PHYSICAL REVIEW B VOLUME 57, NUMBER 13 1 APRIL 1998-I

Phonon-assisted asymmetric tunneling in a double-well potential: Consequences for neutron scattering and diffusion

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(Received 28 August 1997)

We investigate the dynamics of a light interstitial atom in a double-well potential and extend the small polaron theory to include tunneling transitions from the ground state to excited states as well as asymmetry between sites. Starting from a generalized spin-boson Hamiltonian we use the resolvent of the time-development operator to derive formulas for transition rates and neutron-scattering structure factors. We show how with only two parameters the model allows for a quantitative description of hydrogen diffusion in bcc metals up to high temperatures. Asymmetry between the wells strongly reduces the mobility, particularly at low temperatures. [S0163-1829(98)00913-8]

I. INTRODUCTION

Much attention has been focused in recent years on the tunneling and diffusion of light interstitials such as hydrogen (and its isotopes including positive muon) in metals.[1,2] The most clearcut situation, which permits a detailed comparison of experiment and theory, is the one in which H is trapped by other heavier interstitials such as O (or N), in a metal like Nb.[3] In this, the H moves in a double-well potential created by O and the host Nb atoms. In metals the temperature dependence of H tunneling and diffusion at low temperatures is determined by the excitations of the conduction electrons which influence both the coherent and incoherent tunneling rates.[4] These so-called nonadiabatic effects which result, e.g., in an anomalous power-law dependence of the diffusion constant on temperature, are well documented in the literature.[5]

Our emphasis in this paper is on the regime of moderate temperatures [such as $T \geqslant 60$ K, in Nb:$(\mathrm{OH})_x$] where the phonon excitations dominate the electronic ones. This regime is still quantum mechanical and closely resembles the familiar small polaron scenario.[6,7] In this description one assumes that the H follows adiabatically the lattice distortions. It can tunnel from one site to another whenever its energy in both sites is equal, i.e., in a so-called coincidence configuration. Tunneling is allowed to a set of equivalent neighboring sites and the tunneling frequency is taken as a constant, independent of the lattice distortion.

Since the tunneling frequencies are smaller than the host lattice frequencies the host is distorted near the H such as to lower its energy (self-trapping). Neighboring sites of the H are only equivalent if this distortion is transported together with the H. Consequently the H tunneling frequency is ‘‘dressed,’’ causing a reduction by a factor of nearly 10 at the lowest temperatures, in the example of Nb:$(\mathrm{OH})_x$.[3] With increasing temperatures the dressing factor diminishes rapidly and coherent tunneling is suppressed.[5] On the other hand, the same mechanism leads to an increase of the incoherent tunneling rates and thus the H diffusion by the so-called phonon-assisted tunneling. Moreover, as the temperature increases, the rate with which coincidence configurations of the host lattice occur, also increases. In these configurations the H can tunnel from one site to another without additional phonon dressing. The diffusion constant then approaches an Arrhenius behavior at elevated temperatures.

Alltough calculations are normally done by assuming only linear coupling between the H coordinate and the lattice one, quadratic terms can modify the results.[8,9] In addition, even low concentrations of H and O interstitials can lead to long-ranged strain interactions that render the two sites involved in the tunneling transition asymmetric. For small asymmetry and low temperatures this causes otherwise forbidden one-phonon processes.[10] Larger asymmetries can be due to geometry and composition. We will see that at higher temperatures tunneling between strongly inequivalent sites becomes feasible.

The simple small polaron picture breaks down at higher temperatures, in particular as the Condon approximation loses validity. Experimentally, a break in the Arrhenius curve for H diffusion in Nb and Ta is observed (see Fig. 2 further down).[11] Computer simulations have shown that this is due to tunneling in excited states of the H vibration.[12,13] The transition of the H in its ground state in one well to an excited state in the second well is enhanced with the increase of temperature and asymmetry of the wells.

In this paper we will extend the description of the small polaron problem to include both the transition to an excited state and asymmetry. Figure 1 shows schematically the double-well system for the H which is immersed in the phonon bath of the host lattice. Much of the theoretical discussion on the tunneling in such a potential has been hitherto restricted to the truncated Hilbert space of the two lowest energy states, denoted cryptically by $|-\rangle$ and $|+\rangle$, within what is called the spin-boson Hamiltonian.[14] However, if the asymmetry (parametrized by ϵ_1) is large, the possible presence of a nearby state, which is the first vibrational excited state in the deeper of the two wells, such as the left one in Fig. 1, and denoted by $|0\rangle$, cannot be neglected. Therefore, one now has to deal with two tunneling frequencies Δ_0 and Δ_1, indicated in Fig. 1. We study here the consequences of such asymmetric tunneling for the diffusion.

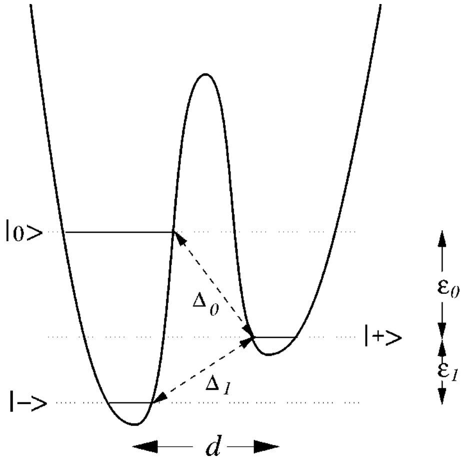

FIG. 1. Schematic representation of the double-well system.

A very accurate method of estimating the diffusion coefficient, especially of an interstitial like H, is neutron scattering[15] When it comes to H the predominant scattering is incoherent[16] such that the data are determined by the so-called self-correlation function, i.e., the time correlation between the position of the *same* scatterer.[17] When the scatterer moves in a restricted domain (e.g., the double-well potential illustrated in Fig. 1) the incoherent scattering cross section is, in general, represented by the following structure factor:[18]

$$S(\mathbf{k},w)=f_1(\mathbf{k}\cdot\mathbf{d})\delta(\omega)+\frac{2}{\pi}\frac{f_2(\mathbf{k}\cdot\mathbf{d})}{1+\exp(\hbar w/k_BT)}\mathrm{Re}[\tilde{C}(-i\omega)], \tag{1}$$

where **k** is the wave-vector transfer and ω is the frequency transfer from the incident to the scattered neutron during the scattering process.

