Relaxation Dynamics of Multi-Level Tunneling Systems*

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Abstract

A quantum mechanical treatment of an asymmetric double-well potential (DWP) interacting with a heat bath is presented for circumstances where the contribution of higher vibrational levels to the relaxation dynamics cannot be excluded from consideration. The deep quantum limit characterized by a discrete energy spectrum near the barrier top is considered. The investigation is motivated by simulations on a computer glass which show that the considered parameter regime is “typical” for DWPs being responsible for the relaxation peak of sound absorption in glasses. Relaxation dynamics resembling the spatial- and energy-diffusion-controlled limit of the classical Kramers’ problem, and Arrhenius-like behavior is found under specific conditions.

*Appears in the Journal of Chemical Physics.
I. INTRODUCTION

Relaxational dynamics of materials which evolve under slow structural change at low temperature can frequently be studied in a double-well potential (DWP) picture that allows tunneling between the two wells. A prototype of such a system, important in many chemical and biological systems, is the transfer of hydrogen atoms along preexisting hydrogen bonds for instance in crystalline benzoic acid and carboxyl dimers. Another example is the tunneling of SiO$_4$- or GeO$_4$-tetraeder in amorphous SiO$_2$ and GeO$_2$.

One of the key issues in understanding the relaxation process is the coupling of the motion of the light tunneling particle to the heavier surrounding atoms constituting the heat bath. In a condensed phase the coupling leads to structural rearrangements of the environment which provides a mechanism of relaxation for the system.

The theoretical description of dissipative DWP-dynamics has been widely elaborated in the low temperature limit where a two-level description (spin-boson model) is sufficient. At higher temperatures where the excitation of vibrational levels can no longer be neglected, the effect of intra-well relaxation has been given explicitly by Silbey and coworkers for a symmetric DWP. Lateron Meyer and Ernst considered a biased DWP with crystalline benzoic acid dimer as an example. In both papers the investigations have been restricted to a regime where the tunneling splitting $\Delta_n$ of all relevant doublets is still very much less than the interdoublet spacing, i.e., $\Delta_n \ll \omega_0$ where $\omega_0$ is the frequency of small oscillations around the two minima of the DWP. They found in the limit of fast intra-well vibrational relaxation – where the population of the doublets is in thermal equilibrium – that the escape rate is the thermally averaged tunneling rate into the lower well,

$$k_t = \frac{1}{2} \langle \Gamma \rangle \beta.$$ (1.1)

In many practical applications, however, whenever the two-state approximation seemed no longer sufficient, a simple classical relaxation over the barrier $V$ with an Arrhenius rate

$$k_{cl} = \frac{\omega_0}{2\pi} e^{-V/k_BT}.$$ (1.2)
has been used successfully.

Hence, concerning the understanding of relaxation dynamics in many chemical and physical systems at higher temperatures, two questions are of major importance: (i) How dense are the energy levels of the DWP as compared to the potential height, i.e., is the classical picture underlying Eq. (1.2) justified, or does the relaxation dynamics depend on the quantum mechanical eigenvalues of the DWP? (ii) Is the DWP coupled to bath modes with frequencies of the order of its potential height, and does the relaxation dynamics depend on the parameters of the heat bath?

In this work these questions are analyzed for the specific example of DWPs in a structural glass. There DWPs correspond to the motion of a local group of atoms or molecules between two local energy minima. Low barrier DWPs are known to be the source for the tunneling properties observed in glasses like SiO$_2$ below 10 K. In contrast, DWPs with higher barriers (in SiO$_2$: $\langle V_{\text{peak}} \rangle / k_B \approx 500$ K) are believed to be responsible for the relaxation peak of sound absorption, observed around 50 K in SiO$_2$. Our goal is to answer the above questions for these DWPs in order to obtain a closer understanding of the relaxation dynamics at the absorption peak.

To this aim we first perform in Sec. 2 computer simulations on a model glass to determine the eigenvalue spectrum and the interaction with phonons of those DWPs which are responsible for the relaxation dynamics in glasses at higher temperatures. We find that DWPs relevant at the sound absorption peak only contain a few energy levels below the their barrier height $V$ and are coupled to bath modes with frequencies as large as $V$. This serves us as a motivation to analyse the relaxation dynamics in a single DWP as depicted in Fig. 1 which is characterized by the parameter regime

$$k_B T \lesssim \hbar \omega_0 \lesssim V,$$

for instance, $T \approx 30 - 50$ K, $V/k_B \approx 300$ K and $V/\hbar \omega_0 \approx 2$. In Sec. 3 a simple model is presented which allows an analytical solution of the relaxation dynamics by applying standard approximation, as shown in Sec. 4. With this model we can discuss in Sec. 5 the
apparent paradox that a classical Arrhenius rate does well in many practical applications although the relaxation dynamics is far from being classical. In Sec. 6 we close with a short summary.

II. SIMULATIONS

In previous work Heuer and Silbey have developed an algorithm which systematically searches for DWPs in glasses simulated on the computer. This algorithm has been readily applied to the specific case of NiP which can be described as a binary Lennard-Jones-type glass. For general reasons one expects that $V_{\text{peak}}$ is approximately proportional to the glass transition temperature. Hence from $T_g(\text{NiP})/T_g(\text{SiO}_2) \approx 2/3$ one may roughly estimate $V_{\text{peak}}(\text{NiP})/k_B \approx 300$ K. We proceed in two steps. First we present a rough estimation of the number of energy levels in DWPs with $V \approx V_{\text{peak}}$. Second we explicitly determine for the NiP computer glass the interaction of the DWP with the heat bath.

