13(c) for c = 10.0 N/m. In this case, the solution $x_t(x_M)$ of Eq. (3.19) displays a sequence of instabilities. These instabilities lead to a stick-slip motion of the tip with increasing x_M , similar to "plucking a string". The hysteresis in the $x_t(x_M)$ relation, shown in Fig. 3.13(c), results in a dependence of the force F_f on the scan direction. The friction force $F_f(x_M)$ in this case is shown by the solid line in Fig. 3.13(d). It is a non-conservative/dissipative force and averages to a non-zero value $\langle F_f \rangle = 3.03 \times 10^{-10}$ N, given by the dashdotted line. The energy released from the elongated spring into heat is represented by the shaded area in Fig. 3.13(d).

The present theory predicts occurrence of friction only for very soft springs or a strongly corrugated potential $V(x_t)$. The latter fact can be verified experimentally since the corrugations $\Delta V(x_t)$ increase strongly with increasing applied load [Zho 90]. Consequently, for a given c, the friction force is zero unless a minimum load F_{ext} is exceeded. On the other hand, for a given F_{ext} , no friction can occur if c exceeds a critical value $c_{crit}(F_{ext})$.

A similar situation occurs during sliding between large commensurate flat surfaces of A on B. In that case, c is given by the elastic constants of A at the interface [Toml 29], hence can not be changed independently. Since c is rather large in many materials, zero friction should be observed for moderate applied loads in the absence of wear and plastic deformations. For a multiatom "tip" which is commensurate with the substrate, the tip-substrate potential is proportional to the number of tip atoms at the interface, n, and so is the critical value c_{crit} for nonzero friction. In this case, the effective FFM spring depends both on the external spring and the elastic response of the tip material. The inverse value of c_{crit} is given by the sum of the inverse values of the corresponding spring constants. For a large tip which is incommensurate with the substrate, no friction should occur [McC 89]. The average friction force $\langle F_f \rangle$ as a function of the load F_{ext} and the force constant c is shown as a contour plot in Fig. 3.14 for a monatomic or a larger commensurate Pd tip on graphite. Clearly, the applicable load range is limited by the underlying assumption of contact without wear. This figure illustrates that not only the friction force F_f , but also the friction coefficient $\mu = \langle F_f \rangle / F_{ext}$, depend strongly both on the interaction potential between the two materials in contact and on the intrinsic force constant c of the Friction Force Microscope. This clearly makes the friction force dependent on the construction parameters of the FFM. There is also one advantage in this fact: c can be chosen in such a way that nonzero friction occurs even at small loads F_{ext} .

Summarizing the results in this Section, I calculated the atomic-scale modulation of the friction force and the corresponding stick-slip motion at the interface during the relative motion between Pd and graphite. I proposed two idealized versions of a Friction Force Microscope. I showed that the friction force depends not only on the Pd-graphite interaction potential, but even more critically on the construction parameters of such a microscope.

3.5 Conclusions

In this Chapter, I have studied theory of atomic force microscopy, using Pd AFM tip and graphite substrate as the model system.

I have calculated interaction between Pd and graphite using *ab initio* density functional theory within local density approximation, with Pd atom placed above hollow and on-top sites of graphite. The precise calculations show that Pd-graphite interaction is characterized by strong close shell repulsion at small distances, which strongly favors hollow site, and very weak chemical bond at larger distance with on-



Figure 3.14: Contour plot of the average friction force $\langle F_f \rangle$ between a Pd tip and graphite, as a function of the load F_{ext} and the force constant c. All forces and the force constant are normalized by the number of tip atoms n in contact with the substrate. (From Ref. [Tom 91c]. (©Les Editions Physique)

top site slightly favored. The total energy results at high symmetry points can be well mapped to a parameterized form, as a function of graphite host charge density. The optimum combination of *ab initio* and parameterized results provides a precise and complete picture of Pd/Graphite interaction.

Using these results, I have studied the limit of resolution of Pd AFM tip on the graphite surface. The calculated trajectories of Pd probing graphite surface under different loads reveals that, the minimum load on Pd is about $5 \times 10^{-9}N$ to produce observable corrugation. Using continuum elasticity theory, I have estimated that the load exceeding $10^{-8}N$ leads to too much deformation and is thus destructive to the surface. So the atomic resolution of graphite from Pd AFM tip is only marginally achievable.

The atomic scale friction between an Pd tip and graphite surface is obtained from the variation of Pd tip energy along the scanning trajectory. There are two contributions to this energy, one is from the work against the load when corrugation is none zero, another comes from adsorption energies difference at different sites. Assuming all the kinetic energy gained by the AFM tip dissipates into heat, I obtain the first quantitative prediction of friction force using *ab initio* techniques. The calculated friction coefficient is in the order of 10^{-2} for loads near 10^{-8} N, and it increases with increasing loads. The calculation is in good agreement with recent experiment.

I further investigate the possible mechanisms of energy dissipation during the friction process. I proposed two models for friction force microscope (FFM). In the more realistic version, I was able to calculate the atomic scale modulation of the friction force, and thus explain the stick-slip motion of the tip. I found the averaged friction force depends not only on the tip-surface interaction potential, but also strongly on the construction parameters of the FFM.

Chapter 4

Structure and Dynamics for H Loaded Pd

As I already mentioned in Chapter 1, the structure and dynamics of H loaded Pd is of great importance to both basic science and technology. While the ultimate goal is to perform the corresponding study completely from first principles, the computational involvement is presently prohibitive for such an endeavor. Therefore, I base the study of the Pd-H system on the Many-Body Alloy (MBA) Hamiltonian, which was derived in Chapter 2, with parameters reproducing the results of an LDA calculation for this system [Tom 86b, Sun 89, Tom 91a]. In Section 4.1, I use the Hamiltonian to calculate the structural properties of bulk Pd and PdH, as well as clean and hydrogen covered Pd surfaces. The results of the surface studies, which have no additional adjustable parameters, are found to be in good agreement with corresponding LDA calculations and experimental data.

In Section 4.2, I use lattice dynamics to calculate the dispersion relations for bulk Pd and PdH, and compare the results to experimental data. The effect of H adsorbates on the phonon spectra of Pd (001) and Pd (110) surfaces is investigated by performing the corresponding lattice dynamics calculations.

In Section 4.3, dynamical properties of Pd-H systems at finite temperature are

investigated using molecular dynamics. I present results for the equilibrium structural and elastic properties of Pd at different temperatures and hydrogen concentrations, and show quantitative results for the mechanical failure and crack formation in hydrogen-free and hydrogen-loaded Pd due to a uniaxially applied load. I will show that a careful analysis of these results can provide valuable insight into the mechanism of "hydrogen embrittlement".

This Chapter contains material which has appeared in the following three publications:

- W. Zhong, Y. S. Li, and D. Tománek, Effect of Adsorbates on Surface Phonon Modes: H on Pd(001) and Pd(110), Phys. Rev. B44, 13053 (1991).
- W. Zhong, Y. Cai, and D. Tománek, Mechanical Stability of Pd-H Systems: A Molecular Dynamics Study, Phys. Rev. B 46 8099 (1992).
- W. Zhong, Y. Cai, and D. Tománek, Computer Simulation of Hydrogen Embrittlement in Metals, Nature 362 435 (1993).

4.1 Application of the Many-Body Alloy Hamiltonian to the Pd–H system

In this Section, I determine the parameters of the MBA Hamiltonian for the Pd-H system, based on previously published *ab initio* results[Tom 86b, Sun 89, Tom 91a] for the equilibrium structure and cohesive energy of bulk Pd and PdH. It should be noted that this procedure does not introduce any free parameters. In the following, I will apply this Hamiltonian next to determine structural properties and vibrational spectra of clean and hydrogen covered Pd surfaces.

Interaction	$q_{lphaeta}$	$p_{lphaeta}$	$r_{lphaeta,0}(\mathrm{\AA})$	$\epsilon^{R}_{lphaeta}(\mathrm{eV})$	$\xi_{lphaeta}(\mathrm{eV})$
Pd-Pd	3.40	14.8	2.758	0.08376	1.2630
H–H	3.22	5.28	2.300	0.1601	0.9093
H-Pd	2.20	5.50	1.769	0.6794	2.5831

Table 4.1: Interaction parameters used in the Many-Body Alloy Hamiltonian for the Pd-H system.

4.1.1 Construction of the Many-Body Alloy Hamiltonian

In the MBA Hamiltonian, each of the H-H, H-Pd and Pd-Pd interactions is characterized by a set of five parameters: $\xi_0, \epsilon_0^R, q, p$ and r_0 (four of these parameters are independent). The Pd-Pd interaction is obtained from the previous *ab initio* calculation[Tom 91a] of the cohesive energy E_{coh} as a function of the lattice constant *a* for bulk Pd. I consider nearest neighbor interactions only and obtain a simplified expression for the bulk cohesive energy,
$$E_{coh}(\text{Pd bulk}) = -\left\{ Z_{\text{bulk}} \xi_{0,PdPd}^{2} \exp[-2q_{Pd,Pd}(\frac{r_{PdPd}}{r_{0,PdPd}} - 1)] \right\}^{1/2} + Z_{\text{bulk}} \epsilon_{0,PdPd}^{R} \exp[-p(\frac{r_{PdPd}}{r_{0,PdPd}} - 1)].$$
(4.1)

Here, $Z_{\text{bulk}} = 12$ for the fcc structure and $r_{0,PdPd} = a\sqrt{2}/2$ is the nearest neighbor distance. The calculated cohesive energy E_{coh} of bulk Pd as a function of the lattice constant *a* is given by the solid line in Fig. 4.1 and compared to corresponding LDA results of Ref. [Tom 91a]. The parameters used in Eq. (4.1) are given in Table 4.1.

The parameters for H-H interaction can be determined in a similar way as those for the Pd-Pd interaction, by mapping the MBA Hamiltonian to the *ab initio* results for molecular hydrogen. The corresponding parameters are given in Table 4.1.