We shall give a derivation of this result and precise meanings of various terms in the sequel. At this stage, however, it suffices to simply state that the first term in Eq. (1) describes the ''elastic'' component, proportional to a δ function of frequency: f_1 and f_2 are the ''form factors'' which depend on the product of **k** and the ''size'' **d** of the scattering region, e.g., the distance between the two minima of the double well in Fig. 1; the denominator in the second term is a detailed balance factor; and $\tilde{C}(-i\omega)$ is the Laplace transform of a certain correlation function which contains all the information about the dynamics of the scatterer.

We postpone the discussion of $\tilde{C}(-i\omega)$ and merely indicate at this point how to extract the diffusion coefficient. It turns out that in the *incoherent tunneling* regime $\tilde{C}(-i\omega)$ can be replaced by its Markovian limit in which case one can write

$$\tilde{C}(-i\omega)=\sum_j \frac{a_j}{-i\omega+\Gamma_j}. \tag{2}$$

Equation (2) then yields a sum of Lorentzians, all centered around $\omega=0$. The net result is a quasielastic component riding on top of the elastic component and the width of which is related to the diffusion coefficient D. Therefore, our task in this paper is to provide a derivation of the form given in Eq. (2) based on the model illustrated in Fig. 1 and explain the crossover phenomenon depicted in Fig. 2 from the derived temperature dependence of Γ_j's.

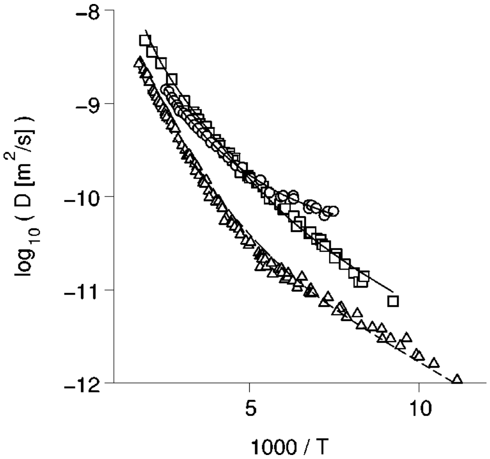

FIG. 2. Diffusion constant of H in bcc metals. Experimental values: Nb:H (Ref. 11), □; Nb:H (Ref. 25), ○; Ta:H (Ref. 11), △. Corresponding theoretical curves with no asymmetry ($\epsilon_1=0$) including transitions from ground state to excited state: solid and dashed lines.

With the aim and scope of the paper in the background an outline is as follows. In Sec. II we formulate the problem by first sketching the steps (in Sec. II A) necessary for calculating the incoherent structure factor and filling-in the gaps in our discussion following Eq. (1). In Sec. II B we motivate the Hamiltonian which generalizes the spin-boson Hamiltonian, in order to be able to treat asymmetric tunneling, as exemplified by Fig. 1. In Sec. II C we set up the notation for the averaged time-development operator required for computing the structure factor. Section III contains the main mathematical results on the structure factor and diffusion. In Sec. IV we analyze the transition rates in the so-called Flynn-Stoneham approximation.[6] Finally, in Sec. V we discuss the results on diffusion and present our conclusions.

II. FORMULATION OF THE PROBLEM

A. The structure factor

The experimentally measured incoherent scattering of neutrons is related to the structure factor[17]

$$S(\mathbf{k},\omega)=(2\pi)^{-1}\int_{-\infty}^{\infty}dt\ \exp(i\omega t)$$
$$\times\langle\exp(-i\mathbf{k}\cdot\mathbf{r}(0))\exp(i\mathbf{k}\cdot\mathbf{r}(t))\rangle, \tag{3}$$

where **k** and ω have been defined previously [following Eq. (1)], $\mathbf{r}(0)$ and $\mathbf{r}(t)$ are the positions of the scatterer (i.e., H in the present instance) at times 0 and t, respectively, and the angular brackets imply thermal averaging over the equilibrium ensemble of the system. The time development of $\mathbf{r}(t)$ is given by the usual Heisenberg picture:

$$\mathbf{r}(t)=\exp(i\mathcal{H}t)\mathbf{r}(0)\exp(-i\mathcal{H}t),\quad \hbar=1, \tag{4}$$

where $\mathcal{H}$ is the Hamiltonian of the system.

We assume that the position of the scatterer coincides with the bottom of the well irrespective of whether the scatterer is in the ground or the excited state. In that case **r** can be assumed to be a three-valued operator:

$$\mathbf{r}=-\frac{\mathbf{d}}{2}\hat{P}_{-}-\frac{\mathbf{d}}{2}\hat{P}_{0}+\frac{\mathbf{d}}{2}\hat{P}_{+}, \tag{5}$$

where the vector **d** is defined in Fig. 1, with the origin chosen at the saddle point and the $\hat{P}$'s are projection operators which have 3×3 matrix representations as follows:

$$\hat{P}_0=\begin{pmatrix}0&0&0\\0&1&0\\0&0&0\end{pmatrix},\quad \hat{P}_{+}=\begin{pmatrix}1&0&0\\0&0&0\\0&0&0\end{pmatrix},$$

$$\hat{P}_{-}=\begin{pmatrix}0&0&0\\0&0&0\\0&0&1\end{pmatrix}. \tag{6}$$

In Eq. (6) the rows and columns are labeled by $|+\rangle$, $|0\rangle$ and $|-\rangle$, respectively.

Equation (5) can be further simplified as

$$\mathbf{r}=-\frac{\mathbf{d}}{2}\hat{1}+\mathbf{d}\hat{P}_{+}, \tag{7}$$

where $\hat{1}$ is the unit matrix. Using the property of the projection operator that

$$\hat{P}_{\alpha}\hat{P}_{\beta}=\hat{P}_{\alpha}\delta_{\alpha\beta},\quad \alpha\beta=0,1,-1, \tag{8}$$

Eq. (3) reduces to

$$S(\mathbf{k},\omega)=(1-4\langle\hat{P}_{+}\rangle)\sin^2\!\left(\frac{1}{2}\mathbf{k}\cdot\mathbf{d}\right)\delta(\omega)+\frac{1}{2\pi}4\sin^2\!\left(\frac{1}{2}\mathbf{k}\cdot\mathbf{d}\right)$$
$$\times\int_{-\infty}^{\infty}dt e^{i\omega t}\langle\hat{P}_{+}(0)\hat{P}_{+}(t)\rangle. \tag{9}$$

