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The self-consistent Mori approach to transport in exciton–phonon systems

H Dolderer and M Wagner

Institut für Theoretische Physik, Universität Stuttgart, Pfaffenwaldring 57, D-70550 Stuttgart, Germany

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Abstract. In earlier calculations of exciton transport in exciton–phonon systems diffusivity in general has been achieved by means of semi-phenomenological elements. The present investigation aims at giving an *ab initio* derivation of the diffusion function, involving only intrinsic characteristics of the model. Using a projection operator technique we have studied a one-dimensional molecular crystal model with site-diagonal coupling to a phonon bath of acoustic type. The relevant memory kernels in the transport equations have been evaluated in a consistent perturbative treatment up to second order in the exciton–phonon interaction for two different kinds of local excitation. The evolution of the second moment of the exciton probability density helps us to discuss coherent ($M_2 \sim t^2$) and diffusive ($M_2 \sim t$) transport. The time dependence of these memory functions displays an oscillatory short-time decay in the case of a broad exciton band, which results in diffusive transport. In the high-temperature limit the diffusion constant is found to decrease with increasing temperature with the power law $D \sim 1/T$. In the opposite case of a small excitonic band the decay remains incomplete and the time dependence of the second moment is governed by the t^2 -law typical of coherent transport processes. Since this is a rigorous second-order result, the vanishing of the second-order term may serve as a check for any non-perturbative calculation of the diffusion constant in this case.

1. Introduction

A great number of quite different approaches to the dynamics of excitons with a linear coupling to a phonon bath have been discussed in the literature. The variety of theoretical concepts includes for example stochastic Liouville equations [13], (generalized) master equations [9, 8, 16], adiabatic approximations [6, 7] and Fulton–Gouterman techniques [14]. We also want to mention a very interesting contribution of Grover and Silbey [5] which describes the motion of excitons, dressed by a phonon cloud, in a renormalized band being scattered by fluctuations in the phonon bath. Since the non-diagonal scattering term is proportional to the exciton transfer J this kind of description seems suitable for narrow-band systems. In this case the velocities in the exciton systems are small and the lattice distortion follows the exciton motion.

The physical situation in systems with a large exciton bandwidth is quite contrasting. An initially created ‘hot’ exciton localized at a single site, for example, spreads out immediately. Since the phonon velocities are small, it is not possible for the lattice to follow this rapid motion and transport is rather like that of a bare (undressed) exciton. Even in systems with smaller bandwidth one could argue that, considering an acoustic phonon branch, the small-wavelength phonons with vanishing group velocity might not follow the excitonic motion. To investigate this in a systematic *ab initio* manner we employ Mori’s formalism.

This allows us to discuss the exciton diffusion by means of a continued-fraction method together with a perturbative calculation of the respective denominator.

The generalized master equation method is especially closely related to our Mori approach yielding an identical general expression for the memory kernels. Unfortunately most of these calculations then proceed by introducing a semi-phenomenological exponential damping factor $\sim e^{-\alpha t}$ in the memory functions simulating the coupling to the thermodynamic bath. This results in the exact (coherent) short-time behaviour and predicts diffusive transport on a long time-scale. On the other hand it clearly fails as regards relating the diffusion constant to the physical parameters of the systems such as coupling strength, bandwidths of the subsystems and temperature. Another critical aspect from the theoretical point of view is the destruction of time-reversal symmetry due to this damping.

In this paper we calculate the leading term of the memory function up to the second power of the coupling constant ($\sim V^2$) for two entirely different initial conditions. In the next section we first describe a molecular crystal model in detail to introduce our notation and present a derivation of the Mori equation. Section 3 gives the description of the transport problem yielding a general relation between the second moment of the exciton probability density and the memory function (see equation (25)). In section 4 we calculate the memory functions of a system with a localized exciton created at time $t = 0$ at site $n = 0$ and the phonon system in the thermal equilibrium pertaining to $t = 0_-$ [17]. In section 5 the memory function of a thermally excited system [18] is evaluated. The resulting expressions for the frequency-dependent memory functions and the static susceptibility have been studied numerically, and a Fourier back-transform yields the time-dependent memories, the time evolution of the second moment and the diffusion constant. Section 6 deals with systems where the exciton bandwidth is larger than the phonon bandwidth; in section 7 the opposite case has been studied. In section 8 we summarize our results and give a short outlook for further applications of the formalism.