To determine the parameters for the Pd-H interaction, I apply the MBA Hamiltonian to bulk PdH. Considering the nearest-neighbor Pd-H, H-H and Pd-Pd interactions, I formally decompose the cohesive energy of the PdH crystal with NaCl



Figure 4.1: Cohesive energy changes $\Delta E_{coh} = E_{coh} - E_{coh,0}$ in bulk Pd and PdH as a function of the lattice constant *a*. Values obtained using the MBA Hamiltonian for Pd (solid line) and PdH (dashed line) are compared to LDA results of Ref. [Tom 91a] for the corresponding systems, given by • and 0. (From Ref. [Zho 91a]. ©American Physical Society)

structure as

$$E_{coh} = E_{coh}(H) + E_{coh}(Pd). \tag{4.2}$$

The binding energies of H and Pd atoms in this structure are given by

$$E_{coh}(H) = -\left\{ Z_{H}(Pd)\xi_{0,PdH}^{2} \exp\left[-2q_{Pd,H}\left(\frac{r_{PdH}}{r_{0,PdH}}-1\right)\right] + Z_{H}(H)\xi_{0,HH}^{2} \exp\left[-2q_{H,H}\left(\frac{r_{HH}}{r_{0,HH}}-1\right)\right]\right\}^{1/2}$$

$$+\left\{ Z_{H}(Pd)\epsilon_{0,PdH}^{R} \exp\left[-p_{Pd,H}\left(\frac{r_{PdH}}{r_{0,PdH}}-1\right)\right] + Z_{H}(H)\epsilon_{0,HH}^{R} \exp\left[-p_{H,H}\left(\frac{r_{HH}}{r_{0,HH}}-1\right)\right]\right\}$$

$$(4.3)$$

and

$$E_{coh}(Pd) = -\left\{ Z_{Pd}(H)\xi_{0,PdH}^{2} \exp\left[-2q_{Pd,H}\left(\frac{r_{PdH}}{r_{0,PdH}}-1\right)\right] + Z_{Pd}(Pd)\xi_{0,PdPd}^{2} \exp\left[-2q_{Pd,Pd}\left(\frac{r_{PdPd}}{r_{0,PdPd}}-1\right)\right]\right\}^{1/2}$$

$$+\left\{ Z_{Pd}(H)\epsilon_{0,PdH}^{R} \exp\left[-p_{Pd,H}\left(\frac{r_{PdH}}{r_{0,PdH}}-1\right)\right] + Z_{Pd}(Pd)\epsilon_{0,PdPd}^{R} \exp\left[-p_{Pd,Pd}\left(\frac{r_{PdPd}}{r_{0,PdPd}}-1\right)\right]\right\}.$$
(4.4)

Here, $Z_{Pd}(H) = 6$, $Z_{Pd}(Pd) = 12$ are the respective numbers of H and Pd nearest neighbors of a Pd atom, and $Z_H(Pd) = 6$, $Z_H(H) = 12$ are the numbers of H and Pd nearest neighbors of a H atom. $r_{0,PdH} = a/2$, $r_{0,PdPd} = a\sqrt{2}/2$ are the Pd - H and Pd - Pd nearest neighbor distances and a is the lattice constant. The values of $\xi_{0,PdH}$, $p_{Pd,H}$, $q_{Pd,H}$, and $\epsilon_{0,PdH}^R$ have been determined by reproducing LDA results of Ref. [Tom 91a] for E_{coh} of bulk PdH and are given in Table 4.1. The corresponding results obtained with the MBA Hamiltonian are given by the dashed line in Fig. 4.1, together with the LDA results given by the data points. The good agreement between results for the bulk systems based on the MBA method and LDA calculations indicates that the model Hamiltonian has sufficient flexibility to describe energy changes accurately.

4.1.2 Structure and stability of clean and hydrogen covered Pd(001) and Pd(110) surfaces

In the previous Subsection, I showed that an appropriately parametrized MBA Hamiltonian reproduces the bulk equilibrium properties very accurately. In this Subsection, I will test the applicability of the MBA Hamiltonian to surfaces, specifically to the calculation of surface energies, surface relaxations, and adsorption energies of H on (001) and (110) surfaces of Pd. These results will be compared to experimental data and to *ab initio* data of Refs. [Tom 86b] and [Tom 91a].

The surface energy of clean Pd surface can be obtained from the cohesive energy of the bulk and that of an n-layer slab using[Tom 91a]

$$E_s = \frac{1}{2} [E_{coh}(\text{Pd slab}) - nE_{coh}(\text{Pd bulk})].$$
(4.5)

This expression is relating values of the slab energy E_{coh} (Pd slab) and the corresponding surface energy E_s per atom in a surface or a layer. Using this equation together with MBA Hamiltonian, one can easily determine the surface energy for a given Pd surface. Multilayer surface relaxations can then be determined by minimizing E_s .

I have calculated the surface energy for Pd slabs with both (001) and (110) surfaces. MBA results for the change of the surface energy ΔE_s due to a relaxation Δd_{12} of the topmost interlayer distance at the (001) and (110) surfaces of Pd are given by the solid lines in Figs. 4.2(c) and (d), respectively. For the sake of simple comparison with the LDA results of Ref. [Tom 91a] [given by the data points in Fig. 4.2(d)], the MBA calculations have also been performed for a 3-layer Pd slab. My results indicate a surface contraction which increases with a decreasing coordination number of the surface atoms, in good quantitative agreement with the LDA data.

It is easy to handle very thick slabs with the MBA Hamiltonian, and I will concentrate on much thicker slabs with n = 25 in the following. This slab thickness is more than sufficient to guarantee that the two slab surfaces do not interact and that the atoms in the middle of the slab are truly in a bulk environment.

These numerical results indicate that the surface energy of Pd(110) (0.73 eV/atom) is much higher than that of Pd(001) (0.48 eV/atom). As discussed in more detail in Ref. [Tom 91a], this can be tracked back to the narrowing of the effective Pd 4d bandwidth, or an increasing number of "dangling bonds", with decreasing coordination number. Since precise experimental data for these surface energies are not available, I will only compare these results to recent LDA calculations[Tom 91a]. For Pd(001), the surface energy value $E_s = 0.48 \text{ eV}/\text{atom}$ is very close to the the LDA result[Tom 91a] of 0.49 eV/atom. The MBA value $E_s = 0.73 \text{ eV}/\text{atom}$ for a Pd(110) surface is significantly lower than the reported LDA result of 1.80 eV/atom. The large discrepancy between these latter results is possibly due to a less adequate basis set and the neglect of surface relaxations in the LDA calculation.

My results for the equilibrium structure of Pd (001) and Pd (110) are summarized in Table 4.2. The values in columns 2-4 of Table 4.2 indicate a damped oscillatory behavior for the surface relaxations. These oscillations occur as a general phenomenon which has been observed[Dav 83, Bar 85, Sko 87] and calculated[Tom 86a, Tom 85b, Boh 90] in many systems. I also find the surface relaxations to be more pronounced on the more open (110) surface than on the close packed (001) surface, in agreement with the general observation that increasing relaxations correspond to larger surface



Figure 4.2: Schematic side view of the Pd(001) (a) and Pd(110) (b) surfaces showing the definitions of the hydrogen adsorption height h and the interlayer spacings d_{12} , d_{23} and d_{34} . Surface energy changes $\Delta E_s = E_s - E_{s,0}$ for clean and H-covered Pd(001) (c) and Pd(110) (d) surfaces, as a function of the first interlayer spacing d_{12} . Values obtained using the MBA Hamiltonian for clean (solid line) and H-covered (dashed line) surfaces are compared to the LDA results of Ref. [Tom 91a] for the corresponding systems, given by \bullet and \circ . (From Ref. [Zho 91a]. ©American Physical Society)

Surface	$\Delta d_{12}(\%)$	$\Delta d_{23}(\%)$	$\Delta d_{34}(\%)$	Reference
Pd(001)	-2.2	0.2	0.0	Present Work
Pd(110)	-5.2	0.7	-0.3	Present Work
$Pd(001) + p(1 \times 1) H$	4.0	0.7	0.0	Present Work
$Pd(110) + p(1 \times 1) H$	1.3	1.3	0.0	Present Work
Pd(110)	-6.0 ± 2	1.0 ± 2		[Bar 85]
Pd(110)	-5.1 ± 1.5	$2.9{\pm}1.5$		[Sko 87]
$Pd(110) + (2 \times 1) H$	-2.2 ± 1.5	$2.9{\pm}1.5$		[Sko 87]

Table 4.2: Relaxations at clean and hydrogen covered Pd surfaces.

energies. As shown in Table 4.2, the surface relaxations, calculated using the MBA technique, are in gratifying agreement with both experimental data[Bar 85, Sko 87] and LDA results[Tom 91a, Boh 90]. This good agreement confirms that the MBA Hamiltonian can accurately describe the equilibrium structure and energy changes of clean Pd(001) and Pd(110) surfaces.

Finally, I use the MBA Hamiltonian to determine the binding energy of hydrogen at different adsorption sites on the Pd(001) and Pd(110) surfaces. These calculations yield the preferential adsorption site and adsorption height, both of which are accessible to experimental verification. In order to simplify the comparison with the LDA calculations of Refs. [Tom 86b] and [Tom 91a], I performed all calculations for a 3-layer Pd slab which was covered by H on both sides. I found the adsorption energy of H on Pd to be typically of the order $E_{ad} \approx -3$ eV. Since the binding energy of a H₂ molecule is only $D_e = 4.75$ eV, the dissociation probability of a H₂ molecule approaching the Pd surface is high. For this reason, the present investigations has been limited to atomic hydrogen on Pd(001) and Pd(110).

The equilibrium structure of hydrogen covered surfaces can be determined in the same way as that of the clean surfaces described above. My results for the surface energies and multilayer relaxations of hydrogen covered surfaces are summarized in Fig. 4.2 and Table 4.2. Hydrogen atoms are assumed to occupy the equilibrium sites during the surface relaxation. The calculated changes of the surface energy at hydrogen covered Pd(001) and Pd(110) surfaces are given by the dashed lines in Figs. 4.2(c) and (d), respectively. For the sake of simple comparison with the LDA results of Ref. [Tom 91a] [given by the data points in Fig. 4.2(d)], also these model calculations have been performed for a 3-layer Pd slab. My results indicate an expansion of the hydrogen covered surfaces, in agreement with the LDA data. The reversal of surface contraction obtained for clean surfaces can be explained by the saturation of Pd dangling bonds by H atoms.

In Fig. 4.3, I display the adsorption energy of H on Pd(001) as a function of the adsorption height h for the on-top site, the bridge site and the hollow site. Results obtained using the MBA Hamiltonian, shown by lines, are compared to LDA data of Ref. [Tom 86b], given by the data points. As discussed above, I represent the substrate by the same 3-layer Pd slab as used in the LDA calculation. Since it is only energy differences which are relevant for the preferential adsorption sites and the vibration frequencies, I concentrate on adsorption energy changes $\Delta E_{ad} = E_{ad} - E_{ad,0}$ with respect to the adsorption energy of H at the equilibrium site. The corresponding results are shown in Fig. 4.3(b). I find the fourfold hollow site to be the equilibrium site on Pd(001), in agreement with the experimental data of Ref. [Beh 80] and the LDA results of Ref. [Tom 86b]. Also the very small equilibrium adsorption height $h_0 =$ 0.18 Å above the first Pd layer is in good agreement with the LDA value[Tom 86b] of 0.24 Å and the experimental result[Bes 87] of 0.30 Å. These small adsorption heights result from the very small atomic radius of hydrogen. More important, the MBA Hamiltonian gives H-Pd interaction potentials (and consequently vibration frequencies) in close agreement with the LDA data.



