Entropy Calculation beyond the Harmonic Approximation: Application to Diffusion by Concerted Exchange in Si

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We present a formulation for calculating entropy based on the application of classical transition-rate theory to quantum-mechanical energy surfaces. Using this approach, which avoids difficulties due to anharmonicity and large energy barriers, we calculate the entropy of concerted exchange (CE) in Si and find it to be $3.3k$ in the high-temperature regime. The relatively high entropy of CE is traced to multiple equivalent exchange paths and to a combination of a stiff mode at the equilibrium and a soft mode at the saddle-point configurations. Comparison to harmonic-approximation results shows substantial differences, both in the low- and in the high-temperature limits.

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The process of diffusion plays a crucial role in the stability of solids, which makes a detailed understanding of diffusion mechanisms highly desirable. Microscopic diffusion mechanisms can be identified, in principle, through comparison of calculated activation energies and entropies of model processes to experimental results. It is essential that both the energy and the entropy of a candidate model are in agreement with experiment. However, the calculation of entropies is a computationally demanding task and is commonly based on the harmonic approximation,[1,2] which at high temperatures (close to the melting point of the solid) may prove unreliable. A more recent approach, that is, direct dynamical simulation of diffusion,[3] is well suited to high temperatures but is limited to processes with very low migration energy barriers (of order a few tenths of an eV). Here, we propose an alternative approach which combines classical diffusion theory with static quantum-mechanical calculations: We compute the entropy of a diffusion process in the context of Vineyard's transition-rate theory,[4] using an accurate energy surface obtained from first-principles total-energy calculations. This formulation of the problem has two important advantages: First, a detailed knowledge of the total-energy surface eliminates any uncertainties due to anharmonicity. Second, the height of the energy barrier is not a limiting factor, which allows the examination of a wide range of physical processes.

Entropy calculations are particularly important to help clarify a long-standing discrepancy concerning self-diffusion in Si. Defect mechanisms (e.g., involving vacancies or interstitials), which are thought to mediate diffusion in Si, have activation energies compatible with experimental results (4-5 eV)[5-7] but preliminary calculations for the entropy give values of less than $1k$,[2] which is much lower than the experimental value of $7k$-$9k$ at high temperatures ($T > 1450$ K; see Ref. 8). Another candidate for diffusion is the concerted-exchange (CE) mechanism, a process which does not involve lattice defects.[9] In this work we calculate the entropy of CE, in an attempt to provide concrete theoretical results for the evaluation of different diffusion mechanisms. We find that the entropy of CE at high temperatures is $3.3k$. The relatively large entropy of CE is due to the existence of multiple equivalent exchange paths in phase space and to the curvature of the energy surface at the equilibrium configuration (a stiff mode) and at the saddle-point configuration (a soft mode). Our result is considerably larger than existing estimates for defect entropies obtained with the harmonic approximation.[2] The latter calculations, however, are not of the same level of accuracy as the present work, and a definitive evaluation of the different mechanisms must await results of comparable quality.

We briefly describe the atomic motion during the CE: Two atoms interchange positions in the Si lattice, in a very specific way without involving any defects. A natural coordinate system to describe the motion of the exchanging atoms consists of the two angular spherical coordinates, the azimuthal angle θ and the polar angle ϕ. The origin of the coordinate system is at the center of mass of the exchanging atoms. During the motion, the bonds of the exchanging atoms to their neighbors are broken in succession and bonds to different atoms are formed. These changes in bonding give variations in the energy of the order of several eV (see Fig. 1). When relaxation is omitted, the motion is completely specified by the angles θ and ϕ. The orientation of the bond between the exchanging atoms in the equilibrium configuration ($\theta=\phi=0$) defines the z axis of the coordinate system.

