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The influence of nonlinear interaction-terms in the spin-boson Hamiltonian for the superohmic case

Andreas Heuer†

Max-Planck-Institut für Med. Forschung, Arbeitsgruppe Molekülkristalle, Jahnstrasse 29, 69 Heidelberg, Federal Republic of Germany

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Abstract. We generalize the conventional spin-boson Hamiltonian by considering additional nonlinear coupling terms between system and heat bath. The equation of motion for the reduced density matrix of the system is calculated in second-order perturbation theory in the tunnelling matrix element and the nonlinear coupling constant. We obtain an explicit expression for the Laplace transform of the function which describes the time evolution of the position of the system. Due to the influence of the nonlinear coupling for temperatures much lower than the Debye temperature a transition from coherent to incoherent dynamics may take place. We fully describe this crossover by our expression.

1. Introduction

The low-temperature dynamics of a particle in a double-well potential has been of considerable interest during the last decade. Often, the dynamics has been analysed in the framework of the spin-boson (SB) Hamiltonian (Leggett *et al* 1987). The particle is described as a two-level system interacting with a heat bath which consists of harmonic oscillators. In most cases the interaction has been chosen linear in the bath coordinates. The two levels correspond to the two lowest eigenstates of the system. Whereas for very asymmetric double-well potentials the dynamics is always incoherent, for symmetric potentials there exist a variety of possibilities, mainly dependent on the spectral density $J(\omega)$ of the heat bath, the temperature T and the coupling strength η. If, for example, the particle is interacting with electrons, the spectral density of the heat bath corresponds to the so-called *ohmic* case (Kondo 1984, Wipf *et al* 1987). It is well known that for this case a temperature-dependent coupling constant $\eta_0(T)$ can be defined such that for $\eta < \eta_0(T)$ the dynamic is coherent and, for $\eta \geqslant \eta_0(T)$, incoherent (Leggett *et al* 1987, Weiss *et al* 1987). With increasing temperature, $\eta_0(T)$ approaches zero. In the incoherent regime, the temperature dependence of the jump rate possesses very interesting properties: in the limit of weak coupling, which is fulfilled in most experimental cases, the jump rate decreases with increasing temperature. The effect of the reduction of the rate with temperature has been observed, for example, in diffusion experiments of positively charged muons in copper for $T < 10$ K (Clawson *et al* 1983). For higher temperatures the interaction is dominated by phonons and the rate increases again.

In the *superohmic* case, which corresponds to coupling to acoustic phonons, the dynamics is coherent for all temperatures much lower than the Debye temperature (Leggett *et*

† Present address: Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Federal Republic of Germany.

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al 1987). This behaviour is independent of the coupling strength η. It somehow contradicts intuition that even a very strong coupling to the heat bath does not suppress the coherent processes.

In contrast to the superohmic case in the ohmic case the spectral density $J(\omega)$ does not vanish for $\omega \to 0$. The interesting question arises in how far consideration of small additional interaction terms, which are quadratic in the bath coordinates, gives a superohmic bath features of an ohmic bath. This might be reasonable, because the spectral density of nonlinear processes possesses a non-vanishing contribution for low frequencies. This property is due to the possibility of a combined absorption and emission process of phonons of similar frequencies.

This problem was first analysed by Kagan and co-workers (Kagan and Klinger 1974, Kagan and Prokof'ev 1986, 1989, 1990, Kagan 1991). They got the interesting result that even for small nonlinear interaction terms the dynamics in incoherent for temperatures much lower than the Debye temperature. Their recent calculations are based on methods known from the polaron theory (Holstein 1959, Mahan 1980). They obtain separate results for the incoherent and for the coherent regime. The crossover region is described by a simple interpolation formula.

We present a full analysis of this problem in the sense that we obtain an expression describing the time evolution of the system for both the coherent and the incoherent regimes. Therefore we can fully describe the crossover between coherent and incoherent dynamics. In the two limiting cases we obtain the same results as Kagan and coworkers. We will show that for the crossover region our results significantly differ from those which are calculated on the basis of the interpolation formula.

Recent diffusion experiments of muonium atoms in NaCl and KCl have been reported where nonlinear interaction terms seem to play a decisive role in explaining the temperature dependence of the diffusion rate (Kiefl *et al* 1989, Kadono *et al* 1990). Therefore the analysis of this paper is not only of academic interest.

