

Vacancies and Diffusion in Solid Hydrogen

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Self-diffusion by a particle-vacancy exchange mechanism is investigated in solid hydrogen and deuterium. The calculations are based on our quantum-crystal formalism published previously. The self-diffusion coefficient is calculated as a function of temperature, and the results compared with values inferred from nuclear-magnetic-resonance measurements; agreement of theory and experiment appears to be satisfactory. The effect of pressure on diffusion is also considered.

I. INTRODUCTION

The distinguishing feature of quantum crystals such as helium and hydrogen is the large-zero-point motion of molecules in the ground state.¹ Wave functions of molecules on neighboring lattice sites overlap appreciably, allowing the particles to exchange positions and thus providing a possible mechanism for self-diffusion by quantum-mechanical tunneling. The tunneling frequency and the self-diffusion coefficient D may be estimated from the exchange interaction J in solid hydrogen. We have previously presented² a calculation of J in bcc He³; using the same formalism, we find that³ $J \cong 10^{-11}$ K in hcp H₂ at a molar volume $V = 22.5$ cm³, corresponding to $P \cong 0$. This leads to a value of $D \sim 10^{-15}$ cm²/sec which is very small; nevertheless, particle exchange is probably the dominant mechanism for diffusion at very small temperature T .

At finite temperatures, there will be vacancies present in the crystal, and diffusion may also proceed by vacancy motion or vacancy-molecule exchange. This is a well-known process in classical solids,⁴ where a molecule on a site j adjacent to a vacancy site i is able to move into the site i by thermal excitation over the intervening potential barrier. In solid hydrogen, this mechanism contributes to D ; in addition, because the molecular mass is small and the potential barrier is not very large, there is also a finite probability for quantum-mechanical tunneling of the molecule from site j to site i . This is the same idea as in the molecular-exchange process described above; however, when only one of the two sites is occupied, the exchange proceeds at a much faster rate. For this case, the analog of the exchange interaction is the energy splitting of the two lowest states in the double-well potential on sites i and j . It is some ten orders of magnitude larger than the exchange interaction, indicating that this "quantum-diffusion" process should dominate at temperatures low enough that thermal excitation over the barrier is frozen out, but high enough that sufficient vacancies are still present to make vacancy-diffusion important.

The model we use is that of localized vacancies. In solid hydrogen this description is probably valid; in solid helium it is not valid because the potential barrier between a vacancy and neighboring atoms is very small (~ 5 K), leading to rapid vacancy motion. In the latter material it is necessary to treat the vacancies as nonlocalized, leading to an energy band of vacancy excitations. Hetherington⁵ has given a description of nonlocalized vacancies in bcc He³.

The remainder of this paper is organized as follows: In Sec. II, we develop an expression for D using the ideas outlined here; Sec. III contains a description of the formalism used to calculate the appropriate energy levels and wave functions in a crystal containing a single vacancy. Finally, in Sec. IV, the numerical results for hcp H₂ and D₂ are presented and comparison is made with experiment.

II. DIFFUSION COEFFICIENT

Following Glyde,⁴ we write the coefficient of self-diffusion as

$$D = \frac{1}{6} a^2 f P_v \sum_n k_n, \quad (1)$$

where P_v is the probability that a given lattice site is vacant, a is the nearest-neighbor distance, and f is a correlation factor that characterizes the extent to which jumps are not random. The jumping rate k has been generalized to a sum over several rates k_n corresponding to different jumping mechanisms described below. The factor $\frac{1}{6}$ is geometrical in origin and applies if the jumps are random in direction⁶; this is not necessarily true in the systems we are considering, but the expression will be correct to within a factor of 2. Similarly, f depends on the crystal structure but is generally of order one. We shall simply set $f = 1$.

The probability that a given site is vacant is

$$P_v = e^{s_v} e^{-h_v/T}, \quad (2)$$

where s_v is the thermal-entropy change of the crystal accompanying vacancy formation and h_v is the

corresponding enthalpy change $h_v = \epsilon_v + P\delta v$. Here, ϵ_v and δv are, respectively, the energy required to produce the vacancy and the concurrent change in crystal volume. For a Schottky defect, δv is approximately the inverse of the molecular number density in the crystal. At the temperatures of interest here, s_v may be disregarded.⁷

To find the jumping rates k_n we suppose that there is a vacancy on site i , located at \vec{R}_i and consider the mechanisms by which a molecule on a neighboring site j at \vec{R}_j can move to \vec{R}_i . This is essentially the problem of a quantum-mechanical particle in a symmetric double-well potential; the particle can cross the barrier between the two wells either by tunneling through it or by being thermally excited over it.