Figure 4.3: (a) Schematic top view of the Pd(001) surface and the assignment of adsorption sites: hollow (×), bridge (•) and on-top(\Box). (b) Adsorption energy changes $\Delta E_{ad} = E_{ad} - E_{ad,0}$ (with respect to the equilibrium adsorption energy) as a function of the hydrogen adsorption height h on Pd(001). Results based on the MBA Hamiltonian for the hollow site (solid line), the bridge site (dashed line) and the on-top site (dotted line) are compared to LDA results of Refs. [Tom 86b] and [Tom 91a], given by the data points. (From Ref. [Zho 91a]. ©American Physical Society)



Figure 4.4: (a) Schematic top view of the Pd(110) surface and the assignment of adsorption sites: hollow (×), long-bridge (•), short-bridge (•) and on-top (□). (b) Adsorption energy changes $\Delta E_{ad} = E_{ad} - E_{ad,0}$ (with respect to the equilibrium adsorption energy) as a function of the hydrogen adsorption height h on Pd(110). Results based on the MBA Hamiltonian for the hollow site (solid line), the long-bridge and the short-bridge sites (dashed line) and the on-top site (dotted line) are compared to LDA results of Ref. [Tom 91a], given by the data points. (From Ref. [Zho 91a]. ©American Physical Society)

Adsorption energies for H on Pd(110) are shown in Fig. 4.4 for the on-top, the short-bridge, the long-bridge and the hollow site. In analogy to Fig. 4.3, the continuous lines represent the MBA Hamiltonian results, and the discrete data points show the LDA values of Ref. [Tom 91a]. Also in this case, the LDA and MBA Hamiltonian calculations have been performed for a 3-layer Pd slab. Similar to the results for the (001) surface, the MBA potentials represent energy differences and adsorption potentials, which are in remarkably good agreement with the LDA data.

Both the MBA technique and the LDA predict the long-bridge site to be the most favored among the adsorption sites considered here. My calculation indicates that in this site, the equilibrium hydrogen adsorption height is only $h_0 = 0.09$ Å above the topmost Pd layer. Recent low-energy electron diffraction (LEED)[Sko 87] and He scattering[Rie 83, Bas 89] experiments suggest that the preferential H adsorption site is the threefold coordinated site in the troughs on the Pd(110) surface. In this site, the separation between the hydrogen atom and the two nearest neighbors in the topmost Pd layer, as well as the closest Pd atom in the second layer, is 2 Å. The mutually repulsive interaction between nearest neighbor hydrogen atoms stabilizes a zig-zag adsorption pattern in the troughs on the surface[Rie 83]. Results based on the MBA Hamiltonian indicate that this adsorption geometry is slightly energetically disfavored when compared to the preferential long-bridge site. While the MBA Hamiltonian clearly can not resolve such minute energy differences, I find that the predicted H-Pd interaction potentials are in remarkably good agreement with *ab initio* calculations and experimental data in view of the simplicity of the approach.

4.2 Phonon structure in the bulk and at the surface of Pd-H systems

In this Section, I present phonon calculation results for bulk Pd and PdH, as well as the clean and H covered (001) and (110) surfaces of Pd. As outlined in Section 2.3, the phonon dispersion relations can be determined directly by diagonalizing the dynamical matrix $D_{\alpha\beta,\kappa\nu}(\vec{k})$, which is basically a Fourier transformed force-constant matrix. According to Eq. (2.26), the force-constant matrix can be determined numerically by calculating total energy differences with respect to the atomic displacements. This can be done even more efficiently using the MBA Hamiltonian which, as shown above, gives reliable potential energies near the equilibrium structure. It is worthwhile to note that the force-constant matrix accounts for effective second- and third-neighbor interactions. This is a consequence of the many-body nature of the MBA Hamiltonian which correctly describes the indirect interaction between two atoms and its mediation through a third atom neighboring the two sites.

In Fig. 4.5(a), I compare the phonon calculations for bulk fcc Pd to measured phonon spectra along the high symmetry lines. The experimental data[Mil 71] have been obtained using inelastic neutron scattering. As shown in this figure, the calculation is in quite good agreement with the experiment throughout the Brillouin zone. While my Hamiltonian is based on LDA calculations for static properties of Pd, and does not contain any adjustable parameters, the good agreement with the experimental data indicates that the MBA Hamiltonian also correctly describes the dynamical properties of this system.

Results of a similar calculation for bulk PdH are shown in Fig. 4.5(b). The net effect of hydrogen on the phonon spectrum is a softening on the acoustic branches. This is partly caused by a 6% increase of the lattice constant upon hydrogen uptake



Figure 4.5: Phonon dispersion relations for bulk Pd (a) and PdH (b). Frequencies calculated using the MBA Hamiltonian are given by the solid lines. The experimental data points of Ref. [Mil 71] for bulk Pd are given by (+). (From Ref. [Zho 91a]. ©American Physical Society)

•

from 3.89 Å in Pd to 4.12 Å in PdH, as shown in Fig. 4.1. Based on the analysis of these results, I find that the presence of hydrogen has a strong effect on the force constant matrix Φ . The force constants describing the restoring forces acting on a Pd atom displaced along a high-symmetry direction are reduced from $c = 10.6 \text{ eV}/\text{Å}^2$ in bulk Pd to only 6.8 eV/Å² in PdH. The effect of the the presence of hydrogen on the bulk modulus is comparably small. I obtain $B = 2.03 \times 10^{12} \text{ dyn/cm}^2$ for bulk Pd which compares well with the experimental value[Kit 86] $B = 1.81 \times 10^{12} \text{ dyn/cm}^2$ and the LDA value of $2.15 \times 10^{12} \text{ dyn/cm}^2$. The corresponding value in PdH is only 3% smaller, $B = 1.98 \times 10^{12} \text{ dyn/cm}^2$, which is in fair agreement with the LDA result $1.95 \times 10^{12} \text{ dyn/cm}^2$ of Ref. [Tom 91a].

Since my main interest is the effect of hydrogen on the Pd modes, I do not include the hydrogen-derived optical modes in Fig. 4.5. These modes have a very high frequency and are well separated from the acoustic Pd-derived modes due to the mass disparity of these atoms. While the hydrogen atoms can be basically thought of as Einstein oscillators, the weak coupling between hydrogen atoms broadens the optical states to a \approx 3 THz broad band. Since the H-H nearest neighbor distance in PdH $r_{0,HH} = 2.06$ Å is much larger than the H-H interaction range (\approx 1 Å), I have neglected the direct H-H interaction in this calculation, but have accounted for the dominant indirect interaction mediated by Pd atoms. A closer analysis of the optical bands reveals that two out of the three bands show no dispersion and represent Einstein modes of hydrogen atoms with no direct coupling. The above mentioned dispersion of the third branch reflects the degree of Pd mediated indirect interaction between H atoms, which is almost equally strong for the first and second neighbors. These effects in the optical band can also be seen in the measured phonon dispersion relations of the related systems PdD_{0.63}[Row 74] and PdT_{0.7}[Row 86]. The calculated phonon spectra for the Pd(100) and Pd(110) surfaces are shown in Figs. 4.6 and 4.7, respectively. These surfaces are represented by relaxed 25layer Pd slabs. Phonon spectra of the clean (001) and (110) Pd surfaces, shown in (a), are compared to results for hydrogen covered surfaces, shown in (b). In order to distinguish surface from bulk states, I are showing phonon bands of bulk Pd in Figs. 4.6(c) and 4.7(c). For the sake of simple comparison, the bulk bands are projected onto the same two-dimensional Brillouin zones in (c) as used in (a) and (b). Note that this procedure yields continuous bulk bands at each \vec{k} -point in the Brillouin zone. The apparent discreteness in Figs. 4.6(c) and 4.7(c) results from a finite \vec{k} -point sampling in a direction perpendicular to the Brillouin zone. For both surfaces, my calculations indicate the presence of surface modes which appear either in the bulk band gaps or are split off from the bulk band edges.

Based on the comparison of phonon spectra for Pd(001) in Fig. 4.6(a) and the projected bulk spectra in Fig. 4.6(c), the presence of the surface introduces a soft Rayleigh mode S_1 which is substantially softer than any bulk mode in the Brillouin zone. At the \overline{M} point, this mode corresponds to vibrations of surface atoms perpendicular to the surface. The origin of the mode softening is a decreased interlayer interaction at the surface, which is only partly compensated by the surface contraction. The analysis of my results indicates that the zone-edge frequency of the S_1 mode increases from 3.72 THz for the unrelaxed surface to 4.11 THz for the relaxed surface. A second surface mode S_4 , which is barely split from the bulk band at \overline{M} , is a transversal mode corresponding to in-plane vibrations. In addition to these soft modes, the surface introduces a phonon mode S_6 with $\nu \approx 6$ THz in the gap of the bulk spectrum near \overline{X} . This mode corresponds to in-plane vibrations of topmost layer atoms, coupled to out-of-plane vibrations of second layer atoms.



Figure 4.6: (a) Calculated phonon dispersion relations for a clean 25-layer Pd slab with a (001) surface. (b) Corresponding results for a H-covered Pd slab (monolayer coverage, hollow site). (c) Bulk phonon dispersion relations of Fig. 4.5(a), projected onto the two-dimensional surface Brillouin zone used in (a) and (b). (From Ref. [Zho 91a]. (c) American Physical Society)



Figure 4.7: (a) Calculated phonon dispersion relations for a clean 25-layer Pd slab with a (110) surface. The experimental data of Ref. [Lah 87] are given by \bullet . (b) Corresponding results for a H-covered Pd slab (monolayer coverage, long-bridge site). (c) Bulk phonon dispersion relations of Fig. 4.5(a), projected onto the two-dimensional surface Brillouin zone used in (a) and (b). (From Ref. [Zho 91a]. ©American Physical Society)

The phonon spectrum of a hydrogen-covered Pd (001) surface has been shown in Fig. 4.6(b). I have assumed a monolayer coverage corresponding to occupying all hollow sites by H atoms. The Pd surface has again been represented by a 25layer slab. Similar to the bulk Pd-H system, I am mainly interested in the effect of hydrogen on the Pd surface modes, and do not show the H-derived high-frequency optical modes which are well separated from the Pd modes. The most striking change in comparison to the H-free surface shown in (a) is a massive softening of the Rayleigh mode. At M, the frequency of the S_1 mode decreases from 4.11 THz to 2.77 THz due to hydrogen adsorption. On the other hand, hydrogen does harden other modes, such as the bulk band gap mode at $\nu \approx 6$ THz which has been discussed above. A detailed analysis of the eigenstates shows that surface phonon modes with a vibration amplitude perpendicular to the surface experience a large amount of softening. Other surface modes with amplitudes restricted to the surface layer, such as the S_6 mode, experience a hardening due to the restricted movement in presence of hydrogen atoms. The eigenvector analysis also indicates that hydrogen adsorption also increases the confinement of surface modes to the few topmost layers and shortens the penetration depth into the bulk.