The plan of this paper is as follows. In section 2 we describe the generalized SB Hamiltonian. In section 3 we first calculate the time evolution of the system without specifying the exact nature of the interaction between system and heat bath. We obtain an expression for the Laplace transform of the expectation value of the position of the system. Then we apply this general expression to the SB Hamiltonian defined in the previous section. In section 4 we discuss this expression and compare our results with those of Kagan and coworkers.

2. The generalized spin-boson Hamiltonian

Our generalized SB Hamiltonian of a double well potential interacting with a heat bath may be written in the following form

$$H_{\mathrm{SB}} = \frac{A}{2}\sigma_z + \frac{\Delta}{2}\exp(-R_s)\sigma_x + \sigma_z\left[\sum_{i=1}^{N}\eta_i(b_i + b_i^+) + \sum_{i=1}^{N}\sum_{j=1}^{N}\mu_{ij}(b_i + b_i^+)(b_j + b_j^+)\right] + \sum_{i=1}^{N}\hbar\omega_i b_i^+ b_i + \hbar\omega_s b_s^+ b_s. \quad (1)$$

Δ denotes the bare tunnelling matrix element, A the static asymmetry. The mode with the index s describes a symmetrically coupled mode which induces a fluctuating tunnelling matrix element via the term

$$\exp(-R_s) \equiv \exp(-\kappa_s(b_s^+ + b_s)). \tag{2}$$

Especially in physical chemistry literature, such as a mode has often been introduced to explain the temperature dependence of rate processes (Siebrand *et al* 1983, 1984). The N modes with frequencies ω_i describe the heat bath. The linear and nonlinear coupling constants between system and heat bath are given by the η_i and μ_{ij}. In the so-called deformation potential approximation (Fetter and Walecka 1971), they can be chosen as

$$\eta_i = \eta\sqrt{\frac{\omega_i}{\omega_D}}\frac{1}{\sqrt{N}} \tag{3}$$

and

$$\mu_{ij} = \mu\frac{\sqrt{\omega_i\omega_j}}{\omega_D}\frac{1}{N}. \tag{4}$$

In these equations overall coupling constants η and μ have been defined. ω_D denotes the Debye frequency. Introducing the variable

$$\phi \equiv \sum_{i=1}^{N}\frac{\eta_i}{\eta}(b_i^+ + b_i) \tag{5}$$

which contains the influence of all oscillators of the heat bath we may conveniently write the SB Hamiltonian as

$$H_{SB} = \frac{A}{2}\sigma_z + \frac{\Delta}{2}\exp(-R_s)\sigma_x + \sigma_z(\eta\phi + \mu\phi^2) + \sum_{i=1}^{N}\hbar\omega_i b_i^+ b_i + \hbar\omega_s b_s^+ b_s. \tag{6}$$

The two level system is expressed in the localized basis. Hence $\omega_z(t)$ describes the time evolution of the position of the system.

As usual we first perform a standard polaron-transform for getting rid of the possibly large linear coupling (Holstein 1959, Mahan 1980). Neglecting a constant term we obtain

$$\tilde{H}_{SB} = x_1\sigma_z + x_2\sigma_+ + x_3\sigma_- + y_1\sigma_z + y_2\sigma_+ + y_3\sigma_- + y_4 1 + H_B \tag{7}$$

with

$$\begin{aligned}
x_1 &= \tfrac{1}{2}A + \mu\langle\phi^2\rangle \\
x_2 &= \tfrac{1}{2}\Delta\langle\exp(2S)\rangle\langle\exp(-R_s)\rangle \\
x_3 &= \tfrac{1}{2}\Delta\langle\exp(-2S)\rangle\langle\exp(-R_s)\rangle \\
y_1 &= \mu[\phi^2 - \langle\phi^2\rangle] \\
y_2 &= \tfrac{1}{2}\Delta[\exp(2S)\exp(-R_s) - \langle\exp(2S)\rangle\langle\exp(-R_s)\rangle] \\
y_3 &= \tfrac{1}{2}\Delta[\exp(-2S)\exp(-R_s) - \langle\exp(-2S)\rangle\langle\exp(-R_s)\rangle] \\
y_4 &= -\frac{4\mu E_r}{\eta}\phi.
\end{aligned} \tag{8}$$

The brackets $\langle . \rangle$ denote the average over the heat bath. We have used the abbreviations

$$E_r \equiv \sum_{i=1}^{N} \frac{\eta_i^2}{\hbar\omega_i} \tag{9}$$

and

$$\exp(\pm 2S) \equiv \exp\left(\pm 2 \sum_{i=1}^{N} \frac{\eta_i}{\hbar\omega_i}(b_i^+ - b_i) \right). \tag{10}$$