2. The model Hamiltonian and Mori formalism

The system considered in this paper is a one-dimensional molecular exciton–phonon system with Hamiltonian

$$H = H_0^{ex} + H_0^{ph} + H_I = \sum_k \epsilon_k c_k^\dagger c_k + \sum_q \Omega_q b_q^\dagger b_q + \sum_{k,q} V_q c_{k+q}^\dagger c_k (b_q + b_{-q}^\dagger) \quad (1)$$

where the dispersion of the excitonic and phononic energies are given by

$$\epsilon_k = -2J \cos k \quad (2)$$

$$\Omega_q = \Omega_D |\sin(q/2)| \quad \Omega_D^2 = 4f/M. \quad (3)$$

The first two parts describe an excitonic system with nearest-neighbour transfer integral $-J$, which yields the usual cosine dispersion in the Bloch representation, and the acoustic harmonic phonon system (molecular mass M , spring constant f). The coupling function is given by [15]

$$V_q = \frac{2iV \sin q}{\sqrt{2(N+1)\Omega_q}} \quad (4)$$

and refers to a diagonal (in excitonic coordinates) linear (in phonon displacement coordinates) coupling (coupling constant V) in the Wannier representation. The operators c_k (c_k^\dagger), b_q (b_q^\dagger) denote exciton and phonon annihilation (creation) operators respectively and obey the usual commutation rules. In equation (1) we have neglected the constant

zero-point energy of the phonons and throughout we use units in which $\hbar = k_B = 1$. At this stage we define the three dimensionless parameters of the system:

$$\alpha := \frac{\Omega_D}{4J} \quad (5)$$

$$\gamma := \beta 4J = \frac{4J}{T} \quad (6)$$

$$\delta := \frac{V^2}{(4J)^3} \quad (7)$$

which correspond to the ratio of bandwidths, the inverse temperature and the coupling strength respectively.

The description of the excitonic transport amounts to the calculation of the time-dependent occupation probabilities at sites n :

$$w_n(t) = \text{Tr}\{\rho(0)c_n^\dagger(t)c_n(t)\} \quad (8)$$

where $\rho(0)$ denotes the density matrix of the system at time $t = 0$ and c_n (c_n^\dagger) is the annihilation (creation) operator of an exciton in the Wannier representation. In this paper we study two different kinds of local excitation. The first one is often used in the literature [17, 8] and describes an exciton created at site $n = 0$ with a phonon system which is still in thermal equilibrium (without any exciton). In this case the density matrix reads

$$\rho(0) = \rho_{ph}c_0^\dagger c_0 \quad (9)$$

where the phonon part is given by:

$$\rho_{ph} = \frac{e^{-\beta H_0^{ph}}}{\text{Tr}\{e^{-\beta H_0^{ph}}\}}. \quad (10)$$

In a second approach we want to study the time evolution of a local thermal excitation in the excitonic system. In this case the density matrix is close to thermal equilibrium and is given by

$$\rho(0) = \frac{e^{-\beta H + \kappa c_0^\dagger c_0}}{\text{Tr}\{e^{-\beta H + \kappa c_0^\dagger c_0}\}}. \quad (11)$$

The operator $\kappa c_0^\dagger c_0$ can be regarded as a small thermal excitation [18] which results in a local enhancement of the excitonic probabilities around site $n = 0$. We note that equation (11) yields an expression for the transport coefficient which is equivalent with the Kubo formula.

In both treatments of the problem we are able to express the occupation probabilities as correlation functions between local observables:

$$w_n(t) = \Phi_{0n}(t) = (A_0(0) \cdot A_n(t)) \quad (12)$$

where both A_i and the definition of the scalar product (\cdot) depend on the specific excitation as will be shown in the next section. The time evolution is governed by the Liouville (super-) operator $A_i(t) = e^{i\mathcal{L}t} A_i(0)$ with $\mathcal{L}A_i = [H, A_i]$. Defining the Laplace transforms $A_i(z)$ of these functions in the standard manner, the evolution of an operator $A_i(z) = R(z)A_i$ is governed by the resolvent

$$R(z) = \frac{1}{z - i\mathcal{L}}. \quad (13)$$

The operator form of the Mori equation is given by [1, 12]