As done above for Pd (001), in Fig. 4.7, I compare the phonon spectra of clean and hydrogen-covered Pd(110) surfaces to bulk phonon spectra. For the hydrogen covered surface, I have assumed a monolayer coverage corresponding to the occupation of all long-bridge sites (the equilibrium adsorption site) and represented the Pd surface by a 25-layer slab.

A comparison between the calculated phonon spectra for clean Pd(110) and inelastic He scattering data of Ref. [Lah 87] is shown in Fig. 4.7(a). The softest surface mode is the Rayleigh mode S_1 . My calculation reproduces the general features of this mode quite well, but the calculated frequencies are $\approx 10\%$ higher than the observed data. While I am aware that the parametrized MBA Hamiltonian may not describe the detailed changes of metal bonding at surfaces to a very high accuracy, I can not exclude the possibility of a slight hydrogen contamination of the Pd sample used in Ref. [Lah 87], which is very hard to detect and would also soften the surface Rayleigh mode.

Since Pd(110) shows the largest surface contraction, the softest surface phonon modes are quite close to the lowest lying bulk bands throughout the surface Brillouin zone. The strongest softening can be observed at the \bar{Y} point, where I obtain three surface modes S_1 , S_2 and E well below the bulk band. My analysis of the eigenstates indicates that these modes correspond to in-plane (along the surface x and y directions) and out-of-plane (along the z direction) vibrations of the topmost layer. The lowest mode is an in-plane mode with an amplitude along the y direction. Similar to the (001) surface, the surface contraction generally hardens the surface phonon modes. This calculation shows that at the \bar{Y} point, because of the relaxation, the lowest surface modes with topmost layer amplitudes along the x, y, and z directions are shifted from 2.36 THz, 2.29 THz and 2.77 THz to 2.71 THz, 2.23 THz and 2.94 THz, respectively.

From the comparison between Figs. 4.7(a) and (c), one can see that the presence of the (110) surface introduces several other vibration modes beyond the Rayleigh mode. The bulk phonon spectrum, shown in Fig. 4.7(c), contains gaps near \bar{X} , at $\nu \approx 5.5$ THz, and near \bar{Y} , at $\nu \approx 4.5$ THz. On Pd(110), three surface states appear in both gaps. The 5.4 THz gap mode at \bar{X} corresponds to topmost layer atoms vibrating along the surface x direction, and the 4.7 THz gap mode at \bar{Y} corresponds to an analogous vibration along the surface y direction. The surface also introduces high frequency states slightly above the top of the bulk bands, well visible at the \bar{X} and \bar{Y} points. These modes have considerable amplitudes deep into the bulk, and correspond to alternating in-plane and out-of-plane vibrations on the individual layers.

Calculated surface phonon dispersion relations for the H covered Pd(110) surface are shown in Fig. 4.7(b). As for bulk PdH and H/Pd(001), I do not show the Hderived high-frequency optical modes for H/Pd(110) in Fig. 4.7(c). The general trends discussed above for the effect of hydrogen on the surface modes of the Pd(001) surface hold also for the (110) surface. Specifically, One can observe a softening of surface modes involving an out-of-plane motion of topmost layer atoms, and a hardening of modes involving an in-plane vibration of surface atoms along the x direction at \bar{X} and the y direction at \bar{Y} . Other vibration modes experience very little change.

Hydrogen-induced bonding changes at the Pd(110) surface can be understood by investigating the three lowest phonon modes S_1 , S_2 and E at the \bar{Y} point. The S_1 mode, which involves in-plane vibrations of the topmost layer along the surface y direction and out-of-plane vibrations of the second layer, has been pushed up in frequency from 2.23 THz for the clean surface to 2.71 THz for the H covered surface. The main reason for this hardening is a restricted freedom of motion of topmost layer Pd atoms due to hydrogen atoms adsorbed in the long-bridge site. The S_2 mode, corresponding to a vibration of topmost layer Pd atoms along the close-packed surface x direction, has been softened by the presence of hydrogen from 2.71 THz for the clean surface to 2.46 THz for the H covered surface. Finally, the E mode, corresponding to out-of-plane vibrations of the topmost layer, experiences the strongest softening from 2.94 THz for the clean surface to 2.56 THz for the H covered surface.

As compared to the (001) surface, phonon modes at the Pd(110) surface are less

affected by hydrogen adsorption. This is especially true for the softening of the Rayleigh mode. This last conclusion may not hold in case of an adsorption in the quasi-threefold site discussed in the previous Section. In that case, I would expect an increasing Rayleigh mode softening with increasing hydrogen coverage, which has been observed at the \bar{Y} point on the related Ni(110) surface in high-resolution EELS experiments[Leh 87].

From this calculation, one can see that hydrogen adsorption has a profound effect on both the equilibrium structure and dynamical properties of Pd surfaces. These two effects are closely related. The presence of hydrogen adsorbates reverses the topmost layer contraction, and the large anharmonicity of the inter-layer interactions causes the effective inter-layer force constant to decrease with increasing inter-layer distance. This results in a softening of the Rayleigh surface phonon mode with an out-of-plane amplitude in the topmost layer. Since the hydrogen-induced expansion is larger on the more densely packed (001) surface than on the (110) surface, the Rayleigh mode softening is also stronger on the Pd(001) surface.

At both Pd(001) and Pd(110) surfaces, the equilibrium adsorption height of hydrogen is close to zero, i.e. hydrogen atoms are buried inside the topmost Pd layer, where they affect the effective Pd-Pd force constants most. There is very little surface stress associated with this adsorption site, due to the small size of the H atoms. Surface phonon modes with in-plane vibration amplitudes are nearly independent of surface relaxations, but are affected by the presence of hydrogen. This latter effect results from the hydrogen-induced change of Pd-Pd force constants, and also the restricted freedom of motion due to the extra adsorbed atoms which hardens some of these modes.

4.3.1 Thermal expansion and the melting transition in Pd

The first nontrivial application of the present formalism is to determine the equilibrium volume of Pd as a function of temperature, and to study the melting transition. In the corresponding molecular dynamics simulation, I consider an originally cubic volume (or simulation box) containing 500 Pd atoms on an fcc lattice. Periodic boundary conditions are used to eliminate surface effects, and the external pressure is set to zero. I start the simulation by first equilibrating the system for 10,000 time steps (corresponding to 2×10^{-11} s) in a VTN canonical ensemble which is in contact with a heat bath at T = 300 K. This simulation is followed by another 20,000 time steps in the TtN canonical ensemble at zero external pressure. The equilibrium volume V per atom is related to the volume of the simulation box, and is obtained from a running average during the simulation. The statistical error based on the last 10,000 time steps is found to be negligible. After V has been determined for the given temperature, the heat bath is gradually warmed up to another temperature, and the equilibrium volume per atom is obtained from a statistical average over 10,000 time steps at the new temperature.

My results, presented in Fig. 4.8(a), indicate a thermal expansion of the lattice in the whole temperature range studied. In the temperature range between T = 2000 - 2050 K, the equilibrium volume per Pd atom shows a discontinuous increase, indicative of a first-order phase transition. This phase transition corresponds to the melting point, as can be verified by inspecting the trajectories of individual Pd atoms at temperatures below and above the critical temperature, shown in Figs. 4.9(b) and 4.9(c). Near the melting point, my calculations show a narrow hysteresis describing



Figure 4.8: (a) Equilibrium volume V of a Pd atom in bulk Pd as a function of temperature T. The dashed line is a guide to the eye connecting the calculated data points. Observed linear expansion of Ag[Pea 58], the neighboring element of Pd, is shown by the dotted line. (b) Equilibrium volume V per Pd atom in bulk PdH_x , as a function of the hydrogen concentration x. The dotted line corresponds to the observed[Pei 78] expansion coefficient of Pd as a function of x. Results of the present molecular dynamics simulations are given by \bullet in (a) and (b). (From Ref. [Zho 92]. (CAmerican Physical Society)



Figure 4.9: Atomic trajectories in bulk Pd at the temperatures (a) T = 300 K and (b) T = 1800 K below the melting temperature T_M , and (c) at T = 2050 K above T_M . Corresponding pair correlation functions $g(\tau)$ at T = 300 K, T = 1800 K and T = 2100 K are shown in (d), (e), and (f), respectively. (From Ref. [Zho 92]. @American Physical Society)

an overheated solid or an undercooled liquid, depending on whether the system is being heated or cooled. The small difference of $\leq 10\%$ between the calculated melting temperature and the experimental value[Kit 86] of $T_M = 1827$ K is impressively small in view of the fact that the interaction potentials are based on T = 0 static properties of Pd. A small positive difference between the calculated and the observed melting point is also expected due to the finite size of the unit cell and absence of large defects or a surface.

In the temperature range T < 1500 K, the thermal expansion of the lattice is nearly linear, corresponding to a thermal (linear) expansion coefficient of $\alpha_l =$ 1.7×10^{-5} K⁻¹. While I could not find any corresponding experimental results for Pd, this value lies very close to $\alpha_l = 1.89 \times 10^{-5}$ K⁻¹ which has been observed in Ag[Pea 58], a neighbor of Pd in the periodic system. At higher temperatures, the volume-temperature relation shows strong deviations from linearity. This relationship bears information about the Pd-Pd interaction potentials at large interatomic separations. Above the melting point, the expansion coefficient of the system experiences an abrupt increase above the solid phase value, correlated with a sharp increase of the interparticle distance at T_M .

In order to illustrate the effect of temperature on the dynamical behavior of the system, I showed the trajectories of individual Pd atoms [projected onto the (100) plane] in Figs. 4.9(a)-(c) at different temperatures. At T = 300 K, all atoms appear to be pinned to their equilibrium site and show negligible fluctuations about this position, reflected in a very small Debye-Waller factor. At T = 1800 K, the fluctuations of Pd atoms about their equilibrium sites are already quite appreciable. The size of these fluctuations is a considerable fraction of the lattice constant, which, according to Lindemann's criterion, is indicative of the proximity to the melting point. A statis-
tically negligible fraction of atoms is also seen to diffuse far away from their site, but the crystalline order still exists. Above the melting point, all atoms diffuse relatively freely throughout the sample, as shown in Fig. 4.9(c), and the long range order is destroyed.

A more quantitative measure of the crystalline order is the pair correlation function g(r) which is shown in Figs. 4.9(d)-(f) for the above temperature values. Clearly, the validity of conclusions related to the long-range order in the crystal is limited by the finite size of the simulation box. At T = 300 K, g(r) consists of a set of sharp peaks which will result in a sharp diffraction pattern. At T = 1800 K, g(r) still shows a substantial amount of structure even for large interatomic distances r, indicative of long-range order, but the peaks are smeared out and begin to overlap. Above the melting transition, the most characteristic feature in the pair correlation function is a peak at the nearest-neighbor distance. For larger interatomic distances, g(r) contains almost no information about the atomic structure and approaches the constant value g(r) = 1 very rapidly. This would justify a treatment of the liquid as a continuous medium beyond the nearest-neighbor distance.