Introducing the symmetrized correlation function as

$$C(t)=\frac{1}{2}\langle\hat{P}_{+}(0)\hat{P}_{+}(t)+\hat{P}_{+}(t)\hat{P}_{+}(0)\rangle, \tag{10}$$

we finally arrive at our earlier expression in Eq. (1), where the Laplace transform of $C(t)$ is defined by

$$\tilde{C}(z)=\int_{0}^{\infty}dt\exp(-zt)C(t),\quad z=-i\omega. \tag{11}$$

B. The Hamiltonian

The energy-level scheme shown in Fig. 1 can be incorporated in the following Hamiltonian:

$$\mathcal{H}_o=(\epsilon_0+\epsilon_1)\hat{P}_0+\epsilon_1\hat{P}_{+}, \tag{12}$$

where the ''zero'' of energy has been set at the level $|-\rangle$. Now, inclusion of two possible tunneling processes with characteristic energies Δ_0 and Δ_1 in Eq. (12) leads to the following form of the ''subsystem'' Hamiltonian:

$$\mathcal{H}_s=(\epsilon_0+\epsilon_1)\hat{P}_0+\epsilon_1\hat{P}_{+}+\Delta_0(\hat{S}_0^{(+)}+\hat{S}_0^{(-)})$$
$$+\Delta_1(\hat{S}_1^{(+)}+\hat{S}_1^{(-)}), \tag{13}$$

where the $\hat{S}$'s are ''ladder'' operators defined by

$$\hat{S}_0^{(+)}=\begin{pmatrix}0&1&0\\0&0&0\\0&0&0\end{pmatrix},\quad \hat{S}_0^{(-)}=\begin{pmatrix}0&0&0\\1&0&0\\0&0&0\end{pmatrix},$$

$$\hat{S}_1^{(+)}=\begin{pmatrix}0&0&1\\0&0&0\\0&0&0\end{pmatrix},\quad \hat{S}_1^{(-)}=\begin{pmatrix}0&0&0\\0&0&0\\1&0&0\end{pmatrix}. \tag{14}$$

Finally, we write down the Hamiltonian for the lattice, taking cognizance of the distortion created by the ''particle'' when it is either in the left or the right well:

$$\mathcal{H}_L=\sum_q\left[\frac{p_q^2}{2m_q}+\frac{1}{2}m_q\omega_q^2(x_q+\hat{P}_0\eta_q+\hat{P}_{-}\xi_q-\hat{P}_{+}\xi_q)^2\right], \tag{15}$$

where p_q, x_q, and m_q are, respectively, the momentum, coordinate, and mass of the normal mode, while $\pm\xi_q$ are the displacements when the particle is in the *ground* state of the right (left) well and η_q is the displacement when the particle is in the *excited* state of the left well. The complete Hamiltonian is then given by the sum of $\mathcal{H}_S$ and $\mathcal{H}_L$. It can be written, in the second quantized notation, as

$$\mathcal{H}=(\epsilon_0+\epsilon_1)\hat{P}_0+\epsilon_1\hat{P}_{+}+\Delta_0(\hat{S}_0^{(+)}+\hat{S}_0^{(-)})+\Delta_1(\hat{S}_1^{(+)}+\hat{S}_1^{(-)})$$
$$+\sum_q\ \omega_q b_q^{+}b_q+\sum_q\ (b_q^{+}+b_q)[\hat{P}_0G_q^0+(\hat{P}_{-}-\hat{P}_{+})G_q^1]$$
$$+\sum_q\ \frac{1}{\omega_q}[\hat{P}_0(G_q^0)^2+(\hat{P}_{+}+\hat{P}_{-})(G_q^1)^2], \tag{16}$$

where $b_q^{+}(b_q)$ are the usual boson creation (annihilation) operators, G_q's are coupling constants given by

$$G_q^0=\sqrt{\frac{m_q}{2}}\omega_q^{3/2}\eta_q\quad\text{and}\quad G_q^1=\sqrt{\frac{m_q}{2}}\omega_q^{3/2}\xi_q, \tag{17}$$

and we have used Eq. (8).

At this stage it is useful to perform a unitary transformation to the Hamiltonian, defined by the operator:

$$U\equiv\exp\left\{-\sum_q\ \frac{(b_q-b_q^{+})}{\omega_q}[\hat{P}_0G_q+(\hat{P}_{-}-\hat{P}_{+})G_q^1]\right\}. \tag{18}$$

It is easy to verify [employing Eq. (8)] that

$$U=\hat{P}_0\exp\left[-\sum_q \frac{(b_q-b_q^+)}{\omega_q}G_q^o\right]$$

$$+\hat{P}_+\exp\left[+\sum_q \frac{(b_q-b_q^+)}{\omega_q}G_q^1\right]$$

$$+\hat{P}_-\exp\left[-\sum_q \frac{(b_q-b_q^+)}{\omega_q}G_q^1\right]. \tag{19}$$

Furthermore,

$$\tilde{\mathcal{H}}=U\mathcal{H}U^{-1}=(\epsilon_o+\epsilon_1)\hat{P}_0+\epsilon_1\hat{P}_++\Delta_0[\hat{C}_-\hat{S}_0^{(+)}+\hat{C}_+\hat{S}_0^{(-)}]$$

$$+\Delta_1[\hat{B}_-\hat{S}-1^{(+)}+\hat{B}_+\hat{S}_1^{(-)}]+\sum_q \omega_q b_q^+ b_q, \tag{20}$$

where

$$\hat{C}_\pm\equiv\exp\left[\pm\sum_q \frac{(G_q^0+G_q^1)}{\omega_q}(b_q^+-b_q)\right],$$

$$\hat{B}_\pm\equiv\exp\left[\pm\sum_q \frac{2G_q^1}{\omega_q}(b_q^+-b_q)\right]. \tag{21}$$

Thus, Eq. (20) allows us to write the total Hamiltonian in a clearcut system-plus-reservoir form:

$$\tilde{\mathcal{H}}=\mathcal{H}_S+\mathcal{H}_R+\mathcal{H}_I, \tag{22}$$

where the subsystem Hamiltonian is

$$\mathcal{H}_s=(\epsilon_0+\epsilon_1)\hat{P}_0+\epsilon_1\hat{P}_+, \tag{23}$$

the reservoir Hamiltonian is

$$\mathcal{H}_R=\sum_q \omega_q b_q^+ b_q, \tag{24}$$

and the interaction Hamiltonian is

$$\mathcal{H}_I=\Delta_0[\hat{C}_-\hat{S}_0^{(+)}+\hat{C}_+\hat{S}_0^{(-)}]+\Delta_1[\hat{B}_-\hat{S}_1^{(+)}+\hat{B}_+\hat{S}_1^{(-)}]. \tag{25}$$