We consider the tunneling mechanism first. The relevant states of the particle in the well are those which have energy eigenvalues below the top of the barrier. Energies will be measured relative to the bottom of the double well; the top of the barrier is designated ϵ_b . The energy levels below ϵ_b occur in nearly degenerate pairs, the lower member of the n th pair $|n, s\rangle$ has even parity along the line between i and j , while the upper member $|n, a\rangle$ has odd parity. Now, in order that the particle be initially on one side of the barrier, the two states $|n, a\rangle$ and $|n, s\rangle$ must be populated with equal amplitude. As time increases, the relative phase of the two states changes because they are not exactly degenerate, and this produces oscillation of the particle back and forth across the barrier. Direct evaluation of the quantum-mechanical probability current in the n th pair of levels shows that $j_n \sim P_n \times \sin J_n t$, where $J_n = \epsilon_n^a - \epsilon_n^s$ is the splitting of the levels and P_n is the probability that this pair is occupied in the first place; we shall take P_n proportional to the Boltzmann factor $P_n \sim e^{-\epsilon_n/T}$, where $\epsilon_n = \frac{1}{2}(\epsilon_n^s + \epsilon_n^a) \cong \epsilon_n^s \cong \epsilon_n^a$. From the expression for j_n , we see that the particle crosses the barrier in a time $\tau_n = \pi/J_n$, and so we have $k_n = (J_n/\pi)P_n$ for the jumping rate in the n th pair of levels.

This approach is valid so long as $\epsilon_n^s \cong \epsilon_n^a$ so that $(1/\sqrt{2})(|ns\rangle + |na\rangle)$ does describe a state well localized on one side of the barrier.

For states above the barrier, a different approach must be used. Particles in these states are so highly excited that motion across the barrier is very rapid, and the picture of discrete energy levels in a rigid double well breaks down. Consequently, we shall adopt the classical description for diffusion over the barrier, writing $k_n = \langle v \rangle / a P_b$, where $P_b \sim e^{-\epsilon_b/T}$ is the probability that a molecule will be thermally excited above the barrier, and $\langle v \rangle$ is a typical velocity of such an excitation $v \cong (\epsilon_b/m)^{1/2}$ where m is the molecular mass.

Assembling the various pieces, we find the following expression for D :

$$D = \frac{1}{6} a^2 e^{-(\epsilon_v - P\delta v)/T} \frac{\sum_n (J_n/\pi) e^{-\epsilon_n/T} + (\epsilon_b/m a^2)^{1/2} e^{-\epsilon_b/T}}{Z}, \quad (3)$$

where $Z = \sum_n e^{-\epsilon_n/T} + e^{-\epsilon_b/T}$. The sum on n is over all pairs of states such that $\epsilon_n < \epsilon_b$. Note that we have given the states above the barrier the statistical weight of a single state which probably underestimates their importance.

III. CALCULATION SCHEME

The evaluation of D from Eq. (3) requires the energy levels and splittings ϵ_n and J_n as well as the barrier height ϵ_b . These energies can be found if the shape of the double-well potential is known. We find this potential function assuming a single vacancy at site i by modifying the formalism developed earlier⁸ for perfect quantum crystals. The principal alteration deals with the distortion of the single-particle wave functions $\phi_j(1)$ for particles on sites j close to the vacancy. As in Ref. 8, the equation for ϕ_j is

$$[-(1/2m)\nabla_1^2 + u_j(1)]\phi_j(1) = \epsilon\phi_j(1), \quad (4)$$

where ϵ is the lowest energy eigenvalue in the single particle effective field $u_j(1)$ given by

$$u_j(1) = \sum_k \int V(1, 2) \phi_k^2(2) \chi_{jk}(1, 2) d^3r_2. \quad (5)$$

Here, V is the interparticle potential, and χ_{jk} is the two-particle correlation function for particles on sites j and k in the presence of a vacancy on site i ; the sum over k omits the terms $k = i, j$.