The energy surface was calculated for a dense grid of 100 points in the (θ,ϕ) configurational space, using

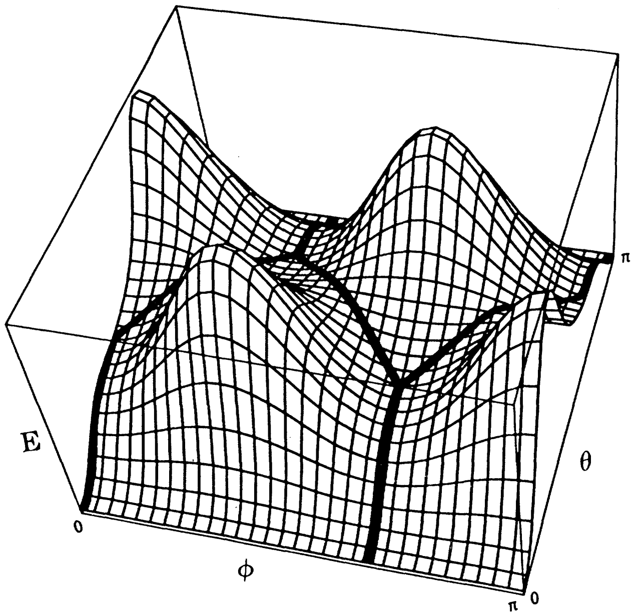

FIG. 1. The energy surface for concerted exchange in a portion of the phase space $0 \leq \theta, \phi \leq \pi$. The remainder of the energy surface is identical by symmetry. Three independent exchange paths are highlighted by thick solid lines. The vertical energy scale (E) ranges from 0 to 11 eV.

first-principles local-density-functional theory and norm-conserving pseudopotentials to represent the atomic cores. A large number of plane waves (with kinetic energy up to 9 Ry) and eight Brillouin-zone sampling points were used for the calculations in a supercell of 54 atoms. This amounted to an extensive computational effort, which was deemed necessary to obtain an accurate representation of the energy surface. A portion of the energy surface for $0 \leq \theta, \phi \leq \pi$ is shown in Fig. 1. The remaining portion is identical, due to symmetry. There are six independent and equivalent exchange paths in the entire phase space, three of which are contained in the portion shown in Fig. 1. The maxima of energy along these paths determine the saddle-point configurations which are given by $\theta = \pi/2$, $\phi = n\pi/6$, $n = 1, 3, \ldots, 11$. The saddle-point energy is equal to the activation energy E_a, which for the *unrelaxed* CE is 5.4 eV (relaxation of the saddle-point configuration lowers the activation energy by 0.7 eV).[9]

In order to perform analytical calculations for the entropy we fitted the first-principles energies by a spherical harmonic expansion. The terms to be included in this series expansion are dictated by the D_{3d} point-group symmetry of the physical process, which is reflected in the symmetry of the energy surface of CE. The fit represents the calculated energy values to better than 1 part in 10^3. We then used Vineyard's transition-rate theory to calculate the entropy. According to this formalism, the rate of diffusion is given by

$$\Gamma = \left(\frac{kT}{2\pi} \right)^{1/2} \frac{\int dU \exp(-E/kT)}{\int dW \exp(-E/kT)}, \quad (1)$$

where the integrations $\int dU$ and $\int dW$ refer to a *surface* around the saddle-point configuration and a *volume* around the equilibrium configuration, and the variables of integration are generalized coordinates (each containing a factor of $m^{1/2}$ in addition to the spatial coordinate).[1] The expression for Γ can be rewritten as

$$\Gamma = \nu \exp(-E_a/kT) \exp(S/k), \quad (2)$$

where ν is the so-called "attempt frequency," E_a is the activation energy, and S defines the entropy associated with the process. The attempt frequency is

$$\nu = (kT/2\pi)^{1/2} \Delta U / \Delta W, \quad (3)$$

where ΔU and ΔW are the integration volumes around the saddle-point and equilibrium configurations, respectively. The entropy S is then given by

$$\frac{S}{k} = \ln \left(\frac{\int du \exp[-(E-E_a)/kT]}{\int dw \exp(-E/kT)} \right). \quad (4)$$

The integration variables in Eqs. (1) and (4) are related by $dU = \Delta U\, du$ and $dW = \Delta W\, dw$ so that the variables du and dw are *dimensionless.* In physical terms, the integration around the saddle-point configuration [numerator of the logarithm in Eq. (4)] measures the number of successful crossings over the saddle-point ridge which can lead to an exchange event (see Fig. 1). The integration around the equilibrium configuration [denominator of the logarithm in Eq. (4)] normalizes the number of successful crossings by the number of departure paths available to the system. In the context of the present formulation, in which dynamical effects are not explicitly included, the possibility of the system returning to the original state rather than crossing the saddle point is neglected. This is equivalent to setting the "efficiency factor" of more elaborate treatments (see, e.g., Ref. 10) equal to 1.