The advantage of the unitary transformation is that in any treatment with $\mathcal{H}_I$ as perturbation, ‘‘strong’’ coupling can be easily incorporated by resumming the perturbation series into a self-energy,[19] as the original coupling constants now occur in the exponential arguments [cf. Eq. (21)]. Such a perturbation theory is similar in spirit to the Lang-Firsov approximation to the polaron problem.[20,21] As stated in the Introduction our focus is on the incoherent tunneling regime, which obtains when the temperature is sufficiently high and the phonon coupling is sufficiently strong, that the renormalized tunneling frequency is vanishingly small. We shall show in the sequel that in the limit of a symmetric two-level system our results for the tunneling rates are identical to those of Flynn and Stoneham.[6] Since our aim is to assess the effect of asymmetry and of tunneling from excited states and its consequences for neutron scattering we restrict our analysis to a straightforward generalization of the Flynn-Stoneham theory. It has been shown recently by de Mello and Ranninger in a simplified version of the two-site polaron problem, in which the phonons are replaced by two localized and independent Einstein oscillators, that the exact quantum mechanics deviates significantly from the Lang-Firsov approximation, in certain parameter regimes.[22] To what extent these deviations are relevant for diffusion of light interstitials is an interesting issue but is beyond the scope of the present investigation.

The energies and frequencies in the Hamiltonian Eq. (16) should be understood as renormalized quantities. A strong coupling between hydrogen and lattice motion has been observed in the vibrational spectrum of the H.[23] It causes a large enhancement of the vibrational mean-square displacement of the H. Its effect has been included, at least partially, in the numerical study of H diffusion,[13,29,5] where the H and its surrounding host atoms are treated as a quasimolecule embedded in the host lattice. Additionally Δ_0 and Δ_1 are renormalized by the coupling to the conduction electrons.[4,5]

C. Averaged time-development operator

As mentioned earlier the angular brackets in Eq. (10) indicate thermal averaging. Thus

$$C(t)=\frac{1}{2}\frac{1}{Z}\mathrm{Tr}[e^{-\beta\mathcal{H}}(\hat{P}_+(0)\hat{P}_+(t)+\hat{P}_+(t)\hat{P}_+(0))], \tag{26}$$

where

$$Z=\mathrm{Tr}(e^{-\beta\mathcal{H}}),\quad \beta=(kT)^{-1}, \tag{27}$$

k being the Boltzmann constant. Recalling that the time-dependent operator $\hat{P}_+(t)$ is defined by an expression similar to Eq. (4) and that the ‘‘trace’’ is invariant under the unitary transformation defined by Eq. (18), we may rewrite Eq. (27) as

$$C(t)=\frac{1}{2}\frac{1}{\tilde{Z}}\mathrm{Tr}[e^{-\beta\tilde{\mathcal{H}}}(\hat{P}_+(0)\tilde{\hat{P}}_+(t)+\tilde{\hat{P}}_+(t)\hat{P}_+(0))], \tag{28}$$

where

$$\tilde{Z}=\mathrm{Tr}(e^{-\beta\tilde{\mathcal{H}}}), \tag{29}$$

and

$$\tilde{\hat{P}}_+(t)=e^{i\tilde{\mathcal{H}}t}\hat{P}_+(0)e^{-i\tilde{\mathcal{H}}t}. \tag{30}$$

In writing Eq. (28) we have also made use of the fact that U commutes with $\hat{P}_+(0)$ (and with other $\hat{P}$’s as well).

It is customary now in the development of perturbation theory to make a factorization assumption, i.e.,

$$e^{-\beta\tilde{\mathcal{H}}}\approx e^{-\beta\mathcal{H}_S}e^{-\beta\mathcal{H}_R}. \tag{31}$$

Correspondingly,

$$\tilde{Z}=Z_S Z_R, \tag{32}$$

with

$$Z_S=1+e^{-\beta\epsilon_1}+e^{-\beta(\epsilon_0+\epsilon_1)} \tag{33}$$

and

$$Z_R = \mathrm{Tr}_R(e^{-\beta \mathcal{H}_R}), \tag{34}$$

where $\mathrm{Tr}_R(\cdots)$ denotes the trace over the reservoir states alone. Using the properties of the projection operator $\hat{P}_+$ [cf. Eq. (8)], we obtain from Eq. (28)

$$C(t) = \frac{e^{-\beta\epsilon_1}}{Z_S}\frac{1}{Z_R}\mathrm{Tr}_R[e^{-\beta\mathcal{H}_R}(++|e^{i\tilde{\mathcal{L}}t}|++)], \tag{35}$$

where $\tilde{\mathcal{L}}$ is the Liouvillean associated with $\mathcal{H}$.[17] (Henceforth, we shall employ $\mathcal{L}$ with an appropriate subscript to denote the Liouvillean associated with $\mathcal{H}_S, \mathcal{H}_I$ or $\mathcal{H}_R$.) In terms of the time-development operator $U(t)$

$$C(t) = \frac{e^{-\beta\epsilon_1}}{Z_S}\frac{1}{Z_R}(++|\mathrm{Tr}_R(e^{-\beta\mathcal{H}_R}\hat{U}(t))|++), \tag{36}$$

where

$$\hat{U}(t) = e^{i\hat{\mathcal{L}}t}. \tag{37}$$

The dynamics of the system is then governed by the *averaged* time-development operator

$$[\hat{U}(t)]_{\mathrm{av}} = \frac{1}{Z_R}\mathrm{Tr}_R(e^{-\beta\mathcal{H}_R}\hat{U}(t)). \tag{38}$$

III. MATHEMATICAL RESULTS

The idea is to treat the interaction $\mathcal{H}_I$ in a systematic perturbation theory treatment and determine the average of $\hat{U}(t)$ upon taking the trace over the eigenstates of the reservoir Hamiltonian $\mathcal{H}_R$. This calculation is most conveniently done in terms of the resolvent of $\hat{U}(t)$ by going over to the Laplace transform of Eq. (38). The resultant averaged time-development operator as a function of the Laplace variable z can be shown to be given, in second-order perturbation theory, by[19]

$$[\hat{U}(z)]_{\mathrm{av}} = [z - i\mathcal{L}s + \hat{\Sigma}(z)]^{-1}, \tag{39}$$

where the ‘‘self-energy’’ $\hat{\Sigma}(z)$ is

$$\hat{\Sigma}(z) = [\mathcal{L}_I(z - i\mathcal{L}_s - i\mathcal{L}_R)^{-1}\mathcal{L}_I]_{\mathrm{av}}. \tag{40}$$