For the estimation of the number of energy levels below the potential height it is sufficient to consider a symmetric DWP. The potential energy along the reaction coordinate $x$, which is defined as the collective coordinate connecting the two local energy minima, can be expressed as a quartic polynomial

$$V(x) = \frac{16V}{d^4}(x - \frac{d}{2})^2(x + \frac{d}{2})^2$$

where $V$ is the potential height and $d$ the distance of both minima. We chose the DWP symmetric around $x = 0$. The length scale $d$ is defined such that the collective dynamics along this DWP can be viewed as the dynamics of a single particle with mass $m$ where $m$ is the average mass of the atoms (for NiP $m = 56m_p$ with $m_p$ the proton mass).

It is straightforward to calculate the vibrational frequency $\omega_0$ in both wells as

$$\omega_0^2 = \frac{32V}{md^2}.$$  \hspace{1cm} (2.2)

In Ref. it has been shown that for NiP the value of the prefactor $16V/d^4$ of the quartic term for symmetric DWPs on average is given by $BA_4/a^4$ with $B/k_B = 4.3 \times 10^4$ K, $A_4 = 0.39$.
and \( d = 2.2 \times 10^{-10} \text{m} \). Elimination of \( d \) in Eq. (2.2) yields \( \omega_0^2 = 8 \sqrt{VBA_4/(ma^2)} \). Inserting the numbers for NiP given above yields for \( V/k_B = 300 \text{ K} \) that

\[ V/h\omega_0 \approx 5.5. \]  (2.3)

This value should be viewed as an upper limit since for DWPs with large barrier heights the quartic contribution is expected to be even larger than the average contribution. However, this would only reduce the number of energy levels below the barrier height.

For evaluating the coupling to the bath modes we analyzed a NiP computer glass with \( N = 500 \) atoms using periodic boundary conditions. The simulations have been performed at zero temperature; details can be found in Refs. 15,16. To first approximation the energy surface of the computer glass adjacent to the DWP can be written as

\[ H = H_0(x) + x \sum_j \lambda_j y_j + \frac{1}{2} m \sum_j \omega_j^2 y_j^2 \]  (2.4)

where \( H_0(x) \) describes the relaxation mode in the DWP, \( \omega_j \) the frequencies, \( y_j \) the coordinates of the bath modes, and \( \lambda_j \) the coupling of the bath modes to the DWP. This potential energy term contains the full anharmonicity with respect to the DWP mode. The other degrees of freedom are only considered up to their harmonic contributions. Of course, in order to obtain the full Hamiltonian of the system one has to add the kinetic energy of the relaxation mode and of the bath modes. For our simulation we chose a DWP with \( V/k_B \approx 300 \text{ K} \). Starting from one minimum we calculated all second derivatives of the energy with respect to the positions of all 500 atoms, yielding a \( 3N \times 3N \) dimensional matrix \( A \). Let \( \hat{d} \) denote the unit vector in the \( 3N \)-dimensional configuration space connecting both minima of the DWP. The matrix \( A \) is diagonalized in the space orthogonal to \( \hat{d} \), yielding eigenvalues \( a_j \) and eigenvectors \( \hat{e}_j \). The corresponding eigenfrequencies \( \omega_j \) are given by \( \omega_j = \sqrt{a_j/m} \). Three eigenvalues equal to zero reflect the periodic boundary conditions. The coupling parameters \( \lambda_j \) are calculated via \( \lambda_j = \hat{d} A \hat{e}_j \). It is worth noting that our vector \( \hat{d} \) which is just a straight line path between the two minima of the DWP is not the reaction path between the two wells, which would be curvilinear. However, the simulations in Refs. 15,16 have shown that the curvature of the reaction path is not very large.
Later on it turns out that the relevant quantities describing the coupling strength of the
bath modes to the DWP is the spectral densities

\[ J(\omega) = \frac{2}{\hbar^2} \sum_j c_j^2 \delta(\omega - \omega_j) \]  

(2.5)

where

\[ c_j = \sqrt{\frac{\hbar}{2m\omega_0}} \sqrt{\frac{\hbar}{2m\omega_j} \lambda_j} . \]  

(2.6)

\( J(\omega) \) is plotted in Fig. 2. One can clearly see that bath modes exist for all frequencies
smaller than 400 K. As a result, DWPs relevant at the sound absorption peak which only
contain a few energy levels below the their barrier height \( V \) are coupled to bath modes with
frequencies as large as \( V \). The high-frequency modes are somewhat more localized that the
average modes and contain the dynamics of the order of 100 atoms. Such an effect has been
already observed in previous simulations.17

A closer inspection of the data shows that the coupling is strongly anharmonic. This
can be easily checked by repeating the above procedure calculating the second derivatives
at different points along the reaction coordinate. It turns out that the \( \lambda_j^2 \) and \( \omega_j \) of the
individual modes strongly vary along \( \hat{d} \) whereas the distribution function \( J(\omega) \) is insensitive.
The reason for this is that \( J(\omega) \) arises from an ensemble average over a large number of
oscillators whose parameter variations are statistically independent in a first approximation.
However, one should keep in mind that due to the finite size of the simulation box we
do not obtain the low-frequency phonons in the Kelvin-regime which are relevant for the
transitions between both minima at low temperatures. For those phonons one expects that
the anharmonic contributions are significantly smaller. A more detailed discussion of the
anharmonicities is beyond the scope of the present paper.

### III. THE MODEL

We now construct a simple model which governs the relaxation dynamics of the relevant
DWPs. For reasons of simplicity we restrict ourselves to only two pairs of tunneling doublets
below the barrier.