$$\left(zP - iP\mathcal{L}P + P\mathcal{L}\frac{1}{z - iQ\mathcal{L}}Q\mathcal{L}P \right) R(z)P = P \quad (14)$$

where P and $Q = 1 - P$ are the projection operators onto the set of local variables $\{A_m\}$, $m = 0, \pm 1, \dots, \pm N/2$, and the anti-projector respectively, defined as

$$P \dots = \sum_{m,n} A_m (A_m \cdot A_n)^{-1} (A_n \cdot \dots) \quad (15)$$

and display the hermiticity and idempotence properties $P = P^\dagger = P^2$, $Q = Q^\dagger = Q^2$. Due to the translational invariance of our model all quantities depend on $|m - n|$ only. Introducing Fourier-transformed operators:

$$A_K = \frac{1}{\sqrt{N+1}} \sum_n A_n e^{-iKn} \quad (16)$$

the projection operator in K -space reads

$$P_K \dots = \sum_K A_K (A_K \cdot A_K)^{-1} (A_K \cdot \dots) \quad (17)$$

and the projection of the Mori equation (14) onto the set of transformed operators (16) yields

$$\Phi_K(z) = \frac{\chi_K}{z - i\omega_K \chi_K^{-1} + \mathcal{M}_K(z) \chi_K^{-1}} \quad (18)$$

where

$$\Phi_K(z) = (A_K \cdot R(z) A_K) \quad (19)$$

$$\chi_K = (A_K \cdot A_K) \quad (20)$$

$$\omega_K = (A_K \cdot \mathcal{L} A_K) \quad (21)$$

$$\mathcal{M}_K(z) = \left(A_K \cdot \mathcal{L} Q_K \frac{1}{z - iQ_K \mathcal{L}} Q_K \mathcal{L} A_K \right) \quad (22)$$

denote the evolution functions $\Phi_K(z)$, the static susceptibilities χ_K , the frequencies ω_K and the memory functions $\mathcal{M}_K(z)$ respectively.

3. Excitonic transport

In the previous section we have presented Mori's formalism for evaluating correlation functions which determine the local time-dependent exciton occupation numbers. The main aim of the present paper is to discuss (energy) transport due to exciton motion. For this purpose we define the normalized moments of the excitonic probability density

$$M_\mu(t) = \sum_m m^\mu w_m(t) / \sum_m w_m(t) \quad (23)$$

which may be written as (using equation (16))

$$M_\mu(t) = (i)^\mu \lim_{K \rightarrow 0} \left\{ \frac{(\partial^\mu / \partial K^\mu) w_K(t)}{w_K(t)} \right\}. \quad (24)$$

We are not interested in the peculiar structure of the excitonic distribution but rather in the mean spread of energy due to the excitonic motion. This requires a discussion of the

second moment only, which can be related to the behaviour of the memory function for small K -values as shown in appendix A:

$$M_2(z) - M_2(t=0) = \frac{1}{z^2} \lim_{K \rightarrow 0} \frac{(\partial^2/\partial K^2)\mathcal{M}_K(z)}{\chi_K}. \quad (25)$$

A perturbative calculation of these memory functions yields

$$\mathcal{M}_K(z) = \left(\mathcal{L}_0 A_K \cdot \frac{1}{z - i\mathcal{L}} \mathcal{L}_0 A_K \right) + \mathcal{O}(K^4, V^4). \quad (26)$$

Inspecting equation (26) we notice that this is a correlation function between the operators $\{\mathcal{L}_0 A_K\}$. Defining a projection operator

$$\tilde{P}_K \dots = \mathcal{L}_0 A_K (\mathcal{L}_0 A_K \cdot \mathcal{L}_0 A_K)^{-1} (\mathcal{L}_0 A_K \cdot \dots) \quad (27)$$

we can use the Mori equation (14) once again to express the memory function (26) in terms of a static susceptibility $\tilde{\chi}_K$ and a second-order memory or self-energy function $\Sigma_K(z)$:

$$\mathcal{M}_K(z) = \frac{\tilde{\chi}_K}{z + \Sigma_K(z)\tilde{\chi}_K^{-1}} + \mathcal{O}(K^4, V^4) \quad (28)$$

with

$$\tilde{\chi}_K = (\mathcal{L}_0 A_K \cdot \mathcal{L}_0 A_K) \quad (29)$$

$$\Sigma_K(z) = \left(\mathcal{L}_0 A_K \cdot \mathcal{L} \tilde{Q}_K \frac{1}{z - i\tilde{Q}_K \mathcal{L}} \tilde{Q}_K \mathcal{L} \mathcal{L}_0 A_K \right). \quad (30)$$