We have shown earlier[19] that the expression in Eq. (39), with the decomposition of the Hamiltonian as in Eq. (22) made possible by the unitary transformation in Eq. (18), leads in a straightforward manner to the results in the so-called dilute bounce gas approximation (DBGA) of an underlying spin-boson Hamiltonian.[14] Considering that DBGA yields excellently accurate results for strong damping and moderately good results even for weak damping especially when the temperature is not too low, we presume the same approach here for the three-level model. Our first task is to evaluate the matrix elements of the ‘‘superoperator’’ $[\hat{U}(z)]_{\mathrm{av}}$ which has a 9×9 matrix representation, for the three-level case. Denoting the states of $\mathcal{H}_S$ by the Greek indices μ, ν, etc., we consider first the elements of $\hat{\Sigma}(z)$. Following the same procedure as in Ref. 19 the requisite 81 elements can be read out from

$$\begin{aligned}(\mu\nu|\hat{\Sigma}(z)|\mu'\nu') = \sum_{nn'}\langle n|\rho_R|n'\rangle\Bigg(&\delta_{\nu\nu'}\sum_{\eta}\frac{\langle\mu n|\mathcal{H}_I|\eta n'\rangle\langle\eta n'|\mathcal{H}_I|\mu' n\rangle}{z - i(E_{n'} - E_n) - i(E_S^{\eta} - E_S^{\nu})} + \delta_{\mu\mu'}\sum_{\eta}\frac{\langle\nu' n|\mathcal{H}_I|\eta n'\rangle\langle\eta n'|\mathcal{H}_I|\nu n\rangle}{z - i(E_n - E_{n'}) - i(E_S^{\mu} - E_S^{\eta})}\\ &-\frac{\langle\mu n|\mathcal{H}_I|\mu' n'\rangle\langle\nu' n'|\mathcal{H}_I|\nu n\rangle}{z - i(E_{n'} - E_n) - i(E_S^{\mu'} - E_S^{\nu})} - \frac{\langle\mu n|\mathcal{H}_I|\mu' n'\rangle\langle\nu' n'|\mathcal{H}_I|\nu n\rangle}{z - i(E_n - E_{n'}) - i(E_S^{\mu} - E_S^{\nu'})}\Bigg).\end{aligned} \tag{41}$$

In the above, we have used the notation $|n\rangle, |n'\rangle$, etc., for the eigenstates of the Hamiltonian $\mathcal{H}_R$ such that

$$\mathcal{H}_R|n\rangle = E_n|n\rangle. \tag{42}$$

In addition, ρ_R is used to designate the density matrix associated with the reservoir:

$$\rho_R = \frac{\exp(-\beta\mathcal{H}_R)}{Z_R}. \tag{43}$$

The strategy now, as indeed in our earlier work,[19] is to write the denominators in Eq. (41) as integrals over time and also to make use of the sum over the reservoir states to express the right-hand side in terms of correlation functions of the reservoir operators $\hat{C}_\pm$ and $\hat{B}_\pm$ [cf. Eq. (21)]. Additionally, we will be interested only in the *incoherent tunneling regime* in which the terms $\mu = \nu$ and $\mu' = \nu'$ are relevant, reducing the number of requisite elements from 81 to 9. Furthermore, the incoherent tunneling regime is the one in which the Markovian approximation is valid and hence we can set z equal to zero. After some algebra, we can collect all the nine terms as follows:

$$(++|\hat{\Sigma}(0)|++) = \Gamma_{0+} + \Gamma_{-+}, \tag{44a}$$

$$(++|\hat{\Sigma}(0)|00) = -\Gamma_{0+}, \tag{44b}$$

$$(++|\hat{\Sigma}(0)|--)=-\Gamma_{-+}, \tag{44c}$$

$$(00|\hat{\Sigma}(0)|00)=\Gamma_{+0}, \tag{44d}$$

$$(00|\hat{\Sigma}(0)|++)=-\Gamma_{+0}, \tag{44e}$$

$$(00|\hat{\Sigma}(0)|--)=0, \tag{44f}$$

$$(--|\hat{\Sigma}(0)|--)=\Gamma_{+-}, \tag{44g}$$

$$(--|\hat{\Sigma}(0)|++)=-\Gamma_{+-}, \tag{44h}$$

$$(--|\hat{\Sigma}(0)|00)=0, \tag{44i}$$

where

$$\Gamma_{0+}=\Delta_0^2\int_{-\infty}^{\infty}dt e^{i\epsilon_0 t}\langle C_-(0)C_+(t)\rangle_R, \tag{45a}$$

$$\Gamma_{+0}=\Delta_0^2\int_{-\infty}^{\infty}dt e^{-i\epsilon_0 t}\langle C_+(0)C_-(t)\rangle_R, \tag{45b}$$

$$\Gamma_{-+}=\Delta_1^2\int_{-\infty}^{\infty}dt e^{-i\epsilon_1 t}\langle B_-(0)B_+(t)\rangle_R, \tag{45c}$$

$$\Gamma_{+-}=\Delta_1^2\int_{-\infty}^{\infty}dt e^{i\epsilon_1 t}\langle B_+(0)B_-(t)\rangle_R. \tag{45d}$$

The quantity $\Gamma_{+0}(\Gamma_{0+})$ has the interpretation of the rate of tunneling from the state $|0\rangle(|+\rangle)$ to $|+\rangle(|0\rangle)$ (cf. Fig. 1). [Similar interpretations can be given for $\Gamma_{-+}(\Gamma_{+-})$.] The correlation functions in Eq. (45) are defined as thermal average over the reservoir states.