The integration around the saddle point involves a phase-space surface perpendicular to the migration path. The migration path is determined by the eigenvector of the dynamical matrix $V - \lambda T$ which corresponds to the lowest eigenvalue λ_0. In terms of the variables θ and ϕ, the kinetic-energy part of the dynamical matrix is given by

$$T_{\theta\theta} = \mu b^2, \quad T_{\phi\phi} = \mu b^2 \sin^2\theta, \quad T_{\theta\phi} = T_{\phi\theta} = 0, \quad (5a)$$

where $\mu = m/2$ (m being the mass of Si atoms) and b is the ideal bond length of bulk Si. The potential-energy part is given by

$$V_{ij} = \partial^2 E(\theta,\phi)/\partial i\, \partial j \text{ with } i,j = \theta,\phi \quad (5b)$$

(see, e.g., Ref. 11). The surface perpendicular to the migration path is determined by the eigenvector which corresponds to the highest eigenvalue λ_1 of the dynamical matrix. Notice that in the present case, since there are only two independent parameters, the phase-space "surface" around the saddle-point configuration is actually a line, determined by the eigenvector corresponding to λ_1 in the neighborhood of the saddle point. In terms of these quantities, the attempt frequency v is given by

$$v=(kT/2\pi\mu b^2)^{1/2}. \qquad (6)$$

With these explicit definitions, the entropy obtained from Eq. (4) at high temperatures ($T>1450$ K) is approximately $3.3k$. The reasons for the relatively large entropy of CE can be traced to several factors. First, there is large configurational degeneracy due to the six equivalent migration paths, which increases the value of the numerator of the logarithm in Eq. (4). Second, the integration around the saddle-point configuration is over a line with very small curvature (this can be seen by examining the energy surface in directions perpendicular to the CE path near the saddle points in Fig. 1), which further enhances the value of the numerator of the logarithm in Eq. (4). Finally, there is a steep increase in the energy for small deviations in θ from the equilibrium configuration. This is due to the fact that the system in the equilibrium configuration of the CE is extremely stable (ideal crystal) and any departure from this configuration results in large energy cost (the curvature of the energy surface near $\theta=0$ is large). Consequently, the value of the denominator of the logarithm in Eq. (4) is small (i.e., the number of possible departure paths for each successful crossing of the saddle point is small), which is also favorable for the entropy. The soft mode (small curvature) near the saddle-point configuration and the stiff mode (large curvature) near the equilibrium configuration combine to produce a relatively large value for the entropy.

Experiments give an entropy for self-diffusion in Si at high temperatures (1450–1650 K) of approximately $7k$–$9k$, a factor of 2–3 higher than the calculated entropy of CE. This could be attributed in part to the approximations employed in the present calculation, and in part to the complex nature of self-diffusion, which may involve several processes at once, making the measurement of entropies subject to large uncertainty. The most severe approximation in the present calculation is the reduction of the phase space to two generalized coordinates (the angles θ and ϕ), i.e., the neglect of relaxation.[12] The validity of this approximation can be checked by including relaxation, which is at present beyond reasonable computational efforts due to the large number of degrees of freedom. The reduction of phase space allows an exact treatment of the integrals in Eq. (4), thus eliminating the effects of anharmonicity, which in a complicated process such as the CE could be important.