The phonons couple to the tunneling coordinate. Their effect is two-fold: They induce vibrational transitions between the eigenstates of the DWP and destruct the tunneling coherence within each doublet. Concerning the first effect we assume that barrier penetrating transitions are negligible. The relevant matrix element between the localized states reads

\[
M = \langle 0\alpha | H | 1\alpha \rangle = \sum_j c_j^{(v)} (b_j + b_j^\dagger)
\]  

(3.1)

with phonon operators satisfying \([b_j, b_{j'}^\dagger] = \delta_{jj'}\) and the coupling constants \(c_j^{(v)} \equiv c_j\) of each mode. Here, the first index labels the doublet and \(\alpha = L, R\) the left and right well. The second effect of the phonon coupling is modeled by a diagonal coupling which detunes \(|nL\rangle\) against \(|nR\rangle\) \((n, m = 0, 1)\). The corresponding matrix elements read

\[
e = \frac{1}{2}(\langle nR | H | nR \rangle - \langle nL | H | nL \rangle) = \sum_j c_j^{(t)} (b_j + b_j^\dagger)
\]

(3.2)

with (note that \(\frac{1}{2}(\langle nR | x | nR \rangle - \langle nL | x | nL \rangle) \approx d\))

\[
\frac{c_j^{(v)}}{c_j^{(t)}} = \frac{\langle 0\alpha | x | 1\alpha \rangle}{d} \equiv \kappa.
\]

(3.3)

Corresponding to \(c_j^{(v)}\) and \(c_j^{(t)}\) we also define the spectral densities \(J_v(\omega) \equiv J(\omega)\) and \(J_t(\omega) \equiv \frac{1}{\kappa^2} J(\omega)\) where \(J(\omega)\) has been defined in (2.5).

In case of our computer glass the factor \(\kappa\) can be estimated for symmetric DWPs as given by Eq. (2.4). Since \(\langle 0\alpha | x | 1\alpha \rangle = \sqrt{\hbar/2m\omega_0}\) one directly obtains from Eq. (2.2) and Eq. (2.3) \(\kappa \approx 0.05\). Hence, though the intra-well vibrational transition \(M\) may be considered as a weak perturbation, the diagonal coupling \(e\), generally, may not. The main reason for this is the “polaron effect”, i.e., the slowing down of the tunneling transition associated with the shift of the oscillator coordinates into the other well.

As mentioned in Refs. 3,13 a suitable decomposition of the Hamiltonian for second order perturbation theory is achieved by the polaron transformation \(\sigma^n_z = |nL\rangle\langle nL| - |nR\rangle\langle nR|\)
\[ e^S = \exp \left[ -\sum_n \sigma_n^z \sum_j \frac{c_j(t)}{\hbar \omega_j} (b_j - b_j^\dagger) \right]. \quad (3.4) \]

We denote the energy separation of the pair of tunneling doublets by \( \Delta E = \hbar \omega_{01}/2 \) and the asymmetry by \( \Delta < \hbar \omega_{01} \) (otherwise the states isolated in the lower well will drop out of the dynamics and the doublets have to be redefined). Now we may eventually define our model Hamiltonian. With the shift operator

\[ B_\pm = \exp \left\{ \pm \sum_j \frac{2c_j(t)}{\hbar \omega_j} (b_j - b_j^\dagger) \right\} \quad (3.5) \]

and the tunneling frequency renormalized by a Debye-Waller factor \( \langle B_\pm \rangle \equiv e^{-W(T)} \) (see Appendix A),

\[ \tilde{\Delta}_n = \Delta_n e^{-W(T)} \quad (3.6) \]

it reads in the localized basis \( |0L\rangle, |0R\rangle, |1L\rangle, |1R\rangle \)

\[ H = H_0 + H_B + H_{\text{int}} \]

\[ = \begin{pmatrix} \frac{1}{2} \Delta & \frac{1}{2} \hbar \tilde{\Delta}_0 & 0 & 0 \\ \frac{1}{2} \hbar \tilde{\Delta}_0 & -\frac{1}{2} \Delta & 0 & 0 \\ 0 & 0 & \hbar \omega_{01} + \frac{1}{2} \Delta & \frac{1}{2} \hbar \tilde{\Delta}_1 \\ 0 & 0 & \frac{1}{2} \hbar \tilde{\Delta}_1 & \hbar \omega_{01} - \frac{1}{2} \Delta \end{pmatrix} + H_B \]

\[ + \begin{pmatrix} 0 & \frac{1}{2} \hbar \Delta_0 \delta B_- & M & 0 \\ \frac{1}{2} \hbar \Delta_0 \delta B_+ & 0 & 0 & M \\ M & 0 & 0 & \frac{1}{2} \hbar \Delta_1 \delta B_- \\ 0 & M & \frac{1}{2} \hbar \Delta_1 \delta B_+ & 0 \end{pmatrix} \quad (3.7) \]

where \( \delta B_\pm = B_\pm - \langle B_\pm \rangle_B \), and \( H_B = \sum_j \hbar \omega_j b_j^\dagger b_j \). Our goal is to apply second order perturbation theory in \( H_{\text{int}} \). In this approximation the intra-well dynamics is governed by the one-phonon transition between the vibrational levels, i.e., by the Orbach process. In case of more than two doublets below \( V \), we have to sum over all pairs (see below). We note in passing that the spectral density \( J(\omega) \) only holds for transitions from level 0 to level 1. For
transitions changing the vibrational quantum number more than one the transition matrix elements are only due to the anharmonicity of the potential and the interaction. This may lead to a somewhat decreased spectral density. However, since we are only interested in an order of magnitude estimation of the coupling to the bath we do not analyse the influence of anharmonicities on the coupling in greater detail. Rather we state that for the observed weak intra-well coupling (as compared to inter-well coupling due to $\kappa \ll 1$) the Orbach process is indeed the dominant relaxation mechanism.