In equation (28) we have already used the fact that the frequency matrix $\tilde{\omega}_K = (\mathcal{L}_0 A_K \cdot \mathcal{L} \mathcal{L}_0 A_K)$ vanishes again due to time-reversal symmetry. The static susceptibility $\tilde{\chi}_K$ turns out to be of order K^2 for small K -values:

$$\lim_{K \rightarrow 0} \tilde{\chi}_K = c_2 K^2 \quad (31)$$

as does the self-energy function $\Sigma_K(z)$:

$$\lim_{K \rightarrow 0} \Sigma_K(z) = S(z) K^2 + \mathcal{O}(K^4, V^4). \quad (32)$$

Inserting equations (31), (32) into equation (28) yields

$$\mathcal{M}_K(z) = \frac{c_2 K^2}{z + S(z)c_2^{-1}} + \mathcal{O}(K^4, V^4). \quad (33)$$

On defining the diffusion function as the first time derivative of the second moment:

$$D(t) = \frac{d}{dt} M_2(t) \quad (34)$$

and considering also the second time derivative

$$\dot{D}(t) = \frac{d}{dt} D(t) = \frac{d^2}{dt^2} M_2(t) \quad (35)$$

equation (33) together with equation (25) yields

$$D(z) = \frac{1}{z} \frac{2c_2/c_0}{z + S(z)c_2^{-1}} \quad (36)$$

$$\dot{D}(z) = \frac{2c_2/c_0}{z + S(z)c_2^{-1}} \quad (37)$$

with

$$c_0 = \lim_{K \rightarrow 0} \chi_K. \quad (38)$$

Equations (36) and (37) will form the basis of our discussion of the excitonic transport. On writing

$$\dot{D}(E) = -i\dot{D}(z = -iE) = \dot{d}'(\omega) + i\dot{d}''(\omega) \quad E = \omega + i\epsilon \quad (39)$$

the inverse Laplace transform of equation (37) is given by

$$\dot{D}(t) = -\frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \dot{d}''(\omega) e^{-i\omega t} \quad (40)$$

where the spectrum $\dot{d}''(\omega)$ may by inserting equation (37) be written as

$$\dot{d}''(\omega) = \frac{2c_2}{c_0} \frac{[\epsilon - s''(\omega)c_2^{-1}]}{[\omega - s'(\omega)c_2^{-1}]^2 + [\epsilon - s''(\omega)c_2^{-1}]^2}. \quad (41)$$

$s'(\omega)$ and $s''(\omega)$ are the real and imaginary parts of the self-energy function $-iS(z = -iE)$ (compare (39)) and obey the Kramers–Kronig relation

$$s'(\omega) = \frac{1}{\pi} \text{P} \int_{-\infty}^{\infty} d\omega' \frac{s''(\omega')}{\omega' - \omega}. \quad (42)$$

The long-time behaviour of the various functions can be discussed studying the low-frequency behaviour of the (symmetric) function $\sigma''(\omega)$, or, to be more precise,

$$\begin{aligned} \lim_{\omega \rightarrow 0} s''(\omega) \sim \omega^0 &\Rightarrow \lim_{\omega \rightarrow 0} \dot{d}(\omega) \sim \omega^0 \Rightarrow \lim_{t \rightarrow \infty} \dot{D}(t) = 0 \Rightarrow \lim_{t \rightarrow \infty} D(t) = D \\ \lim_{\omega \rightarrow 0} s''(\omega) \sim \omega^2 &\Rightarrow \lim_{\omega \rightarrow 0} \dot{d}(\omega) \sim \omega^0 + \delta(\omega) \Rightarrow \lim_{t \rightarrow \infty} \dot{D}(t) = \tilde{D} \Rightarrow \lim_{t \rightarrow \infty} D(t) = \tilde{D}t \end{aligned} \quad (43)$$

which means that transport will be diffusive if $\sigma''(0) = \text{constant}$, whereas in the case of a vanishing zero-frequency value the diffusion function increases linearly with the time, which results in a t^2 -law for the second moment typical for coherent transport processes.

