First-Principles Calculations of Diffusion Coefficients: Hydrogen in Silicon

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(Received 20 October 1989)

Existing calculations of diffusion coefficients in solids have so far relied on empirical potentials and/or dynamical simulations, both of which entail important limitations. We present a practical approach that is based on rate theory and allows the calculation of temperature-dependent diffusion coefficients from static first-principles calculations. Results for hydrogen in silicon are in excellent agreement with recent first-principles dynamical calculations at high temperatures and with experiment. They further elucidate the nature of diffusion pathways and anharmonic effects.

PACS numbers: 66.30.Jt, 61.70.Bv

The reliable calculation of diffusion coefficients in solids has been a long-standing quest driven by both technological needs and the desire to establish the dominant microscopic mechanisms. In the last fifteen years, starting with the pioneering work of Bennett,[1] major strides have been achieved in calculating diffusion constants of *model solids*, defined by a set of empirical interatomic potentials.[2-4] The results of these calculations are usually applicable to metals. Quantitative calculations for real materials are, however, hampered by difficulties in constructing interatomic potentials. These methods have not been used for covalent solids, where significantly more complex potentials are necessary.

In the last few years, the advent of reliable first-principles total-energy calculations for defects in semiconductors has led to calculations of diffusion activation energies.[5-8] In such work, the diffusion coefficient D is expressed as

$$D = D_0 \exp(-Q/k_B T), \tag{1}$$

where Q is the activation energy along a particular path, corresponding to a particular saddle point. The relative contributions of various paths or mechanisms could not be assessed, however, because the corresponding preexponentials D_0, containing entropy terms, could not be calculated.

More recently, first-principles *dynamical* simulations of defects in semiconductors at finite temperatures have been used to obtain diffusion coefficients.[9(a)] These truly impressive calculations literally follow the thermal motion of a H atom in a Si lattice with a full quantum-mechanical description of the changing electronic system and a classical description of the atomic motion. They are, however, limited to systems with small activation energies and, even then, to high temperatures. Otherwise, the time evolution of the system is too slow for practical calculations.

In this paper we develop and implement a practical framework for the first-principles calculation of diffusion constants. The approach is based on existing rate-theory formalisms[1-4,10-12] and invokes a set of well-defined approximations. Since the technique does not involve time-dependent simulations, it is applicable to a wide range of activation energies and temperatures. We report results for H in Si and find them to be in excellent agreement with the recent fully dynamical calculations of Buda *et al.*[9(a)] in the temperature range accessible by the latter. Our calculations, performed for a wide temperature range, show that the effective activation energy changes at high temperatures because of anharmonic terms. The nature of diffusion pathways is elucidated.

The central quantity of the theory is the free energy $F(\mathbf{x},T)$ determined with the impurity frozen at $\mathbf{x}$ and at temperature T. Once this quantity is known, one determines the values $\mathbf{X}_i$ of $\mathbf{x}$ for which F is a minimum. A Wigner-Seitz-like construction then divides all space into cells centered at the stable sites $\mathbf{X}_i$. The diffusion constant is given rigorously by[11]

$$D = \tfrac{1}{6} \sum_{i,j} |\mathbf{X}_j - \mathbf{X}_i|^2 n_i \Gamma_{ij}, \tag{2}$$

where n_i is the probability for the impurity to be at a certain site $\mathbf{X}_i$ and Γ_{ij} is the jump rate from site i to site j. The jump rate can be decomposed into the directional flux Γ^0_{ij} through a *saddle surface* separating sites $\mathbf{X}_i$ and $\mathbf{X}_j$ and an efficiency factor which accounts for immediate return jumps and correlated multiple jumps.[1,11] Transition-state theory[12] gives an exact expression for Γ^0_{ij}:

$$\Gamma^0_{ij} = \left(\frac{k_B T}{2\pi\mu}\right)^{1/2} \frac{1}{n_i} P^S_{ij}. \tag{3}$$

Here μ is the reduced mass of the diffusing particle, which depends on the choice of the relative coordinate $\mathbf{x}$,[13] and P^S_{ij} is the probability for the impurity to be at the saddle surface. The latter is given by

$$P^S_{ij} = n_i \frac{\int_{S_{ij}} d^2x\, P(\mathbf{x})}{\int_{V_i} d^3x\, P(\mathbf{x})}, \tag{4}$$

where $P(\mathbf{x})$ is the probability that the impurity is at $\mathbf{x}$.