Collecting all the terms in Eq. (39) and inverting a 3×3 matrix we obtain

$$(++|[\hat{U}(z)]_{\rm av}|++)=\frac{(z+\Gamma_{+0})(z+\Gamma_{+-})}{z(z+\Lambda_0)(z+\Lambda)}, \tag{46}$$

where the denominator is the determinant of the relevant matrix and $0,\Lambda_0,\Lambda$ are the eigenvalues of the matrix $\hat{\Sigma}(0)$. The latter are given by

$$\Lambda_0+\Lambda=\Gamma_{+0}+\Gamma_{0+}+\Gamma_{+-}+\Gamma_{-+}, \tag{47a}$$

$$\Lambda_0\Lambda=\Gamma_{+0}\Gamma_{+-}+\Gamma_{+0}\Gamma_{-+}+\Gamma_{0+}\Gamma_{+-}, \tag{47b}$$

from which we derive

$$\Lambda_0=\frac{1}{2}(\Gamma_{+0}+\Gamma_{0+}+\Gamma_{+-}+\Gamma_{-+})\left\{1-\left[1-\frac{4(\Gamma_{+0}\Gamma_{+-}+\Gamma_{+0}\Gamma_{-+}+\Gamma_{0+}\Gamma_{+-})}{(\Gamma_{+0}+\Gamma_{0+}+\Gamma_{+-}+\Gamma_{-+})^2}\right]^{1/2}\right\}, \tag{47c}$$

$$\Lambda=\frac{1}{2}(\Gamma_{+0}+\Gamma_{0+}+\Gamma_{+-}+\Gamma_{-+})\left\{1+\left[1-\frac{4(\Gamma_{+0}\Gamma_{+-}+\Gamma_{+0}\Gamma_{-+}+\Gamma_{0+}\Gamma_{+-})}{(\Gamma_{+0}+\Gamma_{0+}+\Gamma_{+-}+\Gamma_{-+})^2}\right]^{1/2}\right\}. \tag{47d}$$

We break Eq. (46) into partial fractions and combine with Eq. (36) to finally write

$$\tilde{C}(z)=\frac{e^{-\beta\epsilon_1}}{Z_S}\left\{\frac{\Gamma_{+0}\Gamma_{+-}}{\Lambda_0\Lambda}\frac{1}{z}+\frac{[\Lambda_0-(\Gamma_{+0}+\Gamma_{+-})+\Gamma_{+0}\Gamma_{+-}/\Lambda_0]}{\Lambda_0-\Lambda}\frac{1}{z+\Lambda_0}+\frac{[\Lambda-(\Gamma_{+0}+\Gamma_{+-})+\Gamma_{+0}\Gamma_{+-}/\Lambda]}{\Lambda-\Lambda_0}\frac{1}{z+\Lambda}\right\}. \tag{48}$$

The transition probabilities have to satisfy the detailed balance relations:

$$p_0\Gamma_{+0}=p_+\Gamma_{0+},\quad p_-\Gamma_{+-}=p_+\Gamma_{-+}, \tag{49}$$

where the p's are the occupation probabilities (Boltzmann factors) given by (see Fig. 1)

$$p_-=\frac{1}{Z_s},\quad p_+=\frac{e^{-\beta\epsilon_1}}{Z_s},\quad p_0=\frac{e^{-\beta(\epsilon_0+\epsilon_1)}}{Z_s}. \tag{50}$$

These relations will be worked out explicitly in Sec. IV. They allow us to simplify the various terms in Eq. (48). For instance, we can show

$$\frac{\Gamma_{+0}\Gamma_{+-}}{\Lambda_0\Lambda}=p_+. \tag{51}$$

Using this and the fact that the first term in Eq. (48) contributes to the elastic component of the structure factor, we find from Eq. (9)

$$S(k,\omega)=\left[1-4(p_+-p_+^2)\sin^2\left(\frac{1}{2}\mathbf{k}\cdot\mathbf{d}\right)\right]\delta(\omega)+\frac{2}{\pi}\frac{\sin^2((1/2)\mathbf{k}\cdot\mathbf{d})}{1+\exp(\omega/kT)}\frac{1}{\Lambda-\Lambda_0}\times\left[\frac{\Lambda^2-\Lambda(\Gamma_{+0}+\Gamma_{+-})+\Gamma_{+0}\Gamma_{+-}}{\omega^2+\Lambda^2}-\frac{\Lambda_0^2-\Lambda_0(\Gamma_{+0}+\Gamma_{+-})+\Gamma_{+0}\Gamma_{+-}}{\omega^2+\Lambda_0^2}\right]. \tag{52}$$

With this, we complete the program set out earlier in Sec. I [see Eqs. (1) and (2)].

The correlation function $C(t)$ can be used to calculate the diffusion constant of H in a lattice. The two wells are viewed to describe two adjacent sites the H can occupy during diffusion, e.g., in the case of Nb:H two tetrahedral interstitial sites in the bcc host. For simplicity we assume that left wells only have right wells as neighbors and vice versa. The diffusion constant is then defined by

$$D=\zeta\left[-\frac{d}{dt}[\langle\mathbf{r}(0)\cdot\mathbf{r}(t)+\mathbf{r}(t)\cdot\mathbf{r}(0)\rangle]\right]_{t=0}$$

$$=2\zeta d^2\left[-\frac{d}{dt}C(t)\right]_{t=0}, \tag{53}$$

where ζ is a geometrical factor for the lattice. From Eq. (53) it is easy to derive that

$$D=\zeta d^2[p_-\Gamma_{+-}+p_0\Gamma_{+0}+p_+(\Gamma_{-+}+\Gamma_{0+})], \tag{54}$$

where the expression inside the square parenthesis is the weighted sum of the partial jump rates.

IV. THE FLYNN-STONEHAM REGIME

In analyzing the correlation function given in Eq. (48) we have to first compute the various transition rates given in Eq. (45). The harmonic nature of the reservoir [cf. Eq. (24)] allows for a calculation of the correlation functions. Thus we have[5]

$$\langle C_-(0)C_+(t)\rangle_R=\langle C_+(0)C_-(t)\rangle_R=\exp\left\{-\sum_{\mathbf{q}}\left(\frac{g_{\mathbf{q}}}{\omega_{\mathbf{q}}}\right)^2\times\left[\coth\left(\frac{1}{2}\beta\omega_{\mathbf{q}}\right)(1-\cos\omega_{\mathbf{q}}t)+i\sin\omega_{\mathbf{q}}t\right]\right\}, \tag{55}$$

where

$$g_{\mathbf{q}}=(G^1_{\mathbf{q}}+G^0_{\mathbf{q}}). \tag{56}$$

Similarly,

$$\langle B_-(0)B_+(t)\rangle_R=\langle B_+(0)B_-(t)\rangle_R=\exp\left\{-\sum_{\mathbf{q}}\left(\frac{G_{\mathbf{q}}}{\omega_{\mathbf{q}}}\right)^2\times\left[\coth\left(\frac{1}{2}\beta\omega_{\mathbf{q}}\right)(1-\cos\omega_{\mathbf{q}}t)+i\sin\omega_{\mathbf{q}}t\right]\right\}, \tag{57}$$

where

$$G_{\mathbf{q}}=2G^1_{\mathbf{q}}. \tag{58}$$

We now go to the continuum limit in which we replace the sum over $\mathbf{q}$ by an integral over the frequency ω of the phonon modes and rearrange the oscillatory terms in the exponents of Eqs. (55) and (57). Thus we have, for example,

$$\langle C_-(0)C_+(t)\rangle_R=\exp\left\{-\frac{1}{2}\int_0^\infty d\omega\frac{j(\omega)}{\omega^2}\left[\coth\left(\frac{1}{2}\beta\omega\right)-\frac{\cos\omega(t-(1/2)i\beta)}{\sinh((1/2)\beta\omega)}\right],\right. \tag{59}$$

where the spectral density of the phonon weight factor is defined as

$$j(\omega)=2\sum_{\mathbf{q}}g^2_{\mathbf{q}}\delta(\omega-\omega_{\mathbf{q}}). \tag{60}$$