As I will discuss later on in connection with fracture, interesting details about the cohesion of the system under different conditions can be learned from the distribution of atomic binding energies. In Figs. 4.10(a) and (b), I compare the binding energy distribution for bulk Pd atoms at T = 300 K and T = 2100 K, just above the melting point. In absence of applied tensile stress, my simulations indicate that binding energies in the system can be characterized by a rather featureless single-peaked distribution function indicating that most atoms have an indistinguishable environment. The small width of this peak at T = 300 K, shown in Fig. 4.10(a), reflects an almost perfect crystalline order at this temperature. Above the melting



Figure 4.10: Distribution of atomic binding energies E_{coh} in bulk Pd at (a) T = 300 K and (b) T = 2100 K at zero pressure. (c) Corresponding data for Pd at T = 300 K at the point of critical uniaxial tensile stress p_c for fracture, discussed in Section 4.3.2 The solid lines give the probability distribution, the dashed lines show the integrated probability. (From Ref. [Zho 92]. ©American Physical Society)

point, this peak is strongly broadened and shifted towards smaller binding energies, as shown in Fig. 4.10(b). The former effect comes from the large variety of binding sites in the liquid, the latter one reflects the loss of cohesion mainly due to a uniform lattice expansion.

4.3.2 Mechanical stability of H-free Pd under tensile stress

One of the most challenging problems related to the mechanical stability of metals is to obtain a quantitative understanding of the fracture process due to uniaxially applied tensile stress. I address this problem by studying the deformation of a metal block (the simulation box) under a uniaxial load, as shown schematically in Fig. 4.11(a). I expect the length z of the metal block first to increase monotonically with increasing load. Once a critical value of the tensile stress p_c is reached, the material can no longer support the load and breaks into parts. In the following, I describe the molecular dynamics simulation of the elastic and plastic deformations in the Pd metal block which is exposed to increasing uniaxial tensile stress, as a function of temperature and – in the following subsection – as a function of hydrogen concentration.

In the present MD simulation, I consider a canonical (TtN) ensemble of 500 Pd atoms in a simulation box which has cubic shape at zero applied stress, but which can vary its shape freely in the case of anisotropic pressure. For a given temperature of the heat bath, I determine the shape changes [especially the elongation of the cell Δz , see Fig. 4.11(a)] in response to uniaxial tensile stress which is described by the stress matrix

$$\underline{\sigma} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & p \end{pmatrix}.$$
 (4.6)

Results for the elongation Δz of the MD unit cell as a function of p are shown in



Figure 4.11: (a) Schematic picture of Pd deformations under tensile stress, showing the length z and deformation Δz of the unit cell. (b) Deformation Δz of bulk Pd as a function of the external tensile stress p, for different temperatures. (c) Deformation Δz of hydrogen loaded bulk Pd at T = 300 K, as a function of the external tensile stress p, for different hydrogen concentrations. The molecular dynamics results are given by the data points. The lines are guides to the eye. (From Ref. [Zho 92]. ©American Physical Society)

Fig. 4.11(b) for temperatures between 77 K and 1800 K. In this simulation, I increased the uniaxial stress p in finite steps of initially $\Delta p = 2.0$ GPa from zero to a load just below the point of fracture. From there on, I decreased the steps Δp to 0.5 - 1 GPa in order to increase the accuracy of the calculated critical tensile stress p_c . At each value of p, the system has been allowed typically 5,000 time steps (or 10^{-11} s) to equilibrate. I observed that the equilibration took longer near the point of fracture and extended the simulation accordingly. The equilibrium shape of the MD unit cell has been obtained by averaging over the last 5,000 time steps.

The first important result of this simulation is the order of magnitude for the critical tensile stress p_c to initiate fracture, typically a few GPa. As shown in Fig. 4.11(b), p_c decreases with increasing temperature, from 11 GPa at T = 77 K to 1 GPa at T = 1800 K. On the other hand, I find an increase in the plasticity, given by $\partial z/\partial p$, with increasing temperature at constant load. I conclude that the Young's modulus Y, defined by $Y = \partial p/\partial z$, decreases as the temperature rises. Both effects indicate that the material becomes softer and easily deformable with increasing temperature, which agrees with the everyday experience. Microscopically, this softening corresponds to the increased probability of activated atomic diffusion leading to a new equilibrium geometry (plastic deformations to a "thin wire" and fracture under excessive uniaxial load). In the elastic region $p \ll p_c$, the $\Delta z - p$ relationship is nearly linear for all temperatures. This Hooke's law type behavior is expected based on the MBA interaction potential which is dominated by harmonic terms close to the equilibrium.

It is interesting to note that the above MD simulations, performed under uniaxial stress, contain the information about the bulk modulus B which describes the elastic response to *isotropic pressure*. For a cubic crystal, the elastic response to a very small

applied uniaxial stress p is

$$p = C_{11}\epsilon_1 + 2C_{12}\epsilon_2 \tag{4.7}$$

along the direction of the load. Here, ϵ_1, ϵ_2 are the strain components along the load direction and perpendicular to the load direction, respectively, and C_{11}, C_{12} are elastic stiffness constants. No stress occurs perpendicular to the load direction [see Fig. 4.11(a)], so

$$0 = C_{12}\epsilon_1 + C_{11}\epsilon_2 + C_{12}\epsilon_2 . (4.8)$$

From Eqs. (4.7) and (4.8) one can derive

$$p = (C_{11} + 2C_{12}) \frac{V(p) - V(p=0)}{V(p=0)} .$$
(4.9)

Using $B = (1/3)(C_{11} + 2C_{12})$ for a cubic crystal leads to

$$B = \frac{1}{3}V\left(\frac{\partial V}{\partial p}\right)_{p=0}^{-1} .$$
(4.10)

As shown in Fig. 4.12(a), the present results for the absolute value of B and the temperature dependence of B are in good agreement with the experimental data of Ref. [Lan 79]. At low temperatures, the bulk modulus is found to be essentially independent of temperature. With rising temperature, however, the present results indicate a strong decrease of B.

I found it instructive to inspect the distribution of binding energies for a signature of atomic fracture at very large tensile loads. In Fig. 4.10(c), I show the distribution at the point of critical tensile stress p_c , for a developed fracture. As compared to the stress-free situation shown in Figs. 4.10(a) and (b), the distribution of binding energies shows several distinctive peaks. The lowest binding energies correspond to



Figure 4.12: (a) Temperature dependence of the bulk modulus B of Pd. The dashed line is a guide to the eye connecting the calculated points, given by \bullet . The dotted line shows the experimental data of Ref. [Lan 79]. (b) Dependence of the bulk modulus of PdH_x on the hydrogen concentration x. (From Ref. [Zho 92]. ©American Physical Society)

sites at the surface of the crack. The highest binding energies, same as in the stressfree sample shown in Fig. 4.10(a), correspond to bulk sites in the intact fragments.

4.3.3 Mechanical stability of H loaded Pd under tensile stress

Hydrogen is well known to dissociate at transition metal surfaces and to penetrate easily into the bulk metal, releasing the heat of hydride formation in many systems such as Pd[Ale 78]. This process makes such metals an ideal medium for hydrogen storage. On the other hand, the presence of hydrogen is known to have an adverse effect on mechanical properties of metals, specifically facilitating the formation of cracks under tensile stress[Bir 79]. In order to obtain a microscopic understanding of the processes associated with hydrogen-assisted crack formation, I simulated the response of hydrogen loaded Pd to uniaxial tensile stress in a molecular dynamics calculation.

I have chosen a cubic simulation box containing 500 Pd atoms as the initial MD unit cell, and occupied the 500 octahedral interstitial sites in the lattice at random with hydrogen atoms. I have considered three different H concentrations in PdH_x, namely x = 0.1, x = 0.25, and x = 0.6, and performed all simulations at room temperature, T = 300 K. At each H concentration, I first let the system equilibrate over a period of more than 30,000 time steps (corresponding to 1.5×10^{-11} s).

First, I study the volume changes due to hydrogen at zero pressure. The free volume V(x) of Pd atoms in PdH_x, shown in Fig. 4.8(b), has been determined for each H concentration x by averaging over 10,000 time steps after reaching the equilibrium. I found the free volume to increase almost linearly with increasing hydrogen concentration x, which agrees with the observed relation [Pei 78] V(x) = V(0)(1 + 0.19x).

In order to understand the effect of dissolved hydrogen on the mechanical stability of Pd, I studied the response of the system to uniaxial tensile stress using molecular dynamics. As in the hydrogen-free samples, the system was first allowed to equilibrate under fixed external tensile stress p and constant temperature of the heat bath T =300 K. Then, the stress-induced elongation Δz of the simulation box was determined by averaging over 10,000 time steps (corresponding to 5×10^{-12} s). The results, presented in Fig. 4.11(c), show an almost linear relationship between p and Δz . I found the slope of the $\Delta z(p)$ curves to be almost independent of x at low values of p, indicating that changes of the hydrogen concentration have little effect on the Young's modulus Y. These results also indicate that the critical tensile stress p_c for the onset of fracture, corresponding to the "end points" of the $\Delta z(p)$ curves, decreases with increasing hydrogen concentration. I found that hydrogen can reduce the critical tensile stress for fracture p_c substantially when compared to the hydrogenfree system, but that the order of magnitude of p_c in the different systems is the same. This hydrogen-induced reduction of the mechanical strength is sometimes called "hydrogen embrittlement" [Bir 79]. As I will discuss later on, the microscopic results indicate that this is a misnomer; I find hydrogen to enhance the *ductility* and plasticity of the metal matrix locally, thereby weakening the structure as a whole.

One can also use the MD results for uniaxial tensile stress to estimate the bulk modulus of the system, following the procedure outlined in the previous subsection. The results, presented in Fig. 4.12(b), indicate that the bulk modulus *B* decreases strongly in the presence of hydrogen. Another quantity of interest is the Poisson's ratio μ which is the ratio of the unit cell deformations along the direction of the applied load, Δz , and perpendicular to it, Δx . In a cubic system, μ relates the Young's and the bulk modulus as $B = Y/(3 - 6\mu)$, which defines μ as

$$\mu = \frac{1}{2} - \frac{Y}{6B} \,. \tag{4.11}$$

My above results for Y(x) and B(x) indicate that the Poisson's ratio decreases strongly with increasing hydrogen concentration in the metal.