Here the two-dimensional integral is performed over the saddle surface S_{ij} separating cells i and j, and the three-dimensional integral is performed over the cell V_i at $\mathbf{X}_i$. The probability distribution is given by

$$P(\mathbf{x}) = Z^{-1}\exp[-F(\mathbf{x},T)/k_BT], \tag{5}$$

where Z is a normalization constant and $F(\mathbf{x},T)$ is the free energy of the system with the impurity constrained to a position $\mathbf{x}$. This free energy is in general given by

$$F(\mathbf{x},T) = -k_BT\ln\lambda_T^{-(3N-6)}\int dq^{3N-3}\delta[\mathbf{x}-\mathbf{x}(\mathbf{q})]\exp\left[-\frac{1}{k_BT}V(\mathbf{q})\right], \tag{6}$$

where $\mathbf{x}(\mathbf{q})$ represents the functional dependence of the impurity's position relative to the host-atom positions, $V(\mathbf{q})$ is the potential energy depending on the positions $\mathbf{q}=(\mathbf{q}_1,\ldots,\mathbf{q}_N)$ of all N atoms in the crystal, and λ_T is the thermal de Broglie wavelength. The total translational degree of freedom has been excluded in the integration.

The above formalism is exact. For a practical implementation we introduce only two approximations. First, we take $\Gamma=\Gamma^0$, setting the so-called efficiency factor equal to 1. Efficiency factors have been studied for model solids and have in many cases been found to change the results for the diffusion constant by only a small fraction.[1,2,11,14] The second approximation of this approach is the way we calculate $F(\mathbf{x},T)$. We note that

$$F(\mathbf{x},T) = F(\mathbf{x},0) - \int_0^T dT S(\mathbf{x},T), \tag{7}$$

where $S(\mathbf{x},T)$ is the entropy of the system *with the impurity fixed at* $\mathbf{x}$. We propose to approximate $F(\mathbf{x},T)$ by its value at $T=0$. The free energy $F(\mathbf{x},0)$ is the total energy obtained with the impurity at $\mathbf{x}$ and all other atoms relaxed. This approximation corresponds to the assumption that the vibrational frequencies of the *host* atoms depend only weakly on the position of the impurity, when the latter is fixed. The second term in Eq. (7) can actually be calculated in a rather straightforward but time-consuming manner in the local harmonic approximation.[15] Such calculations (to be discussed below) show, however, that this contribution to $F(\mathbf{x},T)$ is small. In many cases of interest this term can therefore be neglected, making the method very practical.

The present approach reduces the many-body problem of treating the diffusing particle together with all the particles in the embedding crystal to the problem of diffusion of a single particle in a three-dimensional effective potential. This effective potential has the full space-group symmetry of the crystal, and can, therefore, be expanded in symmetrized plane waves.[7] Thus, calculations of the total energy at only a few selected sites can be used to determine an analytic form for the complete effective potential.

The total-energy surface, which we will use to extract the diffusion constants for H^+, has been obtained from state-of-the-art electronic structure calculations using the local-density approximation and *ab initio* norm-conserving pseudopotentials.[7] The proton is treated, like all other nuclei, as a classical particle. The impurity is placed in a supercell with 32 Si atoms and the atomic positions up to second-nearest neighbors are relaxed. The total energy is calculated for eight inequivalent positions of the impurity. These values have been used to determine the expansion coefficients for a suitable set of symmetrized plane waves. The resulting analytical expression provides the free-energy surface $F(\mathbf{x},0)$ from which we calculate diffusion coefficients. The relevant total-energy surfaces have been published in Ref. 7.