Substituting Eq. (59) in Eq. (45a) and changing the contour of integration over t, we obtain

$$\Gamma_{0+}=\Delta_0^2e^{-(1/2)\beta\epsilon_0}\int_{-\infty}^{\infty}dte^{i\epsilon_0t}\exp\left\{-\frac{1}{2}\int_0^\infty d\omega\frac{j(\omega)}{\omega^2}\times\left[\coth\left(\frac{1}{2}\beta\omega\right)-\frac{\cos\omega t}{\sinh((1/2)\beta\omega)}\right]\right\}. \tag{61}$$

It is evident from Eq. (45b) that Γ_{+0} is obtained from Eq. (61) by simply replacing ϵ_0 by $-\epsilon_0$. Similarly,

$$\Gamma_{-+}=\Delta_1^2e^{(1/2)\beta\epsilon_1}\int_{-\infty}^{\infty}dte^{-i\epsilon_1t}\exp\left\{-\frac{1}{2}\int_0^\infty d\omega\frac{J(\omega)}{\omega^2}\times\left[\coth\left(\frac{1}{2}\beta\omega\right)-\frac{\cos\omega t}{\sinh((1/2)\beta\omega)}\right]\right\}, \tag{62}$$

and Γ_{+-} is obtained from Γ_{-+} by replacing ϵ_1 by $-\epsilon_1$, and $J(\omega)$ is obtained from Eq. (61) by replacing $g_{\mathbf{q}}$ by $G_{\mathbf{q}}$.

The so-called Flynn-Stoneham regime is obtained in the high-temperature limit in which the exponent in the second term under the integral (over t) in Eq. (61) can be replaced by its short-time limit. Thus

$$\Gamma_{0+}\approx\Delta_0^2e^{-(1/2)\beta\epsilon_0}\exp\left(-\frac{1}{2}\int_0^\infty d\omega\frac{j(\omega)}{\omega^2}\tanh\left(\frac{1}{4}\beta\omega\right)\right)\times\int_{-\infty}^{\infty}dte^{i\epsilon_0t}\exp\left(-t^2\left(\frac{1}{4}\int_0^\infty d\omega\frac{j(\omega)}{\sinh((1/2)\beta\omega)}\right)\right)$$

$$\approx\Delta_0^2e^{-(1/kT)[E_0+(1/2)\epsilon_0]}\sqrt{\frac{\pi}{4E_0kT}}e^{-\epsilon_0^2/16E_0kT}, \tag{63}$$

where

$$E_0=\frac{1}{8}\int_0^\infty d\omega\frac{j(\omega)}{\omega}. \tag{64}$$

Similarly,

$$\Gamma_{-+}=\Delta_1^2e^{-(1/kT)[E_1-(1/2)\epsilon_1]}\sqrt{\frac{\pi}{4E_1kT}}e^{-\epsilon_1^2/16E_1kT}, \tag{65}$$

where

$$E_1=\frac{1}{8}\int_0^\infty d\omega\frac{J(\omega)}{\omega}. \tag{66}$$

TABLE I. Input parameters ($\epsilon_0,\Delta_0/\Delta_1,\Delta_2/\Delta_0$) and fit parameters ($\Delta_1,E_1$) for the calculation of the diffusion constants of Nb:H and Ta:H shown in Fig. 2 (first three sets of values) and Fig. 3 (last set of values). The asymmetry parameter $\epsilon_1=0$.

	ϵ_0 (meV)	Δ_0/Δ_1	Δ_2/Δ_0	Δ_1 (meV)	E_1 (meV)
Nb:H (Ref. 11)	107	10		4.6	45
Nb:H (Ref. 25)	107	10		2.7	24
Ta:H (Ref. 11)	114	10		2.8	48
Ta:H (Ref. 11)	114	10	10	2.6	46

The transition rates, Eqs. (63) and (65) are essentially determined by three terms, the ‘‘naked’’ tunneling rate, a thermal activation factor and a line-shape term. The activation factor is given by the energy needed to distort the lattice so as to counteract the self-trapping of the hydrogen, i.e., to create a coincidence configuration. The second exponential term together with the square root factor stems from a ‘‘shape factor’’ appropriate for the vibration-level of the hydrogen.

V. DISCUSSION

In the limit of vanishing asymmetry $\epsilon_1=0$ and large excitation energy ($\epsilon_0 \gg kT$) Eqs. (63) and (65) reduce to the usual Flynn-Stoneham (small polaron) result for Γ_{-+} and $\Gamma_{0+}=0$.[6] The energy E_1 is in harmonic approximation the so-called coincidence energy, i.e., the minimal energy needed to distort the host lattice from the self-trapped configuration such that the potential energy of the H is equal in both wells. The same limit would also be obtain for $\epsilon_1=0$ and $\Delta_0 \ll \Delta_1$. This implies however different site occupancies for the H in its ground and excited states, a situation not fully covered by our model. As long as there is no change of H site $\Delta_0>\Delta_1$ will hold. Estimates for the case of Nb:H give $\Delta_0/\Delta_1 \approx 10$.