IV. DYNAMICS

To determine the time evolution of the tunneling doublets we make use of Mori’s projection operator technique. We adopt throughout the paper the fast vibrational relaxation limit which is relevant for most experimental situations. Denoting the downwards vibrational transition rate between the two doublets by $\gamma_{01}$ and the tunneling escape rate in the other well (inter-doublet transition rate) by $\Gamma_0$ and $\Gamma_1$, this means that we assume

$$\Gamma_0, \Gamma_1 \ll \gamma_{01} \quad (4.1)$$

This guarantees local thermal equilibrium in each well. The relaxation rates are defined in Appendix A. For weak coupling between the vibrational levels and in the temperature regime (1.3), the upwards vibrational rate $\gamma_{10} \equiv \gamma_{01} e^{-\beta \hbar \omega_{01}}$ is typically much smaller than the level spacing

$$\epsilon_n = \sqrt{\Delta^2 / \hbar^2 + \Delta_n^2} \quad (4.2)$$

of the two doublets [cf. Fig. 1]. Furthermore, due to the strong increase of the tunneling matrix element near the barrier top, the ground state spacing is much less than the spacing near the barrier top. Hence we are interested in the regime $\gamma_{10} \ll \epsilon_0 \ll \epsilon_1$ with no fixed relation between $\gamma_{01}$ and $\epsilon_0, \epsilon_1$.

Relaxation dynamics is probed in long time or low frequency experiments where the time scale of the experiment is far off any resonant time scale of the system. Thus, any coherency
has already decayed and the system shows pure decay. The experimentally accessible quantity is the population difference between the two wells. The relevant operator measuring this quantity is

\[ Q = \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & -1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & -1
\end{pmatrix}. \] (4.3)

Its thermal expectation value reads

\[ \langle Q \rangle = -\tanh(\beta \Delta/2). \] (4.4)

In linear response theory all information is contained in the symmetrized correlation function of the relevant operator

\[ C(t) = \frac{1}{2} \langle \delta Q(t) \delta Q \rangle + t \leftrightarrow -t \]
\[ = \frac{1}{2} \text{Tr} \left[ \varrho \delta Q e^{-i\mathcal{L}t} \delta Q \right] + t \leftrightarrow -t \] (4.5)

where \( \delta Q = Q - \langle Q \rangle \), and \( \mathcal{L} = \hbar^{-1}[H,*] \) is the Liouvillian. Due to local thermal equilibrium in each well, the density matrix is given in the canonical form \( \varrho = \exp(-\beta H_d)/\text{Tr} \exp(-\beta H_d) \) with a Hamiltonian \( H_d \) which contains only the diagonal part of \( H_0 \) in the localized basis.

The spectral function \( C(\omega) = (1/2) \int_{-\infty}^{\infty} C(t) e^{i\omega t} dt \) can be directly measured in neutron scattering experiments, or via the dynamical susceptibility in acoustic or dielectric experiments.

In Appendix B we calculate in second order perturbation theory in \( H_{\text{int}} \) the correlation function (4.3) by using Mori’s continued fraction representation for the complex correlation function \( C(\lambda) = \int_0^\infty e^{-\lambda t} C(t) dt \) (Re(\( \lambda \)) > 0). After inverse Laplace transformation we find in the limit \( \lambda \to 0 \) [cf. Eq. B.5] our final result

\[ C(t) = \langle (\delta Q)^2 \rangle e^{-2kt} \] (4.6)

with \( \langle (\delta Q)^2 \rangle = \text{sech}^2(\beta \Delta/2) \) and the escape rate

\[ k = k_t + k_v. \] (4.7)
The tunneling rate $k_t$ is given by the usual small polaron expression averaged over the thermal level occupation

$$k_t = \frac{1}{2} \langle \Gamma_0 + \Gamma_1 \rangle_\beta$$

$$= \frac{1}{\hbar} \int_{-\infty}^{\infty} dt \frac{\langle \tilde{\Delta}_0^2 + \tilde{\Delta}_1^2 \rangle_\beta \cos(\Delta t/\hbar) \left( \cos[g_1(t)] e^{g_2(t)} - 1 \right)}{\cos^2 g_1(t) e^{g_2(t)} - 1}$$

where

$$\langle \tilde{\Delta}_0^2 \rangle_\beta = \frac{\Delta_0^2}{1 + e^{-\beta \hbar \omega_{01}}}$$

$$\langle \tilde{\Delta}_1^2 \rangle_\beta = \frac{\Delta_1^2}{e^{\beta \hbar \omega_{01}} + 1}.$$  

In the fast vibrational relaxation (4.1), the effect of the vibrational transitions enters $k_t$ only through the thermal occupation number of the localized states.

The vibrational relaxation rate

$$k_v = \frac{1}{2} \frac{\tilde{\Delta}_1^2}{\epsilon_1^2 + \gamma_0^2} \frac{\gamma_{01}}{e^{\beta \hbar \omega_{01}} + 1}$$

is characterized by the ratio of the doublet splitting $\epsilon_1$ and the equilibration rate $\gamma_{01}$ between vibrational levels. This type of expression for $k_v$ has first been proposed by Sussmann on ground of a simple wave function argument. For $\Delta = 0$ it is identical to the transition rate between $E$ and $A$ symmetric states in a rotational tunneling problem.