For reasons of simplicity we consider only symmetric potentials so that we choose $x_1 = 0$. The interaction terms y_i have been chosen such that $\langle y_i \rangle = 0$. The average values of the exponentials are given by (Leggett *et al* 1987)

$$\langle \exp(\pm 2S) \rangle = \exp\left(- \int_0^\infty \mathrm{d}\omega \frac{J(\omega)}{\hbar\omega^2}(2N(\omega) + 1) \right) \tag{11}$$

and

$$\langle \exp(-R_s) \rangle = \exp(\tfrac{1}{2}\kappa_s^2(2N(\omega_s) + 1)). \tag{12}$$

We have defined the spectral bath function $J(\omega)$ as

$$J(\omega) \equiv 2 \sum_{i=1}^{N} \frac{\eta_i^2}{\hbar} \delta(\omega - \omega_i) \tag{13}$$

and used the standard definition

$$N(\omega) = \frac{1}{\exp(\beta\hbar\omega) - 1}. \tag{14}$$

In the case of an acoustic heat bath with a density of states

$$\rho(\omega) \equiv N \frac{\omega^2}{\omega_D^3} \exp(-\omega/\omega_D) \tag{15}$$

we obtain

$$J(\omega) = C_J \hbar \frac{\omega^3}{\omega_D^2} \exp(-\omega/\omega_D) \tag{16}$$

with a dimensionless coupling constant $C_J \equiv 2(\eta/\hbar\omega_D)^2$. In the case of the tunnelling of hydrogen atoms in hydrogen bonds C_J is of the order of one (Skinner and Trommsdorff 1988, Heuer and Haeberlen 1991).

For reasons of simplicity we introduce the effective fluctuating tunnelling matrix element

$$\tilde{\Delta}_{fl} \equiv \Delta \langle \exp(2S) \rangle \langle \exp(-R) \rangle. \tag{17}$$

which is non-zero for a superohmic bath.

3. Calculation of the time evolution of the system

In this section we derive an equation of motion for the reduced density matrix of a two-level system. Similar derivations without consideration of the nonlinear term can be found in the literature (Aslangul *et al* 1985, Dattagupta *et al* 1989). The general Hamiltonian in equation (7) may be written as

$$H = H_{\mathrm{A}} + W + H_{\mathrm{B}} \equiv H_0 + W. \tag{18}$$

H_{A} describes the system, H_{B} the heat bath, and W the interaction between system and heat bath. As H is Hermitian, the interaction terms y_i have to fulfill the conditions $y_1 = y_1^+$, $y_4 = y_4^+$, $y_2 = y_3^+$, $y_3 = y_2^+$.

The time evolution of the whole density matrix $\rho(t)$ may be described by the von-Neumann equation

$$\frac{\partial}{\partial t}\rho(t) = -\frac{\mathrm{i}}{\hbar}[H, \rho(t)] \equiv -\frac{\mathrm{i}}{\hbar}\mathcal{H}\rho(t). \tag{19}$$

The reduced density matrix $\rho_{\mathrm{A}}(t)$ which describes the time evolution of the system under the influence of the heat bath is given by

$$\rho_{\mathrm{A}}(t) \equiv \mathrm{tr}_{\mathrm{B}}\rho(t). \tag{20}$$

The equation of motion for $\rho_{\mathrm{A}}(t)$ can be obtained using the projection operator formalism (Kubo and Toda 1987). Assuming a weak coupling between system and heat bath and neglecting a term which describes initial correlations between system and heat bath this equation reads

$$\begin{aligned}\frac{\partial}{\partial t}\rho_{\mathrm{A}}(t) &= -\frac{\mathrm{i}}{\hbar}\mathcal{H}_{\mathrm{A}}\rho_{\mathrm{A}}(t) - \frac{1}{\hbar^2}\int_0^t \mathrm{d}\tau\, \mathrm{tr}_{\mathrm{B}}\mathcal{W}\exp\left[-\frac{\mathrm{i}}{\hbar}\mathcal{H}_0\tau\right]\mathcal{W}\rho_{\mathrm{B}}\rho_{\mathrm{A}}(t-\tau) \\ &\equiv -\frac{\mathrm{i}}{\hbar}\mathcal{H}_{\mathrm{A}}\rho_{\mathrm{A}}(t) - \int_0^t \mathrm{d}\tau\, \mathcal{M}(\tau)\rho_{\mathrm{A}}(t-\tau).\end{aligned} \tag{21}$$