In the present work, we ignore the dependence of χ on the existence of a vacancy at site i and use correlation functions found previously⁹ for hcp H_2 . In the case of D_2 , we use correlation functions found by the same technique as in Ref. 9. The effective field is found in the harmonic approximation by expanding the right-hand side of Eq. (5) around \vec{R}_j . The minimum of $u_j(1)$ will shift away from \vec{R}_j slightly because of the absence of the $k = i$ term in the sum. If we choose axes such that the z direction is parallel to $\vec{R}_{ij} \equiv \vec{R}_i - \vec{R}_j$, then the effective field becomes a constant plus three harmonic-oscillator potentials along the three axes, and in this approximation $\phi_j(1)$ is just the product of three one-dimensional harmonic-oscillator wave functions:

$$\phi_j(1) = \prod_{k=1}^3 \frac{(\alpha_k)^{1/2}}{\pi^{1/4}} \exp\left[-\frac{1}{2}\alpha_{jk}^2(r_{1k} - R_{jk} - \delta_{jk})^2\right], \quad (6)$$

where the subscript k denotes a particular Cartesian component and δ_j is the displacement of the minimum of $u_j(1)$ from \vec{R}_j . Relative to the perfect crystal, the change in the effective force constant is principally along the z direction, and we shall take the force constants along the other two directions the same as in the perfect crystal. With these simplifications, it is not difficult to solve Eqs. (4) and

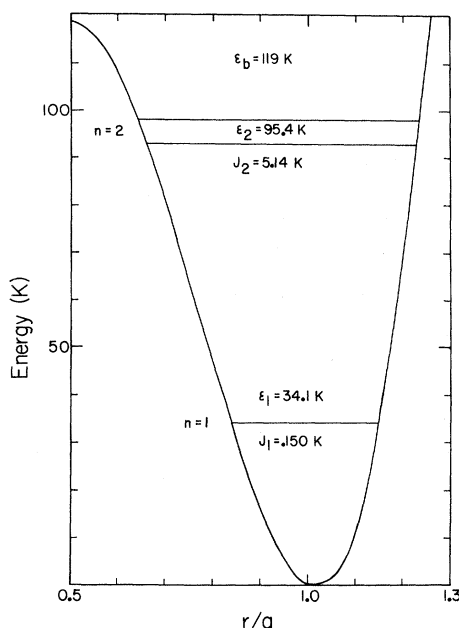


FIG. 1. Double well and energy levels for molecules adjacent to a vacancy in hcp H_2 at $P=0$; r/a is given relative to the vacancy site.

(5) self-consistently from which one finds the harmonic effective field and single-particle wave functions. In this approximation and assuming spherical symmetry around i , the energy ϵ_v required to create a vacancy by removing a molecule to the surface of the crystal is

$$\epsilon_v = \sum_s \left(\frac{1}{2} n_s \delta u_s + \frac{3}{8} \frac{(\delta \alpha_{s3}^2) a^2}{m a^2} \right), \quad (7)$$

where the sum is over all shells of molecules surrounding the vacancy; n_s is the number of molecules in shell s , while δu_s and $\delta \alpha_{s3}^2$ are, respectively, the changes in the effective-field minimum and in α_3^2 in this shell.

The energy levels $\epsilon_n^{(a)}$ in the double well on sites i and j are found by maintaining the harmonic approximation along directions perpendicular to \vec{R}_{ij} and by using Eq. (5) without expanding to find the potential along \vec{R}_{ij} . A typical result is shown in Fig. 1. The barrier height ϵ_b is directly determined from this calculation while the energy levels $\epsilon_n^{(a)}$ are found by solving numerically for the single-particle energy eigenstates in the double well. This provides a check, incidentally, on the harmonic approximation used in finding ϕ_j and ϵ_v , since the wave function of the lowest state in the double well should be nearly identical with $(1/\sqrt{2})(\phi_j + \phi_i)$. This is in fact the case.

IV. NUMERICAL RESULTS AND DISCUSSION

For hcp H_2 at zero pressure, we find $\epsilon_v = 112$ K

and $\epsilon_b = 119$ K. The double-well and energy-level structure for excitations along the direction of \vec{R}_{ij} , are shown in Fig. 1. In principle, states describing excitations along the other two axes also contribute to diffusion, however, for energies below ϵ_b these states have negligible influence and are not included here. The result for D is

$$D = 2 \times 10^{-6} (1 + 34 e^{-61/T} + 300 e^{-85/T}) e^{-112/T} \text{ cm}^2/\text{sec}, \quad (8)$$

where T is in degrees Kelvin. At high T , the last term dominates and gives

$$D = 6 \times 10^{-4} e^{-197/T} \text{ cm}^2/\text{sec}.$$

This is the classical limit in which particles diffuse by thermal excitation across the barrier. At low T , the first term dominates and gives

$$D = 2 \times 10^{-6} e^{-112/T} \text{ cm}^2/\text{sec},$$

which corresponds to diffusion by tunneling in the lowest pair of states in the double well. The temperature at which the transition between these limiting cases occurs is about 14.7 K.