V. DISCUSSION

A. Analogy to the spatial- and energy-diffusion-controlled limit

Our results can be summarized in the following physical picture. There exist two relaxation mechanism for a particle in the energetically instable well: (1) Incoherent tunneling with rate $k_t$ within the thermally occupied tunneling doublets, or (2) vibrational transition to a non-thermally occupied doublet of higher energy, coherent tunneling within the doublet and vibrational decay to the lower well which results in a rate $k_v$. This interpretation also
follows nicely from the projection operator method used in Appendix B. Relevant degrees of freedom are the diagonal terms in $H_0$, i.e., the population in the left and right well. In a projection operator formalism, relevant degrees of freedom (projected out by $\mathcal{P}$ at an earlier time $t' < t$) couple via an interaction ($\mathcal{L}$) to irrelevant degrees of freedom (projected out by $\mathcal{Q}$), which subsequently evolve in time ($\mathcal{QLQ}$) and, due to a second interaction ($\mathcal{L}$), acquire relevancy again, thus influencing the evolution of the relevant degrees of freedom at the present time $t$. Eqs. (B.6) and (B.7) are just the Laplace transform of the kernel describing this process. Now, $k_t$ propagates that part of the irrelevant degrees of freedom which destruct coherence of the relevant degrees of freedom, i.e., $\Delta_n \delta B_\pm$, whereas $k_v$ propagates that part which maintains coherence, i.e., $\tilde{\Delta}_n$.

Process (1) has been discussed by Parris and Silbey\cite{13} and Meyer and Ernst\cite{3}. This process always prevails if $\gamma_{01} \gg \epsilon_1$ because then the particle has no time for tunneling before decaying from the upper doublet. In this case the preexponential factor of $k_v$

$$f_{01} = \frac{1}{2} \frac{\tilde{\Delta}_1^2 \gamma_{01}}{\epsilon_1^2 + \gamma_{01}^2}$$

(5.1)

is approximately $f_{01} \approx \tilde{\Delta}_1^2/2\gamma_{01}$. This is the quantum analog of the spatial-diffusion-controlled limit in the classical Kramers’ problem.\cite{20} The escape to the other well is hindered by the damping of the tunneling motion, i.e., $k \approx k_t$. The tunneling escape rate $k_t$ is given by the Boltzmann-weighted average of the tunneling equilibration rate within each tunneling doublet at given vibrational level. This equilibration is hindered by the distortion of the lattice in the tunneling process, i.e., by the polaron effect. The suppression of the vibrational rate for $\gamma_{01} \gg \epsilon_1$ can be thought off as a phonon bottleneck effect.\cite{23} The physical reason for the suppression of $k_v$ is that phonons resonating between the upper and the lower level of two different tunneling doublets are not distinct because the level width exceeds the doublet spacing. As a result one cannot add up their rates. Instead they can interfere resulting in a suppression of $k_v$.

Process (2) has first been proposed by Sussmann\cite{23} on ground of a simple wave function argument. It prevails provided that (i) the vibrational transition to the upper doublet is
faster than the direct decay via incoherent tunneling,

\[ \gamma_{10} \equiv \gamma_{01} e^{\frac{\hbar \omega_{01} \Gamma}{k_B T}} > \Gamma_0 , \]

and, necessarily, if \( \text{(ii)} \) the decay of the excited state is slower than the tunneling process, \( \gamma_{01} < \epsilon_1 \). In this case the particle has sufficient time for oscillating coherently from and back in the upper level, and, therefore, a maximal, i.e., 50% probability for decaying in the other well. As a result the energy transport to the barrier top becomes the rate limiting process, i.e., \( k \approx k_v \). This is the situation analogous to the energy-diffusion-controlled limit in the classical Kramers’ problem. It should be noted that the quantity which determines the frequency of coherent oscillations is the doublet spacing \( \epsilon_1 = \sqrt{\Delta_1^2 + \Delta^2 / \hbar^2} \) and not the tunneling frequency \( \Delta_1 \). Hence, the asymmetry acts in suppressing the bottleneck effect.

Clearly process (2) becomes increasingly likely with increasing temperature. Eq. (5.2) defines a transition temperature \( T^* \). Furthermore a large \( \epsilon_1 \) is needed. Hence, upper doublets with energies of \( O(V) \) are preferable.

**B. Apparent Arrhenius behavior**

Now we present a derivation of an apparent Arrhenius behavior at higher temperatures with an activation energy \( O(V) \). We still consider the situation where the eigenvalues are discrete and not dense at \( E \approx V \). Our previous results are now generalized to many pairs by noting that the total rate is the sum over all pair rates weighted by the Boltzmann occupation factor of the initial state. We denote the (downwards) equilibration rate between the \( m \)th and the \( n \)th vibrational state \( n < m \) by \( \gamma_{nm} \). This provides the rate

\[ k = k_t + k_v \]

\[ = \left( \frac{1}{2} \sum_n \Gamma_n e^{-\beta E_n} + \sum_{n < m} f_{nm} / [e^{\beta E_m} + e^{\beta E_n}] \right) / \sum_n e^{-\beta E_n} . \]

(5.3)

with

\[ f_{nm} = \frac{1}{2} \frac{\tilde{\Delta}_m^2 \gamma_{nm}}{\epsilon_m^2 + \gamma_{nm}^2} \]

(5.4)
For \((n = 0, m = 1)\) the term for \(k_v\) boils down to Eq. (4.11). Now we consider the relaxation of a single DWP with given parameters. As discussed above for \(T > T^*\) the relaxation is mainly determined by \(k_v\). In order to obtain the temperature dependence one has to check by which doublets \((n, m)\) this term is dominated. As a first approximation we neglect the dependence of \(\gamma_{nm}\) on \(n\) and \(m\), hence introducing a single value of \(\gamma\). Then \(f_{nm}\) only depends on \(m\). This may be a poor approximation. However, since other quantities like the tunneling matrix element or the Boltzmann factor exponentially depend on the indices this approximation is sufficient for our present purposes.