The main task is the calculation of the memory function $\mathcal{M}(\tau)$. The calculation of $\mathcal{M}(\tau)$ is most conveniently performed in the Liouvillian space which is defined by the basis $\sigma_1 = (1+\sigma_z)/2$, $\sigma_2 = (1-\sigma_z)/2$, $\sigma_3 = \sigma_+$, $\sigma_4 = \sigma_-$. In this basis $\rho_{\mathrm{A}}(t)$ can be written as

$$\sum_{i=1}^{4} a_i(t)\sigma_i.$$

After a straightforward calculation we obtain for the matrix elements of $\mathcal{M}$

$$\mathcal{M}_{11}(\tau) = e(\tau)A_{22}(\tau) + e^*(\tau)A_{22}^*(\tau)$$

$$\mathcal{M}_{12}(\tau) = -e(\tau)A_{33}^*(\tau) - e^*(\tau)A_{33}^*(\tau)$$

$$\mathcal{M}_{13}(\tau) = -e^*(\tau)[A_{31}(\tau) + A_{21}^*(\tau) + A_{34}(\tau) - A_{24}^*(\tau)]$$

$$\mathcal{M}_{14}(\tau) = -e(\tau)[A_{21}(\tau) + A_{31}^*(\tau) + A_{34}^*(\tau) - A_{24}(\tau)]$$

$$\mathcal{M}_{2i}(\tau) = -\mathcal{M}_{1i}(\tau) \qquad (i = 1, \ldots, 4)$$

$$\mathcal{M}_{31}(\tau) = -A_{21}(\tau) + A^*_{31}(\tau) - A_{24}(\tau) + A^*_{34}(\tau) - 2e^*(\tau)A^*_{12}(\tau)$$

$$\mathcal{M}_{32}(\tau) = -A_{21}(\tau) + A^*_{31}(\tau) + A_{24}(\tau) - A^*_{34}(\tau) + 2e^*(\tau)A^*_{13}(\tau)$$

$$\mathcal{M}_{33}(\tau) = A_{22}(\tau) + A^*_{33}(\tau) + 2e^*(\tau)[A_{11}(\tau) + A^*_{11}(\tau) + A_{14}(\tau) - A^*_{14}(\tau)]$$

$$\mathcal{M}_{34}(\tau) = -A_{23}(\tau) - A^*_{32}(\tau)$$

$$\mathcal{M}_{41}(\tau) = A_{31}(\tau) - A^*_{21}(\tau) + A_{34}(\tau) - A^*_{24}(\tau) - 2e(\tau)A_{12}(\tau)$$

$$\mathcal{M}_{42}(\tau) = A_{31}(\tau) - A^*_{21}(\tau) - A_{34}(\tau) + A^*_{24}(\tau) + 2e(\tau)A^*_{13}(\tau)$$

$$\mathcal{M}_{43}(\tau) = -A_{32}(\tau) - A^*_{23}(\tau)$$

$$\mathcal{M}_{44}(\tau) = A_{33}(\tau) + A^*_{22}(\tau) + 2e(\tau)[A_{11}(\tau) + A^*_{11}(\tau) - A_{14}(\tau) + A^*_{14}(\tau)]. \tag{22}$$

We defined the correlation functions

$$A_{ij}(\tau) \equiv \langle y_i(\tau) y_j^+ \rangle / \hbar^2 \tag{23}$$

with

$$y_i(\tau) \equiv \exp(\mathrm{i} H_B \tau/\hbar) y_i \exp(-\mathrm{i} H_B \tau/\hbar). \tag{24}$$

Furthermore we have used

$$e(\tau) \equiv \exp(2\mathrm{i} x_1 \tau/\hbar). \tag{25}$$

Analogously $\mathcal{H}_A$ may be written as

$$\mathcal{H}_A = \begin{pmatrix} 0 & 0 & -x_3 & x_2 \\ 0 & 0 & x_3 & -x_2 \\ -x_2 & x_2 & 2x_1 & 0 \\ x_3 & -x_3 & 0 & -2x_1 \end{pmatrix}. \tag{26}$$

By Laplace-transforming both sides of equation (21) we obtain the linear system of equations

$$\lambda \rho_A(\lambda) - \rho_A(0) = \left[-\frac{\mathrm{i}}{\hbar}\mathcal{H}_A - \mathcal{M}(\lambda) \right] \rho_A(\lambda). \tag{27}$$

We denote the Laplace transform of a specific function in the same way as the original function.