The diffusion constant can be determined experimentally from nuclear-magnetic-resonance experiments. According to the Kubo-Tomita formula,¹⁰ in the temperature range where the self-diffusion of the molecules becomes important, and the transverse relaxation time T_2 is much longer than the correlation time Γ which is also much longer than the inverse Larmor frequency ω^{-1} , the longitudinal and transverse relaxation times T_1 and T_2 are given by

$$T_1 = \frac{1}{2} (3 \ln 2) (T_2'')^2 \omega^2 \Gamma \quad (9)$$

and

$$T_2 = (2 \ln 2) (T_2'')^2 / \Gamma, \quad (10)$$

where $(T_2'')^{-1}$ is the linewidth for the rigid lattice.

The experimental data of Bloom¹¹ on T_2 in solid hydrogen at $P=0$ were analyzed by Moriya and Motizuki,¹² and Γ was found to have the behavior

$$\Gamma = \Gamma_0 e^{E_a/T}, \quad (11)$$

for $11 \leq T \leq 14$ K; $E_a = 380$ cal/mole and $\Gamma_0 = 7 \times 10^{-14}$ sec. From this information and the relation

$$\Gamma = a^2 / 12D, \quad (12)$$

one finds $D = (2 \times 10^{-3}) e^{-190/T} \text{ cm}^2/\text{sec}$. We remind the reader that diffusion coefficients determined in this manner are always subject to an uncertainty of about a factor of 2, principally because Eq. (12) is not exact.

Comparison of this result with Eq. (8) indicates that the "classical" diffusion process is being observed. The calculated activation energy of 197 K is quite close to the observed $E_a \approx 190$ K. The temperatures at which this process dominates extend

to lower values than the theory predicts, however. The observed E_a is constant down to $T \cong 11$ K, whereas the theory indicates that it should change to a smaller value at $T \approx 14.5$ K. We suspect that the most likely source of this disagreement lies in the statistical weight assigned to that term in D which describes transitions over the potential barrier. Because the well is three dimensional, the true weight of states above the barrier could be considerably greater. An increase by a factor of 3, for example, would decrease the temperature of the predicted transition from classical to tunneling behavior by about two degrees. The magnitude of the theoretical prediction would also be very close to the results of experiment although this is probably not significant. Another possible source of discrepancy is that our estimate of $\langle v \rangle$ may not be very realistic. While it is not clear where the transition occurs, we do believe that the activation energy for vacancy diffusion will not be the same at all T . It would be interesting in further experimental analyses to see whether the employment of two exponential functions of T is useful.

We have also carried out calculations of D in hcp D_2 at zero pressure. The procedure is identical with that used for H_2 . The results are $\epsilon_v = 132$ K and $\epsilon_b = 192$ K; the energy-level structure is given in Fig. 2, and the corresponding diffusion constant is

$$D = (1.5 \times 10^{-8}) e^{-132/T} (1 + 87 e^{-65/T} + 2380 e^{-122/T} + 46000 e^{-158/T}) \text{ cm}^2/\text{sec}. \quad (13)$$

At high T ,

$$D \cong (7 \times 10^{-4}) e^{-290/T} \text{ cm}^2/\text{sec} ,$$

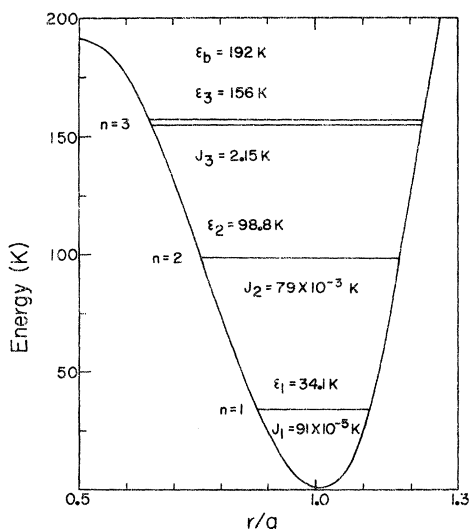


FIG. 2. Double well and energy levels for molecules adjacent to a vacancy in hcp D_2 at $P=0$; r/a is given relative to the vacancy site.

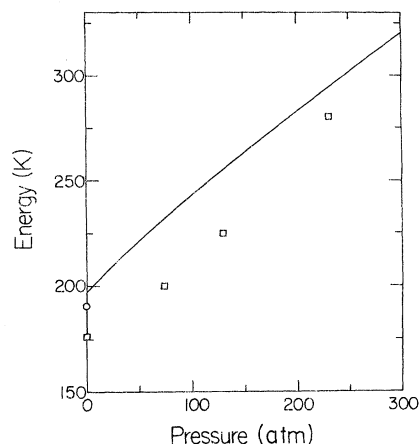


FIG. 3. Activation energy for self-diffusion in hcp H_2 as a function of pressure. The experimental points are \circ (Refs. 11 and 12), \square (Ref. 14).

while for low T ,

$$D \cong (1.5 \times 10^{-8}) e^{-132/T} \text{ cm}^2/\text{sec} ,$$

and the temperature dividing the two regions is once again $T \cong 14.5$ K. Meyer and co-workers¹³ have performed NMR experiments on solid D_2 finding approximately exponential behavior of Γ as a function of T for $13 \leq T \leq 17$ K with an activation energy of 288 K. This energy is once again in striking agreement with our calculated value. However, there is the same problem regarding the temperature at which the tunneling process should take over. The comments made above concerning the source of this discrepancy in H_2 apply in the case of D_2 as well.