As in the hydrogen-free system, I investigated the distribution of binding energies for a signature of atomic fracture at different tensile loads. My results for the PdH_{0.25} system are summarized in Fig. 4.13(a) for zero tensile stress and in Fig. 4.13(b) for critical tensile stress. The structure of the binding energy distribution in the stressfree case reflects the distribution of inequivalent Pd atoms with 0–6 hydrogen nearest neighbors. The relatively featureless distribution of binding energies at the point of critical tensile stress $p = p_c$, displayed in Fig. 4.13(b), is in sharp contrast to the hydrogen-free case shown in Fig. 4.10(c), and is more reminiscent of the results for molten Pd, shown in Fig. 4.10(b). The absence of distinct fracture-related features in the binding energy distribution in Fig. 4.13(b) indicates that all Pd atoms reside in a relatively homogeneous atomic environment. This environment is close to the molten system; it has an amorphous structure and can easily be plastically deformed. I conclude that increased hydrogen concentration has a similar effect on the mechanical properties of Pd as a temperature increase, namely enhanced ductility and plasticity.

An independent microscopic signature of fracture on the atomic scale can be often found in the distribution of Wigner-Seitz volumes associated with the individual atoms in the crystal. Statistical presence of large atomic volumes indicates the occurrence of fracture with no additional assumptions about the number, position or morphology of one or more simultaneous cracks. This information is displayed in Fig. 4.14 for Pd and H atoms in PdH_{0.25} at $p = p_c$. The volumes of Pd atoms, given



Figure 4.13: Distribution of binding energies of Pd atoms in bulk $PdH_{0.25}$ at T = 300 K (a) at zero pressure and (b) at the point of critical uniaxial tensile stress p_c [compare with Fig. 4.11(c)]. The solid lines give the probability distribution, the dashed lines show the integrated probability. (From Ref. [Zho 92]. ©American Physical Society)



Figure 4.14: Distribution of atomic volumes in bulk $PdH_{0.25}$ at T = 300 K. The solid line shows the distribution of atomic volumes associated with Pd atoms, obtained using the Wigner-Seitz cell construction. The dashed line is obtained by first determining, which Pd sites are associated with each of the H atoms in the lattice, and displaying the distribution of these Pd volumes. The dotted line gives the ratio of the values given by the dashed and the solid lines, divided by the volume and multiplied by 3. (From Ref. [Zho 92]. ©American Physical Society)

by the solid line, show a distribution which is characterized by a sharp peak near 15 Å^3 , corresponding to atoms in bulk-like environment, and a wide structureless tail towards larger volumes, associated with atoms near the crack surface. This finding again confirms the previous conclusion that Pd atoms have no preferential binding arrangement in the hydrogen loaded sample, which shows a plastic behavior under critical tensile stress.

The preferential hydrogen sites in this structure are determined in the following way. I enlarged the original Wigner-Seitz volumes of Pd atoms by a factor of 1.5 in each direction and for each hydrogen atom in the crystal, I generated a list of Pd sites which contain this atom in their enlarged unit cell. This definition allows for more than one Pd site to be associated with a given hydrogen atom. Next, I combined the lists of Pd sites associated with each H atom and plotted the distribution of the corresponding Pd Wigner-Seitz volumes. The results are given by the dashed line in Fig. 4.14. A comparison with the solid line for the Pd atoms shows no strong preference of hydrogen atoms for specific sites in the metal structure. The dotted line in Fig. 4.14 represents the probability that a Pd atom, characterized by its atomic volume, is likely to have one or more hydrogen atoms as its closest neighbors. In case that there would be no preferential sites for hydrogen atoms, this curve should be flat. These results indicate a strong preference of hydrogen atoms for sites near highly coordinated Pd atoms in the bulk. From the position of the peak in the dotted curve, which lies at a slightly larger volume than that of bulk Pd atoms, one can infer that hydrogen atoms are more likely to occupy subsurface sites or sites close to the crack tip than sites in the bulk of Pd.

4.3.4 Discussion

The above molecular dynamics calculations, based on the Nosé and Rahman-Parrinello formalism, suggest a useful and consistent picture of the atomic-scale processes which occur in PdH_x at different temperatures and hydrogen concentrations x, specifically in response to large uniaxial tensile stress. Even though the interaction potentials are based on static *ab initio* calculations at T = 0, the finite temperature results of these simulations are in good agreement with experimental data. This increases my confidence that the MBA Hamiltonian describes the interactions in the Pd-H system correctly to a large degree. Since this Hamiltonian has a solid theoretical background, it can provide microscopic insight into the nature of interatomic interaction under different conditions.

These simulations show that the introduction of hydrogen into bulk Pd at room temperature has a similar effect on the structural properties and elastic behavior as a temperature increase in the hydrogen-free metal. Increased hydrogen loading and increased temperature both increase the free volume linearly, decrease the bulk modulus, and reduce the critical tensile stress for fracture. It is plausible to some degree that the presence of hydrogen simulates a temperature increase, since the light H atoms have a much faster dynamics that Pd atoms and can easily excite Pd vibrations in elastic collisions. This effect is enhanced by the fact that hydrogen atoms reduce the bonding strength between Pd atoms and soften the vibrational modes of the Pd lattice[Zho 91a]. I found that hydrogen-induced changes of structural properties and elastic response become more pronounced with increasing hydrogen concentration, as shown in Figs. 4.8(b), 4.12(b) and 4.11(c). At the point of fracture, I found that the presence of hydrogen enhances the plasticity of the system significantly, causing hydrogen-assisted "melting" even at T = 300 K, which is associated with a substantial diffusion of Pd atoms. I found it useful to compare the present results for hydrogen loaded Pd under critical tensile stress to hydrogen-free Pd at the melting point in an animated video movie, and found Pd diffusion at the crack surface of the hydrogen loaded system to be comparable with the atomic diffusion in melting Pd metal.

As mentioned above, a fundamental difference between the effect of hydrogen loading and temperature increase lies in the fact that hydrogen modifies the interaction between Pd atoms. This difference is most obvious in the response to uniaxial tensile stress, shown in Figs. 4.11(b) and 4.11(c). In the hydrogen-free system, one can observe both the bulk and the Young's modulus to decrease with increasing temperature, while the Poisson's ratio μ is nearly constant, consistent with Eq. (4.11). On the other hand, increasing the hydrogen concentration in Pd at a constant temperature T = 300 K still causes the bulk modulus to decrease, but has little effect on the Young's modulus. In this case, the Poisson's ratio decreases with increasing hydrogen loading, indicating an increasing resistance against shape deformations. This effect could also assist in the initial formation of cracks. Based on the results shown in Fig. 4.11(c), I find that the critical value of tensile stress p_c drops at an increasing rate with increasing hydrogen concentration, indicating a continuous ductility increase in the system with increasing number of H atoms in the vicinity of the Pd metal bonds.

The microscopic origin of the ductility increase of Pd in presence of hydrogen is the rehybridization of Pd orbitals in the hydrogen loaded metal. As was found in a previous *ab initio* calculation of atomic binding in bulk Pd and PdH[Sun 89], the hydrogen-induced binding changes of Pd stem mainly from a filling of antibonding states in the Pd4d band, accompanied by a depletion of the partly filled Pd5s band and a small charge transfer towards hydrogen. These effects are considered, albeit in a very approximate way, in the many-body alloy Hamiltonian. Unlike in models based on pairwise interactions, this Hamiltonian does address the different electronic hopping processes to neighboring atoms from the point of view of electronic band formation in the attractive part of the total energy. Hence the binding energy of a Pd atom is not simply proportional to the number of nearest neighbors, but depends in a more complex way on the hybridization with the neighboring atoms and the band filling, which appears to be essential for the understanding of bonding changes in this system.

The calculated values for the critical tensile stress are about one order of magnitude too high when compared to experimental data for single- and polycrystalline samples. There are two reasons for this overestimate of p_c . First, it is impossible to study the dynamics of the fracture process in a molecular dynamics calculation for realistic time scales and large systems. The time spans presently accessible by such simulations fall at least ten orders of magnitude short of a realistic time for the formation of a crack, which is typically seconds. Second, in a realistic system, the fracture process is assisted and proceeds by dislocation motion in the crystal. The presently used unit cell containing 500 Pd atoms, which is large for MD standards, is clearly too small to show the spontaneous formation and motion of dislocations.

I also tried to address the effect of dislocations in a somewhat artificial way, namely removing a single atom from the unit cell, thus creating a defect site and a possible seed for a dislocation or a crack. The corresponding MD simulation did not show a reduction of p_c when compared to the initially "perfect" systems. This is not surprising since the typical atomic fluctuations near the point of fracture are large and comparable to the size of a single atomic vacancy.

In hydrogen loaded Pd, the local decohesion and structural relaxations are medi-

ated by hydrogen which has a very large diffusion constant. I studied the interplay between the time scales for structural changes and the diffusion of hydrogen by considering isotope substitution. I found that replacing H by D atoms in PdH_x has no effect on p_c , probably due to the large difference between the time scales for hydrogen motion and structural relaxation, and possibly also the incoherent motion of hydrogen atoms in the metal which averages out local changes of elastic properties.

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The above microscopic results for the elastic response of hydrogen-loaded Pd to uniaxial tensile stress strongly support one of the previously postulated mechanisms for "hydrogen embrittlement", namely the Hydrogen Enhanced Local Plasticity (HELP) mechanism[Bir]. This mechanism, which has been used to interpret experimental data, postulates that hydrogen concentrates preferentially near the tip of a starting crack. Hydrogen subsequently locally softens the metal matrix in the vicinity of the crack tip, which leads to an increase in the velocity of dislocation motion. This process can lead to a softening over microns over very short time scales. The system will become microscopically ductile, but will appear as brittle on macroscopic length scales.

While the present calculations have been performed for a specific system, namely hydrogen loaded Pd, I expect that the effect of hydrogen on the stability of other fcc metals will be qualitatively the same. The situation in bcc metals (such as Fe) may be somewhat different, since hydrogen is observed to stiffen rather than soften these structures[Bir]. These questions are presently being addressed in corresponding MD simulations[Zho 93b].

4.4 Summary and conclusions

In conclusion, I applied the Many-Body Alloy (MBA) Hamiltonian to Pd-H systems. All parameters have been obtained from *ab initio* Density Functional calculations, with no adjustable parameters for surface properties. I tested this Hamiltonian first and calculated the equilibrium structure and binding energy of bulk Pd and PdH, as well as H-free and H covered Pd(001) and Pd(110) surfaces. I found the calculated results to be in good agreement with experimental data and results of *ab initio* calculations where available.