We now ask by which value of \(m\) the term \(f_{nm}\) is dominated. We first note that only doublets with \(\epsilon_m > \gamma\) can avoid the bottleneck effect, and that, even among those, doublets with \(\Delta m/\Delta \ll 1\) are unimportant. Evidently, \(f_{nm}\) cannot grow beyond \(\gamma/2\) — the strict maximum is only reached for \(\Delta m \to \infty\). However, already for

\[
\Delta m^2 = \Delta^2/\hbar^2 + \gamma^2
\]  

(5.5)

the value \(\gamma/4\) is reached. Hence, Eq. (5.5) is an appropriate criterion that \(f_{nm}\) is close to its maximum value. One can estimate from the numerical data that the average value of \(\pi J(\omega)k_B/\hbar\) is of the order of 30 K. Having in mind that this estimation may be somewhat too large (see Sec. 3) we may estimate \(\gamma h/k_B = O(10\text{ K})\). This is somewhat smaller but of the same order as the numerical value we have found for \(\omega_0\). Hence, at least for asymmetric DWPs, criterion (5.5) can hardly be fulfilled for real systems. However, doublets which come closest to (5.5) will still dominate \(f_{nm}\). Evidently, these are levels \(m\) close to the barrier. This is related to the exponential dependence of the tunneling matrix element on the energy of the corresponding level. Only close to the barrier the maximum value \(\Delta \approx 2\omega_0/\pi\) is reached.

Additionally taking into account the Boltzmann factor one can see that all levels \(n\) contribute as long as \(\exp(\beta E_m) \gg \exp(\beta E_n)\). For \(\beta E_m \gg 1\) this implies that most levels \(n\) indeed contribute.

Summarizing the arguments presented above we obtain
\[ k_v \approx \tau_0^{-1} e^{-\beta \Delta U} \]  \hspace{1cm} (5.6)

with an activation energy \( \Delta U = O(V) \) and a prefactor \( \tau_0^{-1} \) which is of the order \( \gamma/4 \times m \).

The latter factor results from the summation of most of the states below the \( m \)-th level. Since our numerical results indicate that \( \gamma \) is somewhat smaller but close to \( \omega_0 \) we may write \( \tau_0^{-1} \approx O(\omega_0/2\pi) \). As a surprising result, for sufficiently high temperatures, \( T > T^* \) such that \( k_v \gg k_t \), the relaxation rate between the two wells is an effective Arrhenius rate where both the prefactor and the activation energy are of the same order of magnitude as in the classical limit.

VI. SUMMARY AND CONCLUSION

The intension of this work was to investigate the remarkable success of fitting relaxation data of disordered solids at higher temperatures by a simple Arrhenius rate despite the fact the underlying classical picture might not be justified automatically.

Due to the lack of knowledge of microscopic DWPs in disordered solids we have used numerical simulations on a computer glass to characterize the DWP and the bath modes before solving the dynamics for this particular situation. It should be noted that these simulations have proven to be reliable by reproducing characteristic low-temperature properties of glasses\(^{15,16}\). Hence, the parameter regime for which we have solved the dynamics can be considered as “typical” for structurally disordered solids. The simulations have taught us that DWPs relevant at the sound absorption peak, i.e., those with large \( V \), only contain a few energy levels below their barrier height \( V \) and are coupled to bath modes with frequencies as large as \( V \).

To resolve the paradox to the apparent classical behavior we have constructed a simple model of two tunneling doublets which are coupled by intra-well vibrational transitions. Independently of how closely this model reflects the true physical situation in detail, it has provided a simple physical picture how even in this deep quantum mechanical regime an apparent Arrhenius behavior might emerge. Solving our model by standard approximations
we could confirm the suggestion of Sussmann: at high temperatures the vibrational transition to a doublet near the barrier top, followed by coherent tunneling between the wells and vibrational decay to the bottom becomes a faster relaxation mechanism than direct decay via incoherent tunneling. Clearly the derivation which eventually led to the Arrhenius rate (5.6) is very scetchy. In general there will be corrections to the term satisfying (5.3) which are in the present formulation difficult to quantify. Furthermore, if more than two doublets are involved, it is difficult to define quantitatively the transition temperature $T^*$ which separates the tunneling from the vibrational dominated regime. Hence, generally, both terms $k_t$ and $k_v$ may contribute and the Arrhenius rate has to be viewed as an idealization.

However, we believe that the picture drawn provides a physical intuition on the remarkable fact that a simple Arrhenius rate is so successfull in explaining relaxation data even just above temperatures where the quantum mechanical tunneling effect had dominated the relaxation dynamics. In addition to this it is reasonable to expected that in disordered solids like glasses the detailed form of the barrier distribution function has a much greater impact than possible corrections to the Arrhenius rate. Hence, the customary application of this rate for practical purposes can be justified *a posteriori* by the present picture even in the deep quantum regime.

**ACKNOWLEDGMENTS**

Helpful discussion with H. Horner, R. Meyer, D. R. Reichman and R. J. Silbey are gratefully acknowledged. This work has been financially supported by the NSF and the Alexander von Humboldt foundation.