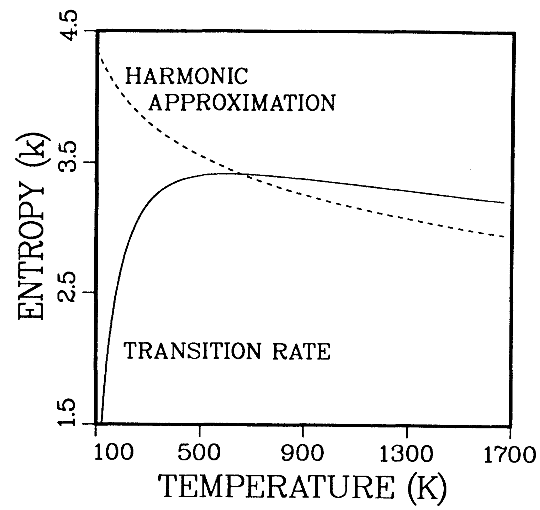

FIG. 2. Entropy of CE from transition-rate theory (solid line) and from the harmonic approximation (dashed line).

In order to evaluate the importance of anharmonic effects, we have performed a calculation for the CE entropy using the harmonic approximation. For a consistent comparison, we have again limited the phase space to the (θ,ϕ) variables and we define the attempt frequency to be the same as in the transition-rate formalism, given by Eq. (6). The temperature dependence of the entropy in the harmonic approximation is

$$S_{\text{harmonic}}/k=\text{const}-\tfrac{1}{2}\ln[T/T_0], \qquad (7)$$

where $kT_0=[V_{\theta\theta}(\theta=0,\phi=0)]^2/|\lambda_1|$. The entropy obtained with the harmonic approximation is shown in Fig. 2, together with results from the transition-rate formalism, for temperatures up to the melting point of Si (1687 K). The harmonic-approximation results exhibit good agreement with those of transition-rate theory (less than a 5% difference) only in the range 500 K $<T<$ 1000 K. The origin of the difference between the two approaches can be elucidated by examining the temperature dependence of the integrals appearing in Eq. (4). The values of these integrals are shown in Fig. 3. The results of the two approaches are indistinguishable for the equilibrium configuration and they exhibit a linear dependence on temperature. In contrast, the harmonic approximation fails to give accurate results for the saddle-point integral and shows large deviations from the transition-rate results both in the low- and in the high-temperature limits. In the harmonic approximation, the entropy has an unphysical singularity in the $T\to 0$ limit [Eq. (7)]. This singularity is exactly canceled by the temperature dependence of the attempt frequency in the expression for the diffusion rate Γ [cf. Eq. (2)], which then becomes independent of temperature. Thus, the low-temperature singularity of the entropy in the harmonic approximation

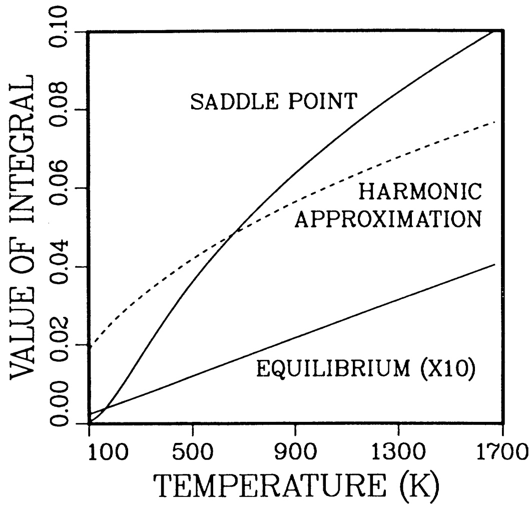

FIG. 3. Values of the integrals of Eq. (4) obtained from the harmonic approximation (dashed line) and from transition-rate theory (solid lines). The value of the equilibrium integral is multiplied by a factor of 10 to make it visible on the scale of the figure.

will not lead to unphysical results for the diffusion constant.

In conclusion, we have calculated the entropy of self-diffusion in Si for the CE process, in the context of Vineyard's transition-rate theory, using an accurate quantum-mechanical energy surface obtained from first principles. This combination of techniques enabled us to overcome difficulties associated with anharmonic effects and with a large migration energy barrier. The value for the CE entropy obtained from our calculation at high temperatures is $3.3k$, a factor of 2–3 lower than experimental results. A comparison with results from the harmonic approximation reveals that the latter fails both in the low- and in the high-temperature limits and gives accurate results for a narrow temperature range.

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Note added.—After this work was completed, we found that Blöchl, Van de Walle, and Pantelides[13] used a similar method to calculate the entropy of hydrogen diffusion in Si.

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