Next, I studied the effect of hydrogen on the vibration spectra of bulk Pd and the Pd(001) and Pd(110) surfaces, by constructing the dynamical matrix based on the MBA Hamiltonian. I found that in the bulk systems, hydrogen softens the Pd vibration modes, as seen in the comparison of bulk Pd and PdH phonon spectra. The results for the clean and H covered (001) and (110) surfaces of Pd are not as clear-cut. I found the most pronounced effect of hydrogen coverage to be the softening of the surface Rayleigh mode with out-of-plane vibration amplitudes on the topmost layer. Other surface modes, such as in-plane vibrations of the topmost layer, are affected to a lesser degree or occur at higher vibration frequencies in the presence of hydrogen.

Finally, I have used the Nosé and Rahman-Parrinello molecular dynamics formalism to study the equilibrium structure and elastic properties of bulk Pd as a function of temperature and hydrogen concentration. I have used this formalism first to predict the elastic constants, thermal expansion and melting temperature of hydrogen-free and hydrogen loaded bulk Pd. I found my results to be in good agreement with available experimental data.

Introducing uniaxial tensile stress as an independent variable into this formalism

has enabled me also to study the elastic deformations as a function of the applied load at different temperatures and hydrogen concentrations. At small applied loads, I found that the bulk and the Young's moduli decrease with increasing temperature in hydrogen-free bulk Pd. Increased hydrogen concentration at constant temperature has a very similar effect as the temperature increase in the hydrogen-free metal: The system gets softer, which is reflected in a decreased bulk modulus. While hydrogen softens the Pd-Pd bonds, its presence does not affect the Young's modulus. Consequently, the Poisson's ratio decreases with increasing hydrogen loading, indicating an increasing resistance towards shape deformations. This behavior might assist in the formation of cracks.

At large values of the uniaxial tensile stress, one can observe the onset of crack formation. I find that the critical tensile stress for fracture decreases both with increasing temperature and increasing hydrogen concentration. Near the point of fracture, however, the elastic response of hydrogen-free and hydrogen-loaded Pd is vastly different. Following the fracture, Pd atoms can be found in well-defined "crystalline" sites in the fragments or at the crack surface for the Pd system which is free of hydrogen. In hydrogen-loaded Pd, the metal structure can be called amorphous at the point of fracture. One can find a broad distribution of Pd sites in this system which can easily be deformed plastically. I conclude that the hydrogen-induced reduction of the mechanical stability of Pd (and likely also other metals) originates from an increased *ductility* and *plasticity* in parts of the sample with a large hydrogen concentration, such as regions near grain boundaries and dislocations. These conclusions agree with one of the previously postulated mechanisms for "hydrogen embrittlement", namely the Hydrogen Enhanced Local Plasticity (HELP) mechanism[Bir]. More detailed studies will be necessary to confirm this behavior also in bcc metals (such as iron). A comparison with corresponding experimental data, stemming from atomic resolution studies of single crystals would be highly desirable.

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Bibliography

- [Abr 89] F.F. Abraham and I.P. Batra, Surf. Sci. 209, L125 (1989).
- [Alb 87] T.R. Albrecht and C.F. Quate, J. Appl. Phys. 62, 2599 (1987).
- [Ale 78] G. Alefeld and J. Völkl, Eds., Hydrogen in Metals I and II, Vols. 28 and 29 of *Topics in Applied Physics* (Springer-Verlag, Berlin, 1978).
- [All 90] M.P. Allen and D.J. Tildesley, Computer Simulation of Liquids (Oxford Press, New York, 1990).
- [And] M. Anders and C. Heiden (submitted for publication).
- [And 80] H.C. Andersen, J. Chem. Phys. 72, 2384 (1980).
- [Arn 66] R.D. Arnell, J.W. Midgley, and D.G. Teer, Proc. Inst. Mech. Eng. 179, 115 (1966).
- [Bac 82] G.B. Bachelet, D.R. Hamann, and M. Shlüter, Phys. Rev. B 26, 4199 (1982).
- [Bar 85] C.J.Barnes, M.Q. Ding, M. Lindroos, R.D. Diehl, and D.A. King, Surf. Sci. 162, 59 (1985).
- [Bas 89] R. Bastasz, T.E. Felter, and W.P. Ellis, Phys. Rev. Lett. 63, 558 (1989).
- [Bat 88] I.P. Batra and S. Ciraci, J. Vac. Sci. Technol. A 6, 313 (1988).

- [Bea 72] C.D. Beachem, Metall. Trans. 3, 437 (1972).
- [Beh 80] R.J. Behm, K. Christmann and G. Ertl, Surf. Sci. 99, 320 (1980).
- [Bes 87] F. Besenbacher, I. Stensgaard and K. Mortensen, Surf. Sci. 191, 288 (1987).
- [Bin 82] G. Binnig, H. Rohrer, Ch. Gerber and E. Weibel, Phys. Rev. Lett. 49, 57 (1982).
- [Bin 86] G. Binnig, C.F. Quate and Ch. Gerber, Phys. Rev. Lett. 56, 930 (1986), and Appl. Phys. Lett. 40, 178 (1982).
- [Bin 87] G. Binnig, C. Gerber, E. Stoll, T. R. Albrecht, C. F. Quate, Europhys. lett.3, 1281 (1987).
- [Bir 73] H. K. Birnbaum, M. Grossbeck, and S. Gahr, in: Hydrogen in Metals, M. Bernstein and A. Thompson, eds., A.S.M. Metals Park, Ohio, 1973, p. 303.
- [Bir 79] H.K. Birnbaum, in: Environmentally Sensitive Fracture of Engineering Materials, Z. A. Foroulis, eds., T.M.S. New York, 1979, p. 326.
- [Bir 84] H.K. Birnbaum, J. Less Common Metals 103, 31 (1984).
- [Bir] Howard K. Birnbaum, private communication.
- [Boh 90] K.P. Bohnen, Th. Rodach, and K.M. Ho, in The Structure of Surfaces III, edited by M.A. Van Hove, K. Takanayagi, and X. Xie (Springer-Verlag, Heidelberg, 1990), and references cited therein.
- [Bor 84] V. Bortolani, G. Santoro, U. Harten, and J.P. Tonnies, Surf. Sci. 148, 82 (1984).

- [Bor 85] V. Bortolani, A. Franchini, F. Nizzoli, and G. Santoro, Surf. Sci. 152/153, 811 (1985).
- [Bre 89] D.W. Brenner, Phys. Rev. Lett. 63, 1022 (1989).
- [Cal 72] Langlinais and J. Callaway, Phys. Rev. B 5 124 (1972).
- [Cal 84] J. Callaway and N.H. March, Solid State Phys. 38, 135 (1984).
- [Car 90] A.E. Carlsson, in Solid State Physics, Vol. 43, Academic Press (New York, 1990), p. 1.
- [Cat 83] M.G. Cattania, K. Christmann, V. Penka and G. Ertl, Gazz. Chim. Ital. 113, 433 (1983).
- [Cep 80] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. 45 566 (1980).
- [Cha 73] D.J. Chadi and M.L. Cohen, Phys. Rev. B 8, 5747 (1973).
- [Cha 86a] C.T. Chan, D. Vanderbilt, and S. G. Louie, Phys. Rev. B 33, 2455 (1986).
- [Cha 86b] C.T. Chan, D. Vanderbilt, S.G. Louie and J.R. Chelikowsky, Phys. Rev. B33, 7941 (1986).
- [Che 84] J. R. Chelikowsky and S. G. Louie, Phys. Rev. B 29, 3470 (1984).
- [Cir 90] S. Ciraci, A. Baratoff and I.P. Batra, Phys. Rev. B 41, 2763 (1990).
- [Dav 83] H.L. Davis, J.R. Noonan, Surf. Sci. 126, 245 (1983).
- [Daw 84] M.S. Daw and M.I. Baskes, Phys. Rev. B 29, 6443 (1984).
- [Daw 89] M.S. Daw, Phys. Rev. **B39**, 7441 (1989).
- [Doa 83] R.B. Doak, U. Harten and J.P. Toennis, Phys. Rev. Lett. 51, 578 (1983).

- [Dre 90] R.M. Dreizler and E.K.U. Gross, Density Functional Theory (Springer-Verlag, 1990).
- [Fah 86] S. Fahy, S.G. Louie and M.L. Cohen, Phys. Rev. B 34, 1191 (1986).
- [Foi 85] S.M. Foiles, Phys. Rev. **B32**, 3409 (1985).
- [Foi 86] S.M. Foiles, M.I. Baskes, and M.S. Daw, Phys. Rev. B 33, 7983 (1986).
- [Foi 87] S.M. Foiles, Surf. Sci. 191, L779 (1987).
- [Foi 89] S.M. Foiles and J.B. Adams, Phys. Rev. **B40**, 5909 (1989).
- [Gea] C.W. Gear, private communication.
- [Gou 89] S. Gould, K. Burke, P.K. Hansma, Phys. Rev. B 40 5363 (1989).
- [Gru 89] M. Grunze and H.J. Kreuzer, Eds., Adhesion and Friction, Springer Series in Surface Sciences, Vol. 17 (Springer-Verlag, Berlin 1989).
- [Hal 88] B.M. Hall, D.L. Mills, M.H. Mohamed, and L.L. Kesmodel, Phys. Rev. B38, 5856 (1988).
- [Ham 79] D.R. Hamann, M. Schlüter and C. Chiang, Phys. Rev. Lett. 43, 1494 (1979).
- [Har 82] B. Harmon, W. Weber, and D. R. Hamann. Phys. Rev. B 25, 1109 (1982).
- [Har 85] U. Harten, J.P. Toennis, Ch. Wöll and G. Zhang, Phys. Rev. Lett. 55, 2308 (1985).
- [He 88] J.-W. He, D.A. Harrington, K. Griffiths, and P.R. Norton, Surf. Sci. 198, 413 (1988).
- [Hed 71] L. Hedin and B.J. Lundqvist, J. Phys. C4, 2064 (1971).

[Ho 86] K.-M. Ho and K.P. Bohnen, Phys. Rev. Lett. 56, 934 (1986).

- [Hoh 64] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).
- [Hor 92] C. Horie and H. Miyazaki (submitted for publication).
- [Iba 87] H. Ibach, J. Vaccum Sci. Technol. A5 419 (1987).
- [Joh 72] R.A. Johnson, Phys. Rev. B6, 2094 (1972).
- [Jon 89] R.O. Jones and O. Gunnarsson, Rev. Mod. Phys. 61, 689 (1989).
- [Kit 86] Ch. Kittel, Introduction to Solid State Physics, 6th edition (John Wiley, New York, 1986).
- [Koh 65] W. Kohn and L.J. Sham, Phys. Rev. 140 A1133 (1965).
- [Kus 90] D. Kusnezov, A. Bulgac and W. Bauer, Ann. Phys. 204, 155 (1990).
- [Laf 71] Lafon, R.C. Chaney, and C.C. Lin, in Computational Methods in Band Theory, edt. P.M. Marcus, D.F. Janak, and A.R. Williams (Plenum, New York, 1971), p. 284.
- [Lah 87] A.M. Lahee, J.P. Toennies and Ch. Wöll, Surf. Sci. 191, 529 (1987).
- [Lan 60] L.D. Landau and E.M. Lifshitz, Course of Theoretical Physics, Volume 1: Mechanics (Pergamon, Oxford 1960), p. 122.
- [Lan 86] L.D. Landau and E.M. Lifshitz, Course of Theoretical Physics, Volume 7: Theory of Elasticity, (Pergamon, Oxford 1986), p. 53.
- [Lan 79] Landolt-Börnstein (new series), edited by K.-H. Hellwege (Springer-Verlag, New York, 1979), Vol. III/11, pp. 10, 114.