4. Fast single-site excitation (FSSE)

In this section we present the explicit calculation of the memory function for the initial condition given by equation (9). The time-dependent occupation probabilities are written as [17]

$$w_m(t) = (A_0|A_m(t)) \quad (44)$$

where

$$A_i = c_i^\dagger c_i \quad (45)$$

and the scalar product between two operators now is specified to be $(\cdot) \equiv (| \cdot)$

$$(A|B) = \text{Tr}(\rho_{ph} A^\dagger B) \quad (46)$$

where $\text{Tr}(\cdot \cdot \cdot)$ means the product trace over all phonon states combined with the single-exciton states, and ρ_{ph} is given by equation (10). We want to note that for this definition of the scalar product the Liouville operator does not display the hermiticity property

$$(A|\mathcal{L}B) \neq (\mathcal{L}A|B) \quad (47)$$

since the interaction part \mathcal{L}_I does not commute with the phonon density matrix. On inserting equation (16) into the definition of the scalar product, the static susceptibility χ_K is given by

$$\chi_K = (A_K|A_K) = \frac{1}{N+1} \sum_{kk'} \text{Tr}\{\rho_{ph} c_k^\dagger c_{k+K} c_{k'+K}^\dagger c_{k'}\} = 1 \quad (48)$$

and the memory function in K -space reads (see equation (22))

$$\mathcal{M}_K(z) = (A_K|\mathcal{L}Q_K[1/(z - iQ_K\mathcal{L})]Q_K\mathcal{L}A_K) = (A_K|\mathcal{L}Q_K[1/(z - i\mathcal{L}Q_K)]Q_K\mathcal{L}A_K) \quad (49)$$

with

$$A_K = \frac{1}{\sqrt{N+1}} \sum_n c_n^\dagger c_n e^{-iKn} = \frac{1}{\sqrt{N+1}} \sum_k c_{k+K}^\dagger c_k. \quad (50)$$

The last equality in equation (49), with the reversed order of the Liouvillian and the anti-projector in the denominator, is due to the idempotency property of the projection operators. In a first step we remove the anti-projectors Q_K in equation (49). For this purpose we use the algebraic identity

$$R_{Q_K}(z) = Q_K \frac{1}{z - i\mathcal{L}Q_K} = Q_K \frac{1}{z - i\mathcal{L}(1 - P_K)} = Q_K R(z) - iR_{Q_K}(z)\mathcal{L}P_K R(z) \quad (51)$$

which, on inserting into equation (49), yields for the memory function

$$\mathcal{M}_K(z) = \frac{(A_K|\mathcal{L}Q_K R(z)\mathcal{L}A_K)}{1 + i(A_K|R(z)\mathcal{L}A_K)}. \quad (52)$$

The remaining anti-projector in the numerator of equation (52) can also be removed, because for an arbitrary operator B we have the property that

$$(A_K|\mathcal{L}Q_K B) = (A_K|\mathcal{L}B) - (A_K|\mathcal{L}P_K B) = (A_K|\mathcal{L}B) - \underbrace{(A_K|\mathcal{L}A_K)}_{=0} (A_K|A_K)^{-1} (A_K|B). \quad (53)$$

Employing

$$\mathcal{L}A_K = \mathcal{L}_0 A_K = \frac{1}{\sqrt{N+1}} \sum_k (\epsilon_{k+K} - \epsilon_k) c_{k+K}^\dagger c_k \quad (54)$$

as well as the hermiticity of the unperturbed Liouvillian \mathcal{L}_0 with respect to the scalar product

$$(A|\mathcal{L}_0 B) = (\mathcal{L}_0 A|B) \quad (55)$$

the memory function is written as

$$\mathcal{M}_K(z) = \frac{(\mathcal{L}_0 A_K|R(z)\mathcal{L}_0 A_K)}{1 + i(A_K|R(z)\mathcal{L}_0 A_K)} + \frac{(A_K|\mathcal{L}_I R(z)\mathcal{L}_0 A_K)}{1 + i(A_K|R(z)\mathcal{L}_0 A_K)}. \quad (56)$$