**APPENDIX A: BATH CORRELATION FUNCTIONS AND RELAXATION RATES**

Assuming that the bath is not disturbed by the DWP we can calculate bath correlation functions with $H_B$ and $e_B = \exp(-\beta H_B)/Z_B$. Defining
\[ g(t) = \frac{\hbar^2}{2} \int_0^\infty d\omega \ J_v(\omega) \left( n(\omega) e^{i\omega t} + (n(\omega) + 1) e^{-i\omega t} \right) \]  
(A.1)

\[ g_1(t) = 2 \int_0^\infty d\omega \frac{J_1(\omega)}{\omega^2} \sin(\omega t) \]  
(A.2)

\[ g_2(t) = 2 \int_0^\infty d\omega \frac{J_1(\omega)}{\omega^2} \coth(\beta \hbar \omega / 2) \cos(\omega t) \]  
(A.3)

\[ W(T) = \frac{1}{2} g_2(0) \]  
(A.4)

the bath correlation functions read

\[ \langle B_+(t) B_- \rangle_B = \langle B_-(t) B_+ \rangle_B = \langle B_+ B_- (t) \rangle_B^* = \langle B_- B_+ (t) \rangle_B^* \]

\[ = \exp \left[ g_2(t) - i g_1(t) \right] e^{-2W(T)} \]  
(A.5)

\[ \langle M(t) M \rangle_B = g(t) \]  
(A.6)

Furthermore, we need the following modification of the vibrational relaxation function

\[ g_\pm(\omega_0, t) = e^{i\omega_0 t} \frac{\hbar^2}{2} \int_0^\infty d\omega \ J_v(\omega) \left( n(\omega) e^{\pm i\omega t} + (n(\omega) + 1) e^{\mp i\omega t} \right) . \]  
(A.7)

In the following two kind of relaxation rates are needed. First, the transition rate within the nth doublet (inter-well transition)

\[ \Gamma_n = \frac{1}{2\hbar} \int_{-\infty}^\infty dt \ (\Delta_n^2 \cos(\Delta t/\hbar) \left( \cos[g_1(t)] e^{g_2(t)} - 1 \right) . \]  
(A.8)

This expression is well-known from small polaron theory.

The second rate is the transition rate between the doublets (intra-well transition)

\[ \gamma_{10} = \frac{1}{2\hbar} \int_{-\infty}^\infty dt \left( g_-(\omega_{01}, t) + g_+(-\omega_{01}, t) \right) \]  
(A.9)

\[ \gamma_{01} = \frac{1}{2\hbar} \int_{-\infty}^\infty dt \left( g_-(\omega_{01}, t) + g_+(\omega_{01}, t) \right) . \]  
(A.10)

\[ \gamma_{10} \] is the transition rate from the zeroth to the first vibrational level and given by

\[ \gamma_{10} = \pi J_v(\omega_{01}) n(\omega_{01}) . \]  
(A.11)

Here, \( n(\omega_{01}) \equiv [\exp(\beta \hbar \omega_{01}) - 1]^{-1} \) is the Bose factor. \( \gamma_{01} \) and \( \gamma_{10} \) satisfy the principle of detailed balance \( \gamma_{10} = \gamma_{01} e^{-\beta \hbar \omega_{01}} \).
APPENDIX B: FORMULATION OF THE DYNAMICS IN THE MORI SCHEME

If we define the symmetrized scalar product $(A|B) := \frac{1}{2}(A^\dagger B + BA^\dagger)$ we can write the complex correlation function $C(\lambda) = \int_0^\infty e^{-\lambda t} C(t) dt$ (Re($\lambda$) > 0) as a resolvent matrix element

$$C(\lambda) = (\delta Q|\lambda + i\mathcal{L})^{-1}|\delta Q) . \quad (B.1)$$

We define the projector $\mathcal{P} = |\delta Q\rangle\eta^{-1}(\delta Q\rangle = \mathcal{I} - Q$ and its complement $Q$ with the normalization $\eta = (\delta Q|\delta Q\rangle \equiv \text{sech}^2(\beta \Delta/2)$. The resolvent identity

$$[\lambda + i\mathcal{L}_{\mathcal{P}\mathcal{P}} + \mathcal{L}_{\mathcal{P}\mathcal{Q}}[\lambda + i\mathcal{L}_{\mathcal{Q}\mathcal{Q}}]^{-1}\mathcal{L}_{\mathcal{Q}\mathcal{P}}]\mathcal{P}[\lambda + i\mathcal{L}]^{-1}\mathcal{P} = \mathcal{P} \quad (B.2)$$

where $\mathcal{L}_{\mathcal{A}\mathcal{B}} = \mathcal{A}\mathcal{L}\mathcal{B}$ with $\mathcal{A}, \mathcal{B} \in \{\mathcal{P}, \mathcal{Q}\}$ defines a relaxation kernel $k(\lambda)$. With $(\delta Q|\mathcal{L}|\delta Q\rangle = 0$ we find

$$C(\lambda) = \frac{\eta}{\lambda + 2k(\lambda)} \quad (B.3)$$

where the relaxation kernel is given by

$$2k(\lambda) = (\delta Q|\mathcal{L}_{\mathcal{P}\mathcal{Q}}[\lambda + i\mathcal{L}_{\mathcal{Q}\mathcal{Q}}]^{-1}|\mathcal{L}_{\mathcal{Q}\mathcal{P}}\delta Q\rangle \eta^{-1} . \quad (B.4)$$

For long times the transition rate $k$ between the left and right well is given by the limit $\lambda \to 0$

$$k = \lim_{\lambda \to 0} k(\lambda) . \quad (B.5)$$

To calculate this function, we first separate $k(\lambda)$ into two terms $k(\lambda) = k_t(\lambda) + k_v(\lambda)$ with

$$2k_t(\lambda) = (\delta Q|\mathcal{L}_{\mathcal{P}\mathcal{Q}}[\lambda + i\mathcal{L}_{\mathcal{Q}\mathcal{Q}}]^{-1}|\delta R\rangle \eta^{-1} \quad (B.6)$$

$$2k_v(\lambda) = (\delta Q|\mathcal{L}_{\mathcal{P}\mathcal{Q}}[\lambda + i\mathcal{L}_{\mathcal{Q}\mathcal{Q}}]^{-1}|\tilde{R}\rangle \eta^{-1} \quad (B.7)$$

where $\delta R$ contains all matrix elements of $\mathcal{L}_{\mathcal{Q}\mathcal{P}}\delta Q$ arising from $H^{(i)}_{\text{int}}$ and $\tilde{R}$ contains all matrix elements of $\mathcal{L}_{\mathcal{Q}\mathcal{P}}\delta Q$ arising from the non-diagonal part of $H_0$. Note that $H^{(v)}_{\text{int}}$ does not contribute to $\mathcal{L}_{\mathcal{Q}\mathcal{P}}\delta Q$. 