As we have already mentioned we are mainly interested in the time development of the expectation value of $\sigma_z(t)$, which, in our basis, describes the time development of the position of the system. In our notation we may write

$$P(t) \equiv \langle \sigma_z(t) \rangle = a_1(t) - a_2(t). \tag{28}$$

The initial condition $\langle\sigma_z(0)\rangle = 1$ corresponds to $a_i(0) = \delta_{1i}$. After a tedious but straightforward calculation we obtain for $P(\lambda)$ the following expression

$$P(\lambda) = \frac{1 + \left[\mathcal{M}_{11}(\lambda) + \mathcal{M}_{12}(\lambda) + \dfrac{\left[\mathcal{M}_{14}(\lambda) + \mathrm{i}\frac{x_2}{\hbar}\right] z_5(\lambda) + \left[\mathcal{M}_{13}(\lambda) - \mathrm{i}\frac{x_3}{\hbar}\right] z_3(\lambda)}{z_1(\lambda)}\right]\lambda^{-1}}{\lambda + \mathcal{M}_{11}(\lambda) - \mathcal{M}_{12}(\lambda) - \dfrac{\left[\mathcal{M}_{14}(\lambda) + \mathrm{i}\frac{x_2}{\hbar}\right] z_4(\lambda) + \left[\mathcal{M}_{13}(\lambda) - \mathrm{i}\frac{x_3}{\hbar}\right] z_2(\lambda)}{z_1(\lambda)}} \tag{29}$$

with

$$z_1(\lambda) = \left[\lambda + \mathcal{M}_{44}(\lambda) - 2\mathrm{i}\frac{x_1}{\hbar}\right]\left[\lambda + \mathcal{M}_{33}(\lambda) + 2\mathrm{i}\frac{x_1}{\hbar}\right] - \mathcal{M}_{34}(\lambda)\mathcal{M}_{43}(\lambda)$$

$$z_2(\lambda) = \mathcal{M}_{34}(\lambda)\left[\mathcal{M}_{42}(\lambda) - \mathcal{M}_{41}(\lambda) - 2\mathrm{i}\frac{x_3}{\hbar}\right] + \left[\lambda + \mathcal{M}_{44}(\lambda) - 2\mathrm{i}\frac{x_1}{\hbar}\right] \times \left[\mathcal{M}_{31}(\lambda) - \mathcal{M}_{32}(\lambda) - 2\mathrm{i}\frac{x_2}{\hbar}\right]$$

$$z_3(\lambda) = \mathcal{M}_{34}(\lambda)[\mathcal{M}_{42}(\lambda) + \mathcal{M}_{41}(\lambda)] - \left[\lambda + \mathcal{M}_{44}(\lambda) - 2\mathrm{i}\frac{x_1}{\hbar}\right][\mathcal{M}_{32}(\lambda) + \mathcal{M}_{31}(\lambda)]$$

$$z_4(\lambda) = \mathcal{M}_{43}(\lambda)\left[\mathcal{M}_{32}(\lambda) - \mathcal{M}_{31}(\lambda) + 2\mathrm{i}\frac{x_2}{\hbar}\right] + \left[\lambda + \mathcal{M}_{33}(\lambda) + 2\mathrm{i}\frac{x_1}{\hbar}\right] \times \left[\mathcal{M}_{41}(\lambda) - \mathcal{M}_{42}(\lambda) + 2\mathrm{i}\frac{x_3}{\hbar}\right]$$

$$z_5(\lambda) = \mathcal{M}_{43}(\lambda)[\mathcal{M}_{32}(\lambda) + \mathcal{M}_{31}(\lambda)] - \left[\lambda + \mathcal{M}_{33}(\lambda) + 2\mathrm{i}\frac{x_1}{\hbar}\right][\mathcal{M}_{42}(\lambda) + \mathcal{M}_{41}(\lambda)]. \tag{30}$$

It can be easily checked that $P(\lambda)$ is real for real λ, which gives some confidence in the correctness of the above equations.