In order to test the approximation of neglecting the host-atom entropy [second term of Eq. (7)], we calculated the vibrational frequencies of the host atoms. Even though this can, in principle, be done with *ab initio* calculations, we have used here a generalized Keating potential[16] for the Si-Si interactions and a suitably chosen Morse potential for the H-Si interactions.[17] The resulting entropy, obtained within the local harmonic approximation, was found to differ by $\sim 1k_B$ between the most dissimilar sites [e.g., the bond-center (BC) and tetrahedral sites] and significantly less between rather similar sites. At 1000 K these differences translate into corrections of less than ~ 0.1 eV for $F(\mathbf{x},T)$. That is precisely the level of accuracy with which $F(\mathbf{x},0)$ can be calculated from first principles.[7] We expect this to be a conservative estimate for other impurities as well because of the relatively large relaxations of neighboring Si atoms when H is at the BC position. Thus a time-consuming calculation of this term from first principles is not warranted. We did test, however, the effect of 0.1-eV uncertainty in $F(\mathbf{x},0)$ on the final diffusion coefficients and results are given below.

For the calculation of the diffusion coefficient, we first determine the minima $\mathbf{X}_i$ in the total-energy surface. These form the so-called diffusion-site lattice. A Wigner-Seitz-like construction then yields the volumes V_i, related to the sites $\mathbf{X}_i$, and the saddle surfaces S_{ij} as the faces of the Wigner-Seitz polyhedra. For the positively charged state of H there exists only one set of equivalent minima $\mathbf{X}_i$. These lie in a disk-shaped region of almost degenerate sites centered at the BC position.[18] H atoms can hop from bond to bond via the so-called C site, which is located midway between two second-nearest Si neighbors. The Wigner-Seitz cell of the diffusion-site lattice formed by the BC sites has the shape of a rhombohedron (see Fig. 1). Every face con-

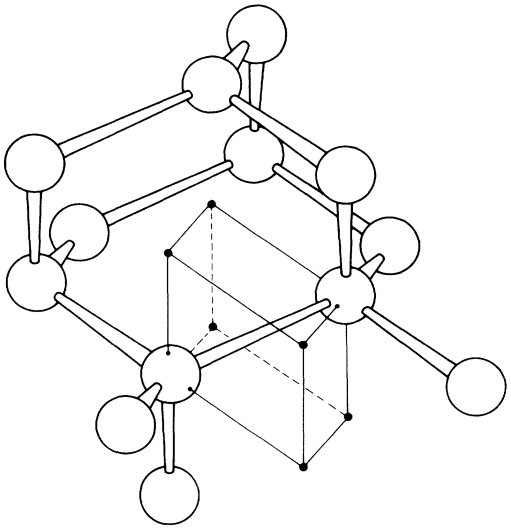

FIG. 1. Wigner-Seitz cell for the diffusion-site lattice of H^+ in Si. All six faces are equivalent. The corners of the cell are formed by six tetrahedral interstitial sites and two atomic sites. C sites are located in the center of the faces. The hexagonal interstitial sites lie on the edges of the cell, midway between two neighboring tetrahedral interstitial sites.