17
We now apply lowest order perturbation theory in $H_{\text{int}} = H^{(t)}_{\text{int}} + H^{(v)}_{\text{int}}$, i.e., in $\Delta_n \delta B_{\pm}$ and $M$. Since terms which are proportional to the product of these two perturbations are of higher order, we neglect the vibrational coupling $M$ in the tunneling part $k_t$, and the tunneling coupling $\Delta_n \delta B_{\pm}$ in the vibrational part $k_v$.

It is a standard result of spin-boson literature that for a single tunneling doublet the tunneling transition rate defined by $k_t \equiv k_t(\lambda = 0)$ is given by expression (A.8) in second order perturbation theory in the tunneling matrix element. Repeating the same kind of calculation for the pair of doublets one easily finds (4.8) in case of fast vibrational relaxation (4.1).

The calculation of the vibrational rate is essentially identical to the calculation of the transition rate between E and A symmetric states in a XH$_2$ rotational tunneling problem. Let us introduce the notation that $E_{nm}$ denotes a matrix with a one in the $n$-th row and the $m$-th column and zeros elsewhere. With this, we separate $\tilde{R}$ into two part $\tilde{R} = \tilde{\Delta}_0 R_0 + \tilde{\Delta}_1 R_1$ with $R_0 = E_{21} - E_{12}$ and $R_1 = E_{43} - E_{34}$. Inserting this and the projector

$$P' = \sum_{\alpha=0,1} |R_\alpha\rangle \eta_\alpha^{-1} \langle R_\alpha| $$

(B.8)

with $\eta_0 = [1 + e^{-\beta\hbar\omega_{01}}]^{-1}$ and $\eta_1 = [e^{\beta\hbar\omega_{01}} + 1]^{-1}$ into $k_v(\lambda)$ and noting that $(\delta Q|\mathcal{L}|R_0)\eta_0^{-1}\eta^{-1} = \tilde{\Delta}_0$ and $(\delta Q|\mathcal{L}|R_1)\eta_1^{-1}\eta^{-1} = \tilde{\Delta}_1$ one finds that the vibrational part of the relaxation kernel becomes

$$k_v(\lambda) \approx \tilde{\Delta}_1^2 G_{11}(\lambda) $$

(B.9)

with

$$G_{11}(\lambda) = (R_1 [\lambda + i\mathcal{L}_{QQ}]^{-1}|R_1) $$

(B.10)

Because of $\tilde{\Delta}_1 \gg \tilde{\Delta}_0$, we have neglect all terms $\propto \tilde{\Delta}_0$. The calculation of this function in second order perturbation theory in the vibrational coupling $M$ allows the replacement

$\mathcal{L}_{QQ} \rightarrow \mathcal{L}' = \hbar^{-1}[H_0 + H^{(v)}_{\text{int}}]$, where $H_0 + H^{(v)}_{\text{int}}$ have been defined in (3.7). The problem is now essentially identical to the calculation of the scattering function in a XH$_2$ rotational
tunneling system. Details of this can be found in Refs. \textsuperscript{24,25}. Following essentially their lines one finds with the definition $k_v \equiv k_v(\lambda = 0)$ the result (4.11).
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The resulting polaron factor for the vibrational coupling $M$ can be neglected, since there is almost no lattice distortion in this transition – the transfer distance is essentially zero in this case. Furthermore, the resulting energy shift $\sum_j c_j^{(t)}^2/\hbar \omega_j$ for the diagonal elements can be neglected since this shift is almost the same for all energy levels.

For this simplified model $\omega_{01}$ is identical to the zero-point frequency $\omega_0$. In the original DWP, however, the energy difference between doublets constituting a pair may exceed several $\omega_0$ because the coupled doublets are not necessarily adjacent.

In the classical regime, Kramers has determined the effect of friction on the preexponential factor in (1.2) for a particle subject to frequency independent damping $\gamma$ and Gaussian noise [for a review see Refs. 10,21]. In the strong damping limit $\gamma \gg \omega_b$, where $\omega_b$ is the barrier frequency, the prefactor is reduced as compared to $\omega_0/2\pi$ by a factor $\omega_b/\gamma$ because of diffusive barrier recrossings. This has been termed spatial-diffusion-controlled limit. On the other hand, for weak friction, typically $\gamma \lesssim \omega_b k_B T/V$, the influence of the heat bath is not strong enough to maintain thermal equilibrium at the top of the barrier. In this case the energy flow to the barrier top works as a bottleneck which reduces the prefactor as compared to $\omega_0/2\pi$ approximately by $\gamma V/\omega_b k_B T$. This situation has been termed energy-diffusion-controlled limit. Since this seminal work, quantum corrections to the classical escape rate have been elaborated showing explicitly the crossover between the quantum and the classical regime [see for instance Refs. 6,10,21,22 and references therein].

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**FIGURE CAPTIONS**

FIG. 1: Schematic representation of a biased double-well potential with \( V \approx 2\hbar\omega_0 \). The ground state and first excited state tunneling doublets are separated by an energy \( \Delta E \approx \hbar\omega_0 \).

FIG. 2: Spectral density \( J_v(\omega) \equiv J(\omega) \) for the NiP Lennard-Jones computer glass.