So far our treatment has been exact, without any approximations. Now we use perturbation theory and draw attention to the behaviour of the memory function for small K -values, or, being more precise, we want to extract the leading term $\propto K^2$. In appendix B it is shown that the second part of equation (56) does not contribute in this order, and from equation (54) we deduce that

$$\lim_{K \rightarrow 0} \mathcal{L}_0 A_K = \frac{1}{\sqrt{N+1}} \sum_k v_k c_k^\dagger c_k K \quad (57)$$

where the v_k represent the group velocities in the excitonic system:

$$v_k = \frac{d\epsilon_k}{dk} = 2J \sin k. \quad (58)$$

This means that the numerator in equation (56) is of order K^2 and

$$\mathcal{M}_K(z) = (\mathcal{L}_0 A_K | [1/(z - i\mathcal{L})] \mathcal{L}_0 A_K) + \mathcal{O}(K^4, V^4). \quad (59)$$

This is the result given in equation (26). We are thus able to use the Mori formalism once again with the projection operator \tilde{P}_K defined in equation (27). The static susceptibility (29) is easily calculated, using equation (54), and the definition of the scalar product (46):

$$\lim_{K \rightarrow 0} \tilde{\chi}_K = \frac{1}{N+1} \sum_k v_k^2 K^2 = 2J^2 K^2 \quad (60)$$

which determines c_2 as defined in equation (31). The self-energy function $\Sigma_K(z)$ is given by (cf. (30)):

$$\begin{aligned} \Sigma_K(z) &= (\mathcal{L}_0 A_K | \mathcal{L} R_{\tilde{Q}_K}(z) \mathcal{L} \mathcal{L}_0 A_K) \\ &= (\mathcal{L}_0^2 A_K | R_{\tilde{Q}_K}(z) \mathcal{L}_0^2 A_K) + (\mathcal{L}_0^2 A_K | R_{\tilde{Q}_K}(z) \mathcal{L}_I \mathcal{L}_0 A_K) \\ &\quad + (\mathcal{L}_0 A_K | \mathcal{L}_I R_{\tilde{Q}_K}(z) \mathcal{L}_0^2 A_K) + (\mathcal{L}_0 A_K | \mathcal{L}_I R_{\tilde{Q}_K}(z) \mathcal{L}_I \mathcal{L}_0 A_K) \end{aligned} \quad (61)$$

with

$$R_{\tilde{Q}_K}(z) = \tilde{Q}_K \frac{1}{z - i\mathcal{L}\tilde{Q}_K}. \quad (62)$$

The first three terms in equation (61) are of fourth or higher order in K which means that

$$\Sigma_K(z) = (\mathcal{L}_0 A_K | \mathcal{L}_I R_{\tilde{Q}_K}(z) \mathcal{L}_I \mathcal{L}_0 A_K) + \mathcal{O}(K^4, V^4). \quad (63)$$

Note that both interactions \mathcal{L}_I are on the right-hand side of the scalar product which is in contrast to a similar formula given in [17]. Since equation (63) is of order V^2 due to the two interaction operators \mathcal{L}_I we are able to replace the full Liouvillian \mathcal{L} in the resolvent by the unperturbed \mathcal{L}_0 . On the other hand this allows us to remove the anti-projectors $\tilde{Q}_K = 1 - \tilde{P}_K$ since

$$\tilde{P}_K \mathcal{L}_0^v \mathcal{L}_I \mathcal{L}_0 A_K = \mathcal{L}_0 A_K \tilde{\chi}_K^{-1} (\mathcal{L}_0 A_K | \mathcal{L}_0^v \mathcal{L}_I A_K) \sim \text{Tr}\{\rho_{ph}(b_q + b_{-q}^\dagger)\} = 0 \quad (64)$$

and we finally arrive at

$$\Sigma_K(z) = (\mathcal{L}_0 A_K | \mathcal{L}_I [1/(z - i\mathcal{L}_0)] \mathcal{L}_I \mathcal{L}_0 A_K) + \mathcal{O}(K^4, V^4). \quad (65)$$