For applying equation (29) to our system of interest we first have to calculate the correlation functions $A_{ij}(\tau)$. We obtain

$$
\begin{aligned}
A_{11}(\tau) &= \frac{\mu^2}{2\eta^4}\left[\int_0^\infty d\omega\, J(\omega) f^+(\omega,\tau)\right]^2 \\
A_{12}(\tau) &= \frac{\mu\tilde{\Delta}_{\mathrm{fl}}}{2\hbar^2\eta^2}\left[\int_0^\infty d\omega \frac{J(\omega)}{\omega} f^-(\omega,\tau)\right]^2 \\
&= A_{21}(\tau) = A_{13}(\tau) = A_{31}(\tau) \\
A_{14}(\tau) &= 0 \\
A_{22}(\tau) &= \frac{\tilde{\Delta}_{\mathrm{fl}}^2}{4\hbar^2}\left[\exp\left(2\int_0^\infty d\omega \frac{J(\omega)}{\hbar\omega^2} f^+(\omega,\tau) + \kappa_s^2 f^+(\omega_s,\tau)\right) - 1\right] \\
&= A_{33}(\tau) \\
A_{23}(\tau) &= \frac{\tilde{\Delta}_{\mathrm{fl}}^2}{4\hbar^2}\left[\exp\left(-2\int_0^\infty d\omega \frac{J(\omega)}{\hbar\omega^2} f^+(\omega,\tau) + \kappa_s^2 f^+(\omega_s,\tau)\right) - 1\right] \\
&= A_{32}(\tau) \\
A_{24}(\tau) &= -\frac{2\mu E_r \tilde{\Delta}_{\mathrm{fl}}}{\hbar^2\eta^2}\int_0^\infty d\omega \frac{J(\omega)}{\omega} f^-(\omega,\tau) \\
&= A_{42}(\tau) = -A_{34}(\tau) = -A_{43}(\tau).
\end{aligned}
\tag{31}
$$

We have used

$$
f^{\pm}(\omega,\tau) = \cos(\omega\tau)\coth\left(\frac{\beta\hbar\omega}{2}\right) \mp \mathrm{i}\sin(\omega\tau). \tag{32}
$$

Fortunately it turns out for our case that, due to the symmetries among the correlation functions $A_{ij}(\tau)$, the resulting expression for $P(\lambda)$ substantially simplifies. We obtain

$$
P(\lambda) = 1 \Bigg/ \left(\lambda + 4A_{22}^{\mathrm{re}}(\lambda) + \frac{\tilde{\Delta}_{\mathrm{fl}}^2/\hbar^2}{\lambda + d^+(\lambda)} + \frac{(4A_{24}^{\mathrm{re}}(\lambda))^2 - (4A_{12}^{\mathrm{re}}(\lambda))^2}{\lambda + d^-(\lambda)}\right) \tag{33}
$$

with

$$
d^{\pm}(\lambda) = 4A_{11}^{\mathrm{re}}(\lambda) + 2A_{22}^{\mathrm{re}}(\lambda) \pm 2A_{23}^{\mathrm{re}}(\lambda). \tag{34}
$$

The index re denotes the real part of the correlation functions. Equation (33) is the main result of this article.

4. Discussion

The time-dependence of $P(t)$ can be obtained by calculation of the poles of $P(\lambda)$. We note that in the superohmic case the $A_{ij}(\lambda)$ may be substituted by $A_{ij}(\lambda = 0)$ (Leggett *et al* 1987). The underlying reason is that the time scale of the dynamics of the system, which is proportional to $\tilde{\Delta}_{\mathrm{fl}}^2$, is slow compared with the time scale of the bath dynamics $1/\omega_{\mathrm{D}}$. For reasons of simplicity we will use the notation A_{ij} instead of $A_{ij}^{\mathrm{re}}(\lambda = 0)$.

For the discussion of $P(\lambda)$ the following theorem turns out to be very useful

$$
A_{ii} \cdot A_{jj} \geqslant A_{ij}^2. \tag{35}
$$

The proof will be sketched in the appendix.

We first consider the limit of vanishing nonlinear interaction. Then we obtain from equation (33)

$$P(\lambda) = 1 \Bigg/ \left(\lambda + 4A_{22} + \frac{\tilde{\Delta}_{\mathrm{fl}}^2/\hbar^2}{\lambda + 2A_{22} + 2A_{23}}\right). \tag{36}$$

This expression has been already given by Aslangul *et al* (1985). From (35) follows $A_{23} \leqslant A_{22}$.