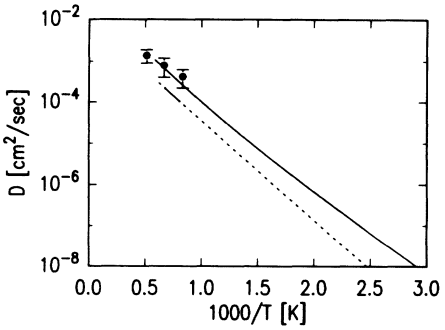

FIG. 2. Diffusion coefficients for H^+ in c-Si as a function of inverse temperature. Solid line: present calculation for H^+; solid circles, theoretical results of Buda *et al.* (Ref. 9); dotted line: $D = 9.41 \times 10^{-5} \exp[(-0.48\ \text{eV})/k_B T]$ as obtained by van Wieringen and Warmoltz (Ref. 19) (the solid part indicates the actual temperature range of the experiments).

tains one C site as the only saddle point. The occupation and the saddle-surface probability are obtained from integrals over the Wigner-Seitz polyhedron and one of its faces, respectively.

Our results for the diffusion constant are shown in Fig. 2. They agree with the theoretical results of Buda *et al.*[9(a)] within their error bars, and with the experimental results of van Wieringen and Warmoltz[19] within a factor of 3, which is within the expectations for the accuracy of the method and the accuracy of the measurements.

The number of distinct diffusion pathways can always be obtained from the number of inequivalent saddle points on the saddle surface. Their relative contribution can be obtained from partial integrals over the saddle surface. The total-energy surface of H^+ in Si has only equivalent minima and only identical saddle points. Thus, according to our definition, we have only one pathway. At higher temperatures, however, the impurity need not pass through total-energy minima or saddle points, giving rise to a variety of trajectories. For example, the impurity may diffuse by cutting through bonds or it may merely "rub" against the bond without actually crossing it. Anharmonic effects in the effective potential, which are evident from the curvature in the Arrhenius plot of Fig. 2, enhance the possibility of trajectories that avoid the bond region at high temperatures.

Our approach does not seek to determine the actual trajectories. Instead, it determines the diffusion coefficient as an integral over all possible trajectories. The approach assumes implicitly that the motion of H is randomized after each saddle-surface crossing. Thus, it neglects the effect of dynamical correlations, i.e., trajectories in which successive saddle-surface crossings occur in a correlated fashion. In contrast, Buda *et al.* carry out a time integral over the trajectories that actually occur. The two "paths" identified by them are, in our terminology, two dynamical trajectories. The excellent agreement between the results in Ref. 9(a) and ours seems to indicate that dynamical correlations, even though extremely important for the time evolution of the system, do not substantially affect the value for the diffusion constant. This result is consistent with earlier findings.[14]

The accuracy of our calculation depends of course on the accuracy of the energy surface used as input. The error bar is related to the accuracy of the individual total-energy calculations, as well as to the number of calculated points used for the analytic representation of the energy surface. Both contributions have been estimated to be on the order of 0.1 eV.[7] As we saw above, the correction from the host-atom entropy is even smaller. In order to see how sensitive our results are to these uncertainties, we have artificially introduced changes of the order of 0.1 eV in the regions where they count the most, i.e., the stable site and the saddle surface. The resulting changes in the activation barrier are comparable to the changes in the total-energy surface. The preexponential, obtained from the Arrhenius plot at high temperatures, however, is surprisingly insensitive and varies only by a factor of 5. This is understandable because at high temperatures the impurity explores a large region of phase space and is therefore insensitive to small local changes in the total-energy surface.

In conclusion, we have shown that diffusion constants can be calculated with considerable accuracy from static total-energy calculations. The technique is applicable to systems with low or high activation barriers and is valid over a wide temperature range. We have applied this approach to the calculation of the diffusion constant of

H in Si. Our results compare well with experiment and recent calculations of Buda *et al.*,[9(a)] which describe the time evolution of all particles without approximations.

This work was supported in part by the Office of Naval Research Contract No. N00014-84-0396. We are grateful to R. Car and J. Tersoff for helpful discussions.

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$$\frac{1}{\mu}=\sum_{i}^{3N}\left(\mathbf{n}\frac{\partial \mathbf{x}}{\partial q_i}\right)^2\frac{1}{m_i},$$

where $\mathbf{n}$ is the normal vector of the saddle surface.

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