The evaluation of the commutators in equation (65) is straightforward and yields for the function $S(z)$, defined in equation (32),

$$S(z) = \frac{1}{N+1} \sum_{k,q} |V_q|^2 (v_k - v_{k+q}) \left\{ \frac{n_q v_k - (n_q + 1)v_{k+q}}{z - i(\epsilon_{k+q} - \epsilon_k - \Omega_q)} + \frac{(n_q + 1)v_k - n_q v_{k+q}}{z - i(\epsilon_{k+q} - \epsilon_k + \Omega_q)} \right\} \quad (66)$$

with the Bose occupation

$$n_q = 1/(e^{\beta\Omega_q} - 1). \quad (67)$$

The imaginary part (see equation (39)) is given as a sum over δ -functions

$$\begin{aligned} s''(\omega) &= \frac{1}{N+1} \sum_{k,q} |V_q|^2 (v_k - v_{k+q}) \{ (n_q v_k - (n_q + 1)v_{k+q}) \delta[\omega + (\epsilon_{k+q} - \epsilon_k - \Omega_q)] \\ &\quad + ((n_q + 1)v_k - n_q v_{k+q}) \delta[\omega + (\epsilon_{k+q} - \epsilon_k + \Omega_q)] \} \end{aligned} \quad (68)$$

and the evaluation of equation (68) can be performed by the procedure presented in appendix B, yielding

$$s''(\omega) = \frac{V^2}{\alpha} \{s^+(\omega) + s^-(\omega)\} \quad (69)$$

with

$$s^\pm(\omega) = -\frac{1}{\pi} \int_{\substack{q \in [0, \pi] \\ |u_q^\pm| < 1}} dq \sin^2(q) \coth \left\{ \frac{1}{2} \gamma \alpha \sin \left(\frac{q}{2} \right) \right\} \sqrt{1 - (u_q^\pm)^2} \quad (70)$$

and the abbreviations

$$u_q^\pm = \frac{\omega \pm \Omega_D |\sin q/2|}{4J \sin q/2}. \quad (71)$$

The remaining q -integration has to be performed numerically, and the real part of the self-energy function is calculated using a principal-value integration.

5. Thermal site excitation (TSE)

The evaluation of the site occupation probabilities for an initial condition of type (11) requires more effort. In contrast to the previous section here we have to make the additional assumption that the operator $\kappa c_0^\dagger c_0$ in the exponent is ‘small’, i.e. that the system is close to thermal equilibrium. In this case in a previous paper [18] it has been shown that a Goldberger–Adams expansion of the density matrix yields in a linearized theory the following expression for the deviation of the expectation values from the stationary equilibrium value:

$$A_n(t) = \langle c_n^\dagger(t) c_n(t) \rangle_T - \langle c_n^\dagger c_n \rangle_T = \kappa (A_0(0); A_n(t)) \quad (72)$$

where $(\cdot) \equiv (\cdot; \cdot)$ denotes the Mori product which has been exploited in the original papers [11, 19]

$$(A; B) = \frac{1}{\beta} \int_0^\beta d\lambda \langle A^\dagger(0) B(i\lambda) \rangle_T \quad (73)$$

and the thermal expectation values are defined in the conventional manner:

$$\langle A \rangle_T = \text{Tr} \{ \rho_T A \} \quad \rho_T = \frac{e^{-\beta H}}{\text{Tr}(e^{-\beta H})} \quad (74)$$

and the Liouville operator now displays hermiticity:

$$(A; \mathcal{L}B) = (\mathcal{L}A; B). \quad (75)$$

Note that with the definition of the normalized second moment (equation (23)) the factor κ cancels out, and the constant c_0 , as defined in (38) is given by

$$c_0 = \frac{1}{N+1} \sum_{kk'} \langle c_k^\dagger c_k c_{k'}^\dagger c_{k'} \rangle_T = \frac{1}{N+1} \sum_k \langle N_k \rangle_T = \frac{1}{N+1} \quad (76)$$

since the total exciton number equals one. The memory function is given as

$$\mathcal{M}_K(z) = (\mathcal{L}A_K; Q_K [1/(z - i\mathcal{L}Q_K)] Q_K \mathcal{L}A_K) \quad (77)$$

where we have used equation (75). Again the anti-projectors can be removed by the same procedure as in the previous section (see equations (51) and (53)), yielding

$$\mathcal{M}_K(z) = (\mathcal{L}_0 A_K; [1/(z - i\mathcal{L})] \mathcal{L}_0 A_K) + O(K^4). \quad (78)$$