For $\kappa_s = 0$ and $k_B T \ll \hbar\omega_D$ it may be easily verified that $A_{22} \gg \tilde{\Delta}_{\mathrm{fl}}/\hbar$ (Leggett *et al* 1987). In this limit the dynamics is coherent. Only for temperatures of the order of the Debye temperature A_{22} may increase beyond $\tilde{\Delta}_{\mathrm{fl}}/\hbar$, turning the dynamics into incoherent motion. If the frequency of the symmetric mode ω_s is sufficiently small and the coupling constant κ_s sufficiently large the jump rate can be strongly modified by the fact that during the jump process the symmetric mode may be in an excited state. The effective tunnelling matrix element of this jump process is strongly enhanced compared with the process in which the symmetric mode is in its ground state (Siebrand *et al* 1983, 1984, Suarez and Silbey 1991). A similar effect can be observed for a single antisymmetric mode which is strongly coupled to the system (Heuer and Haeberlen 1991). Therefore, for a strongly fluctuating tunnelling matrix element, A_{22} increases much faster with temperature than without this coupling, so that the crossover to incoherent motion may take place at lower temperatures. For the incoherent regime we obtain $P(t) = \exp(-\Gamma_{\mathrm{lin}} t)$ with

$$\Gamma_{\mathrm{lin}} \equiv 4A_{22}. \tag{37}$$

It can be easily checked that for the whole temperature range the term $2A_{22} + 2A_{23}$ may be neglected except for the small temperature range for which $A_{22} \approx \tilde{\Delta}_{\mathrm{fl}}/\hbar$.

After this brief repetition we additionally consider the influence of the nonlinear interaction. A_{11} turns out to be the most important term. From the definition of A_{11} in equation (31) we directly obtain

$$A_{11} = \frac{\pi\mu^2}{\eta^4}\int_0^\infty \mathrm{d}\omega\, J(\omega)J(\omega)N(\omega)[N(\omega)+1]. \tag{38}$$

For $k_B T \ll \hbar\omega_D$ this may be approximated by

$$A_{11} \approx 10^3 \times \frac{\mu^2\pi}{\hbar^2\omega_D}\left(\frac{k_B T}{\hbar\omega_D}\right)^7. \tag{39}$$

Hence, for low temperatures, A_{11} strongly increases with temperature. A_{11} is a measure of the probability that the nonlinear interaction term simultaneously induces an absorption and emission process of the same frequency.

For our further discussion let us define

$$\tilde{P}(\lambda) \equiv 1 \Bigg/ \left(\lambda + 4A_{22} + \frac{\tilde{\Delta}_{\mathrm{fl}}^2/\hbar^2}{\lambda + 4A_{11}}\right) \tag{40}$$

and

$$\Gamma_{\mathrm{nl}} \equiv \frac{\tilde{\Delta}_{\mathrm{fl}}^2}{4A_{11}\hbar^2}. \tag{41}$$

We will first discuss the poles of $\tilde{P}(\lambda)$ and show afterwards they are approximately the same as the poles of $P(\lambda)$.

For $T \to 0$ A_{11} may be neglected so that according to our above discussion we obtain a coherent behaviour with tunnelling frequency $\tilde{\Delta}_{\text{fi}}/\hbar$. Now let us assume that for some temperature T_0 we have $4A_{22} \ll \tilde{\Delta}_{\text{fi}}/\hbar$ and $2A_{11} = \tilde{\Delta}_{\text{fi}}/\hbar$. Whereas the first inequality is in general fulfilled for $k_B T_0 \ll \hbar\omega_D$ (see our discussion above) the second inequality holds only if μ exceeds a critical value μ_0. For a given T_0 this value may be easily calculated from equation (39). Then for $T \approx T_0$ A_{22} may be neglected and the poles are determined by

$$\lambda_\pm = -[2A_{11} \pm (4A_{11}^2 - \tilde{\Delta}_{\text{fi}}^2/\hbar^2)^{1/2}]. \tag{42}$$

It is easy to see that for $T \to T_0$ the frequency of the coherent motion decreases and the damping increases. Finally, for $2A_{11} = \tilde{\Delta}_{\text{fi}}/\hbar$ we obtain two real poles. Hence, the crossover from coherent to incoherent motion has taken place. In the incoherent regime of the crossover region, $P(t)$ is the sum of two exponentials. With further increasing temperature we may finally write

$$\tilde{P}(\lambda) = \frac{1}{\lambda + \Gamma_{\text{nl}} + \Gamma_{\text{lin}}}. \tag{43}$$

Hence, the rate constant of the incoherent motion has one contribution from the linear and one from the nonlinear interaction. For temperatures slightly above T_0, the rate may be described by Γ_{nl} and therefore decreases with temperature. Very soon the term Γ_{lin} will be dominant so that the rate increases again. The whole scenario is identical to that of a particle which is coupled to an electronic as well as to a phonon bath, which we briefly presented in the introduction.