[Lan 89a] U. Landman, W.D. Luedtke, A. Nitzan, Surf. Sci. 210, L177 (1989).

- [Lan 89b] Uzi Landman, W.D. Luedtke, and M.W. Ribarsky, J. Vac. Sci. Technol. A 7, 2829 (1989).
- [Lan 90] U. Landman, W.D. Luedtke, N.A. Burnham, and R.J. Colton, Science 248, 454 (1990).
- [Lee 89] S. Lee, H. Miyazaki, S.D. Mahanti and S.A. Solin, Phys. Rev. Lett. 62, 3066 (1989).
- [Leh 83] S. Lehwald, J.M. Szeftel, H. Ibach, T.S. Rahman and D.L. Mills, Phys. Rev. Lett. 50, 518 (1983).
- [Leh 87] S. Lehwald, B. Voigtländer, and H. Ibach, Phys. Rev. B 36, 2446 (1987).
- [Lev 79] M. Levy, Proc. Natl. Acad. Sci. (USA) 76, 6062 (1979).
- [Lun 83] S. Lundqvist and N.H. March, Theory of the Inhomogeneous Electron Gas (Plenum, 1983).
- [Luo 88] N. Luo, W. Xu, and S.C. Shen, Solid State Commun. 67, 837 (1988).
- [Lyn 86] S.P. Lynch, J. Mat. Sci. 21, 692 (1986).
- [Mah 90] G.D. Mahan and K.R. Subbaswamy, Local Density Theory of Polarizability (Plenum, 1990).
- [Mam 86] H.J. Mamin, E. Ganz, D.W. Abraham, R.E. Thomson, and J. Clarke, Phys. Rev. B 34, 9015 (1986).
- [Mar 63] A.A. Maradudin, E.W. Montroll, and G.H. Weiss, Theory of Lattice Dynamics in the Harmonic Approximation (Academic Press, New York, 1963).

- [Mat 87] C. Mathew Mate, Gary M. McClelland, Ragnar Erlandsson and Shirley Chiang, Phys. Rev. Lett. 59, 1942 (1987).
- [McC 89] G.M. McClelland in Adhension and friction, edited by M. Grunze and H. j. Kreuzer, Springer Series in Surface Science, Vol. 17 (Springer-Verlag, Berlin) 1989.
- [Mey 88] E. Meyer, H. Heinzelmann, P. Grütter, Th. Jung, Th. Weiskopf, H.-R. Hidber, R. Lapka, H. Rudin, and H.-J. Güntherodt, J. Microsc. 152, 269 (1988).
- [Mey 90] G. Meyer and N. M. Amer, Appl. Phys. Lett. 56, 2100 (1990).
- [Mil 71] A.P. Miller and B.N. Brockhouse, Can. J. Phys. 49,704 (1971).
- [Nel 77] J.S. Nelson, E.C. Sowa, M.S. Daw, Phys. Rev. Lett. 61, 1977 (1988).
- [Nel 89] J.S. Nelson, M.S. Daw, and E.C. Sowa, Phys. Rev. B40, 1465 (1989).
- [Nos 84] S. Nosé, J. Chem. Phys. 81, 511(1984); Mod. Phys. 52, 255 (1984).
- [Nyb 83] C. Nyberg and C.G. Tengstål, Phys. Rev. Lett. 50, 1680 (1983).
- [Ori 77] R.A. Oriani and P.H. Josephic, Acta Metall. 25, 979 (1977).
- [Ove 92] R.M. Overney, E. Meyer, J. Frommer, D. Brodbeck, R. Luthi, L. Howald, H.-J. Guntherodt, M. Fujihira, H. Takano, and Y. Gotoh, Nature 359, 133 (1992)
- [Par 80] M. Parrinello and A. Rahman, Phys. Rev. Lett. 45, 1196 (1980).
- [Par 81] M. Parrinello and A. Rahman, J. Appl. Phys. 52, 7182 (1981).
- [Par 82] M. Parrinello and A. Rahman, J. Chem. Phys. 76, 2662 (1982).

- [Pea 58] W.B. Pearson, A Handbook of Lattice Spacings and Structures of Metals and Alloys, Pergamon, New York, 1958.
- [Pei 78] H. Peisl in Hydrogen in Metals I, Vol. 28 of Topics in Applied Physics, edited by G. Alefeld and J. Völkl (Springer-Verlag, Berlin, 1978), p. 69.
- [Pet 87] J.B. Pethica, W.C. Oliver, Physica Scripta **T** 19, 61 (1987).
- [Pra 89] L.R. Pratt and J. Eckert, Phys. Rev. B 39, 13170 (1989).
- [Ray 84] J.R. Ray and A. Rahman, J. Chem. Phys. 80, 4423 (1984).
- [Ray 88] J.R. Ray, Comp. Phys. Rep. 8, 109 (1988).
- [Rie 83] K.H. Rieder, M. Baumberger and W. Stocker, Phys. Rev. Lett. 51, 1799 (1983).
- [Rie 84] K.H. Rieder and W. Stocker, Surf. Sci. 148, 139 (1984).
- [Roc 84] S. M. Rocca, S. Lehwald, H. Ibach and T.R. Rahman, Surf. Sci. 138, L123 (1984).
- [Row 74] J.M. Rowe, J.J. Rush, H.G. Smith, M. Mostoller, and H.E. Flotow, Phys. Rev. Lett. 33, 1297 (1974).
- [Row 86] J.M. Rowe, J.J. Rush, J.E. Schirber and J.M. Mintz, Phys. Rev. Lett. 57, 2955 (1986).
- [Ski 71] J. Skinner, N. Gane, and D. Tabor, Nat. Phys. Sci. 232, 195 (1971).
- [Sko 87] M. Skottke, R.J. Behm, G. Ertl, V. Penka, and W. Moritz, J. Chem. Phys. 87, 6191 (1987).

- [Sla 93] M. Slameron, R. Overeny, E. Meyer, M.O. Robbins, P.A. Thompson, G.C. Crest, J.A. Harrison, C.T. White, R.J. Colton, D.W. Brenner, J. Belak, D.B. Boercker, I.F. Stowers, U. Landman and W.D. Luedtke, MRS Bulletin, May 1993, p. 15.
- [Smo 41] R. Smoluchowski, Phys. Rev. 60, 661 (1941).
- [Spa 84] D. Spanjaard and M.C. Desjonquères, Phys. Rev. B30, 4822 (1984).
- [Spr 62] J. Spreadborough, Wear 5, 18 (1962).
- [Ste 60] E.A. Steigerwald, F.W. Schaller, and A.R. Troiano, Trans. Metall. Soc.. A.I.M.E. 218, 832 (1960).
- [Sto 89] P. Stoltze, J.K. Nørskov and Uzi Landman, Surf. Sci. Lett. 220, L693 (1989).
- [Sun 89] Z. Sun and D. Tománek, Phys. Rev. Lett. 63, 59 (1989).
- [Tab 84] T. Tabata and H.K. Birnbaum, Scripta Metall. 18, 231 (1984).
- [Tar 86] B. Tardy, J.C. Bertolini, C.R. Acad. Sci., Ser. 2, 302 813 (1986).
- [Ter 83] J. Tersoff and D.R. Hamann, Phys. Rev. Lett. 50, 1998 (1983), and Phys. Rev. B31, 805 (1985).
- [Toe 87] J.P. Toennies, J. Vacuum Sci. Technol. A5, 440 (1987); ibid. A2, 1055 (1984).
- [Tom 83] D. Tománek, S. Mukherjee and K.H. Bennemann, Phys. Rev. B28, 665 (1983); *ibid.* B29, 1076 (1984) (E).

[Tom 85a] D. Tománek, A.A. Aligia and C.A. Balseiro, Phys. Rev. B32, 5051 (1985).

[Tom 85b] D. Tománek and K.H. Bennemann, Surf. Sci. 163, 503 (1985).

[Tom 86a] D. Tománek, Phys. Lett. 113 A, 445 (1986).

[Tom 86b] D. Tománek, S.G. Louie, and C.T. Chan, Phys. Rev. Lett. 57, 2594 (1986).

- [Tom 86c] D. Tománek and S.G. Louie, Phys. Rev. Lett. 57, 2594 (1986).
- [Tom 89] D. Tománek, G. Overney, H. Miyazaki, S.D. Mahanti and H.J. Güntherodt,
 Phys. Rev. Lett. 63, 876 (1989) and ibid. 63, 1896(E) (1989).
- [Tom 91a] D. Tománek, Z. Sun, and S.G. Louie, Phys. Rev. B43, 4699 (1991).
- [Tom 91b] D. Tománek and W. Zhong, Physical Review B (in press).
- [Tom 91c] D. Tománek, W. Zhong, and H. Thomas, Europhys. Lett. 15, 887 (1991).
- [Toml 29] G.A. Tomlinson, Phil. Mag. S. 7, Vol. 7, 905 (1929).
- [Wes 69] D.G. Westlake, Trans. Am. Soc. Metals 62, 1000 (1969).
- [Wig 38] E.P. Wigner, Trans. Faraday Soc. 34 678 (1938).
- [Wut 86] M. Wuttig, R. Franchy and H. Ibach, Solid State Commun. 57, 445 (1986).
- [Yan 91] Liquiu Yang, Talat S. Rahman and Murray S. Daw, Phys. Rev. B44, 13725 (1991).
- [Yos 88] J. Yoshinobu, M. Onchi and M. Nishijima, Phys. Rev. B 38, 1520 (1988).
- [Zab 89] H. Zabel in Graphite Intercalation Compounds, Topics in Current Physics, edited by H. Zabel and S.A. Solin (Springer-Verlag, New York, 1989).
- [Zho 90] W. Zhong and D. Tománek, Phys. Rev. Lett. 64, 3054 (1990).
- [Zho 91a] W. Zhong, Y.S. Li and D. Tománek, Phys. Rev. B 44, 13053 (1991).
- [Zho 91b] W. Zhong, G. Overney, and D. Tománek, Europhys. Lett. 15, 49 (1991).

[Zho 93a] W. Zhong, G. Overney, and D. Tománek, Phys. Rev. B 47 (1993).

[Zho 93b] W. Zhong and D. Tománek, in preparation.