To test our results we fitted Eqs. (63) and (65) to the experimentally measured diffusion constants of H in Nb and Ta using expression (54). For the sake of simplicity in the analysis, we assume low hydrogen concentrations (α phase) and no trapping sites. The asymmetry will, therefore, play little role and we set $\epsilon_1=0$. The excitation energy of the hydrogen is then given by ϵ_0 for which we take the experimental values.[24] We neglect the difference in the coupling to the lattice of the H in its ground state and its excited state, i.e., we put $E_0=E_1$. To reduce the number of fitting parameters further we use a fixed ratio of the naked tunnel splittings, $\Delta_0=10\Delta_1$. The two remaining fitting parameters for each curve are the ‘‘naked’’ ground-state tunneling rate Δ_1 and the coincidence energy E_1. Figure 2 shows the resulting fit to the experimental values for Ta:H (Ref. 11) and to both the Gorski effect[11] and NMR (Ref. 25) values of Nb:H. The input and the resultant parameters are shown in Table I. Given the simplicity of the model the fit is excellent. The deviations at very high temperatures have to be expected.

The tunneling rate Δ_1 has the magnitude expected from earlier estimates.[12,26] It has been shown in simulations that the second tunneling channel described by Δ_0 is the first one to drive the diffusion rate up, with increasing temperature.[13] Also at higher temperatures other processes such as tunneling between excited states set in. These will have yet higher tunneling rates which counterbalance at high temperatures the higher effective activation energy of $\approx \epsilon_0+E_1$.

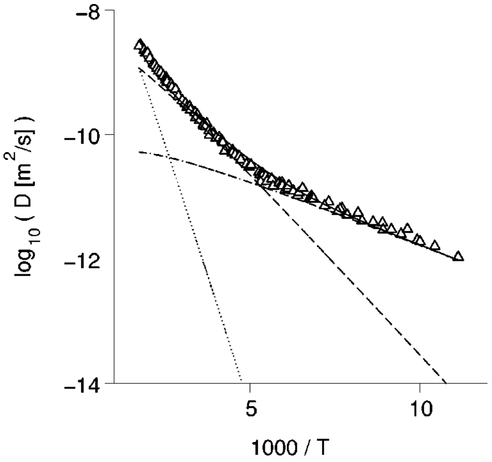

FIG. 3. Diffusion constant of H in Ta (△ indicates experiment (Ref. 11), full line indicates theory including transitions between excited states) and partial diffusion constants (dash dotted indicates ground state – ground state, dashed indicates ground state – excited state, dotted indicates excited state – excited state).

To check this conjecture and the stability of the parameters we repeated the fit including tunneling between excited states as an additional channel. For the rate $\Gamma_{0'0}$ we take the same form as for Γ_{-+} [Eq. (65)] with $\epsilon_1=0$ and Δ_1 replaced by Δ_2. Here $|0'\rangle$ stands for the excited level in the right well. Figure 3 shows the results for Ta:H. The fit is now excellent even at the high temperatures. To show the influence of the three processes, the partial diffusion constants are also shown. With increasing temperature, first ground-state–ground-state, then ground-state–excited state, and finally, excited-state—excited-state processes dominate. As evidenced by the small change in the fit parameters given in Table I the model is fairly stable with regard to inclusion of additional tunneling channels.

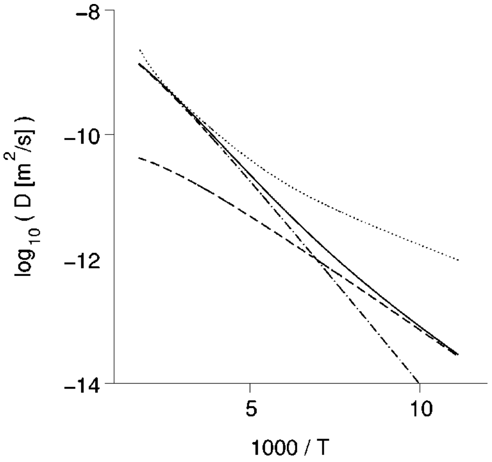

FIG. 4. Diffusion with asymmetric wells, $\epsilon_1=\epsilon_0=1/2\times 114$ meV (solid line). Dashed line indicates ground-state–ground-state contribution, dash dotted line indicates ground-state–excited-state contribution, dotted line indicates the corresponding symmetric case (Ta:H of Fig. 2).

Our model relates directly to the numerical extension[13] of the small polaron model and gives the same interpretation of the mechanisms underlying diffusion. The relation to the ''occurrence probability'' method[27,12] is not so direct. In that method the excitation of the phonon bath providing the energy ϵ_0 needed for the H to tunnel from state $|+\rangle$ to state $|0\rangle$ is included only partially in the averaging over coincidence configurations. The overall conclusion that high-temperature diffusion is by tunneling to excited states also holds in that approach.

A different mechanism for high-temperature diffusion was proposed by Kagan and co-workers.[28,8] There the tunneling rate is increased due to fluctuations in the tunneling barrier. This corresponds to nonlinear terms in the Hamiltonian not included in Eq. (16). The nonlinear terms were however in our earlier simulation[29] found to be too small.

At temperatures where the excited state of the H becomes thermally occupied a delocalization of this state seems to occur.[30,26,12,31] On the other hand, well defined excited states are observed in neutron scattering. Whereas in the first case the lattice relaxes to its thermal equilibrium configuration with respect to the H, involving major displacements of the host atoms, only slight adjustments of the host atom positions are involved in the second case. The H delocalization involves large anharmonic couplings between the H and the lattice not present in our Hamiltonian. Our model is therefore, limited to temperatures where the anharmonicity is not yet too important.

Tunneling in strongly asymmetric potentials ($\epsilon_1 \gg \Delta_1$) will be important for diffusion in alloys. At present, sufficient data are not available[3] to get reliable parameters for an interpretation in terms of our model. To get a qualitative picture of the effect we calculated the diffusion constant using the parameters gained for Ta:H but setting the asymmetry energy to half the excitation energy, $\epsilon_0 = \epsilon_1 = 1/2 \times 114$ meV. The results are shown in Fig. 4 together with the symmetric case. Diffusion is suppressed by asymmetry, particularly at low temperatures, due to the reduction in the thermal occupation of the right well and of the rate Γ_{+-}. The transitions to the excited state in the left well and hence diffusion at higher temperatures are less affected. The additional contribution, not shown in Fig. 4, due to transitions between excited states would again be strongly reduced by asymmetry. On the other hand, at high temperatures, asymmetry might facilitate transitions to other excited states. These effects cannot be incorporated in a simple model such as ours without additional parameters.

ACKNOWLEDGMENTS

This work was carried out when S.D. was a visitor to the Forschungszentrum Jülich. He thanks the Alexander von Humboldt Stiftung for financial support, and Professor H. Müller-Krumbhaar and his group for their warm hospitality. He and H.R.S. acknowledge lasting collaborations with Professor H. Grabert and Professor A. M. Stoneham.

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