It turns out that for $T \ll T_0$ as well as for $T \gg T_0$ our results are identical with the results of Kagan and coworkers. For $T \approx T_0$ they proposed an interpolation formula for the rate, which in our notation for the incoherent regime may be written as (Kagan and Prokofev 1990)

$$\Gamma = \frac{\tilde{\Delta}_{\text{fi}}/\hbar}{\sqrt{2} + 4A_{11}\hbar/\tilde{\Delta}_{\text{fi}}}. \tag{44}$$

In the limit $A_{11} \to \infty$ this turns out to be the correct expression for the rate. For the crossover temperature, hence for $2A_{11} = \tilde{\Delta}_{\text{fi}}/\hbar$, equation (44) gives $\tilde{\Gamma} \approx \tilde{\Delta}_{\text{fi}}/3.4\hbar$, whereas the exact solution reads $\Gamma = \tilde{\Delta}_{\text{fi}}/\hbar$. This shows that for $T \approx T_0$ the interpolation formula only has limited accuracy.

It remains to justify that the additional terms in $P(\lambda)$ do not change the above results. From (35) follows $A_{12}^2 \leqslant A_{11}A_{22}$. Furthermore we have $A_{24} = 0$. For $T \approx T_0$ we have $2A_{11} \approx \tilde{\Delta}_{\text{fi}}/\hbar$ and $4A_{22} \ll \tilde{\Delta}_{\text{fi}}/\hbar$ so that $4A_{12} \ll \tilde{\Delta}_{\text{fi}}/\hbar$. Therefore the fourth term in the denominator of $P(\lambda)$ can be neglected in this temperature range. Since $A_{11} \gg A_{22} \geqslant A_{23}$ also the term $2A_{22} + 2A_{23}$ has no influence. Therefore for $T \approx T_0$, $\tilde{P}(\lambda)$ is an excellent approximation of $P(\lambda)$. For higher temperatures the fourth term in the denominator of $P(\lambda)$ may become more important than the third term. However, it turns out that in the high-temperature limit $A_{22} \gg A_{12}^2/A_{11}$ so that the fourth term may neglected compared with the second term. This can be easily checked numerically but can be also simply derived from the fact that in contrast to A_{12} and A_{11} the value of A_{22} exponentially increases with temperature at high temperatures. Indeed, at high temperatures one may approximate

$A_{22} \propto \exp(-E/k_B T)$ with some activation energy E (Leggett *et al* 1987). Since we are mainly interested in the transition region we will not discuss the high-temperature behaviour any further.

In summary, the nonlinear coupling terms play a decisive role in the description of a particle in a double-well potential which is coupled to a superohmic bath. We have presented an expression for the Laplace transform of $P(t)$ which allows one to describe the dynamics for all temperatures and especially for the crossover regime between coherent and incoherent dynamics.

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Appendix

Let y_u and y_v be two real operators in a countable Hilbert-space with Hamiltonian H. The eigenvalues are denoted by E_i, the density matrix by ρ. Our goal is to prove

$$A_{uu} \cdot A_{vv} \geqslant A_{uv}^2. \tag{45}$$

Since the operators are real we can write

$$A_{uv} = \pi \sum_{ij} (y_u)_{ij} (y_v)_{ij} \rho_{ii} \delta(E_i - E_j) \tag{46}$$

where we have introduced the matrix elements of the operators with respect to the eigenbasis of H. Let us formally define

$$(x_u)_{ij} \equiv (y_u)_{ij} (\rho_{ii} \delta(E_i - E_j))^{1/2}. \tag{47}$$

Since we are interested only in even products of these expressions we do not have to worry about the square-root of the δ-distribution. Now A_{uv} may be rewritten as

$$A_{uv} = \pi \sum_{ij} (x_u)_{ij} (x_v)_{ij}. \tag{48}$$

Let c_u be a vector which contains all elements of $(x_u)_{ij}$. Then the original statement is equivalent to

$$|c_1|^2 |c_2|^2 \geqslant |c_1 \cdot c_2|^2. \tag{49}$$

This relation is trivially fulfilled.

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