We have also considered the behavior of the diffusion coefficient if pressure is applied to the crystals. The energy ϵ_v turns out to be quite insensitive to P , decreasing slightly as P increases. The production of vacancies is strongly inhibited, however, because of the term $P\delta v$ in the enthalpy of vacancy formation. Also, the energy splittings J_n are strongly reduced, and the barrier height ϵ_b increases sharply. These changes simply reflect the fact that molecules become more localized in solid hydrogen crystals as the molar volume is decreased. If we write $D = D_0 e^{-\epsilon_a/T}$ in the high-temperature regime, then the net effect is that D_0 increases slowly with pressure, changing by less than a factor of 2 for $P \leq 10^4$ atm; ϵ_a increases with pressure and produces the dominant pressure dependence of D . In Fig. 3 we have plotted calculated values of ϵ_a vs P in solid H_2 . The experimental points at $P \neq 0$ were determined by Smith and Squire from their NMR measurements.¹⁴

Finally, we should mention that experimental samples usually contain comparable amounts of orthohydrogen (o - H_2) and parahydrogen (p - H_2). Dif-

ferent lattice sites are therefore not equivalent, because the $o\text{-H}_2\text{-}p\text{-H}_2$ interaction is not quite the same as the $o\text{-H}_2\text{-}o\text{-H}_2$ interaction. In our calculations, on the other hand, we have assumed equivalence of all sites. The difference between the interactions should produce a small correction to the activation energy ($\delta\epsilon_a \lesssim 5$ K) at the low pressures we have treated here. This expectation is supported by the NMR work of Hass, Poulis, and Borleffs,¹⁵ who find that the $o\text{-H}_2$ concentration has almost no effect on ϵ_a at $P=0$. They find that $(T_2')^{-2}$ is proportional to the concentration of orthohydrogen in agreement with Van Vleck's theory.¹⁵ The result shows that D_0 is independent of the concentration of orthohydrogen at low pressures as we expect. As the pressure becomes larger ($P \sim 10^4$ atm), however, the corrections increase in relative importance and should be taken into account. This involves a fairly large amount of numerical work and is currently under

investigation in the broader context of the effect of anisotropic interactions in solid H_2 .

In summary, we have given a first principles calculation of the self-diffusion constant in solid hcp D_2 and H_2 , where diffusion proceeds by a vacancy-molecule interchange mechanism. The calculated activation energy for thermal diffusion is in quite good agreement with experiment in both materials. In addition, we find that at low temperatures diffusion should proceed by a tunneling mechanism with a lower activation energy, suggesting that analyses of experimental data may be improved by using a sum of two exponential terms.

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Asymptotic Form of the Pair-Correlation Function in Liquids*

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Recently, several authors have contended that the pair-correlation function for a simple liquid asymptotically goes to zero in a way proportional to the two-particle potential. We critically examine the basis of their assertion and find that the conclusion is unfounded. Existing x-ray and neutron-diffraction data on liquids are inconclusive insofar as the asymptotic form of the pair correlation is concerned. We propose an experiment which may shed some light upon the large- r behavior of this important quantity.

There have recently appeared in the literature several papers¹⁻⁵ in which the assertion is made that the radial distribution function $g_2(r)$ approaches unity, its limiting value at large r , in the following way:

$$g_2(r) - 1 \approx \phi(r) \text{ for large } r. \quad (1)$$

Here $\phi(r)$ is the two-body potential. Unfortunately, the validity of Eq. (1) for liquids is rather muddled. This is because of the methods used in arriving at

the conclusion embodied in Eq. (1). In this article we seek to clarify the logical position of Eq. (1) relative to the theory of the liquid state, and we suggest an experiment which might provide insight as to how $g_2(r) - 1$ approaches zero as r becomes large.

Equation (1) has been obtained^{1,2} from model equations such as the Percus-Yevick equation.⁶ One starts with a model statement relating the direct correlation $c(r)$, the potential $\phi(r)$, and the