As pointed out by Forster [2] equation (78) together with equation (25) ‘is nothing but a funny way of writing down the Kubo formula [10]’. Using the projection operator formalism once again, the static susceptibility is given by

$$\tilde{\chi}_K = (\mathcal{L}_0 A_K; \mathcal{L}_0 A_K) = (\mathcal{L}_0 A_K; \mathcal{L} A_K) \quad (79)$$

which, on employing equation (57), relates the constant c_2 to the thermal occupation numbers

$$c_2 = \frac{1}{N+1} \sum_k v_k^2 \langle N_k \rangle_T \quad \langle N_k \rangle_T = \langle c_k^\dagger c_k \rangle_T. \quad (80)$$

The evaluation of the thermal expectation values up to second order in the coupling using the Goldberger–Adams expansion of the density matrix with respect to the interaction Hamiltonian H_I is presented in appendix C.

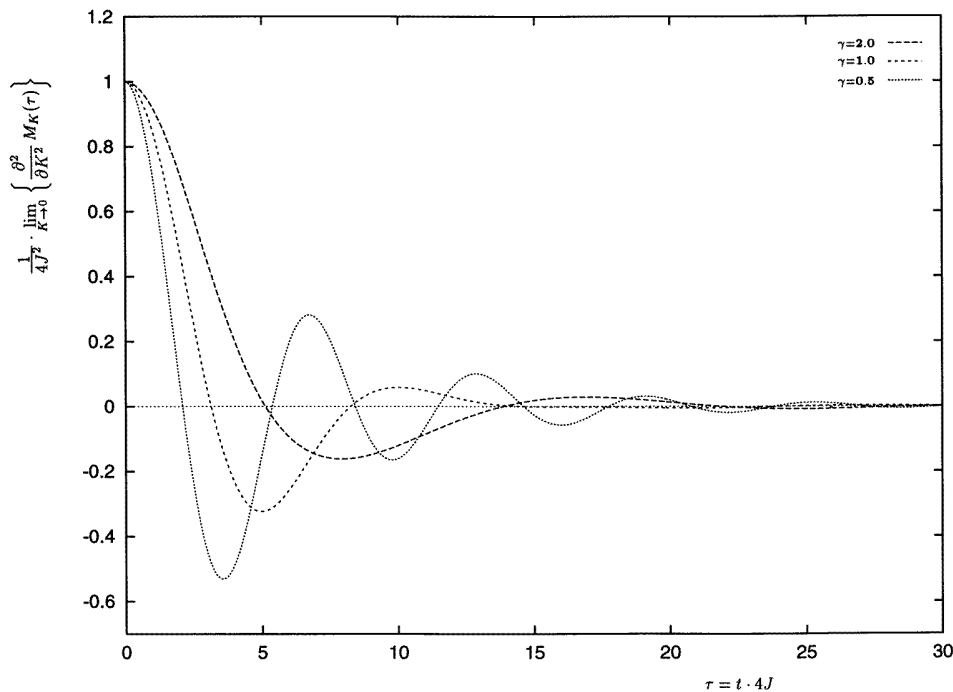


Figure 1. FSSE: here we show the time dependence of the K^2 -term of the memory function $((1/4J^2) \lim_{K \rightarrow 0} (\partial^2/\partial K^2) M_K(\tau))$, $\tau = 4Jt$ for three different temperatures $\gamma = 4J/T$ (0.5, 1.0, 2.0), bandwidth parameter $\alpha = \Omega_D/(4J) = 0.5$ and coupling $\delta = D^2/(4Jf) = 0.01$. The decay of the memories is complete and is faster with increasing temperature.

We can use the same arguments as in the case of a FSSE yielding equation (65) from equation (61), but with the difference that now the complete Liouvillian, and not only \mathcal{L}_0 , displays hermiticity to arrive at the following expression for the self-energy function:

$$\Sigma_K(z) = (\mathcal{L}_I \mathcal{L}_0 A_K | [1/(z - i\mathcal{L}_0)] \mathcal{L}_I \mathcal{L}_0 A_K) + O(K^4, V^4). \quad (81)$$

We use the dissipation-fluctuation theorem [1] corresponding to definition (73):

$$\sigma_K''(\omega) = -\pi \frac{\sinh(\beta\omega/2)}{\beta\omega/2} \exp(\beta\omega/2) J_K(\omega) \quad (82)$$

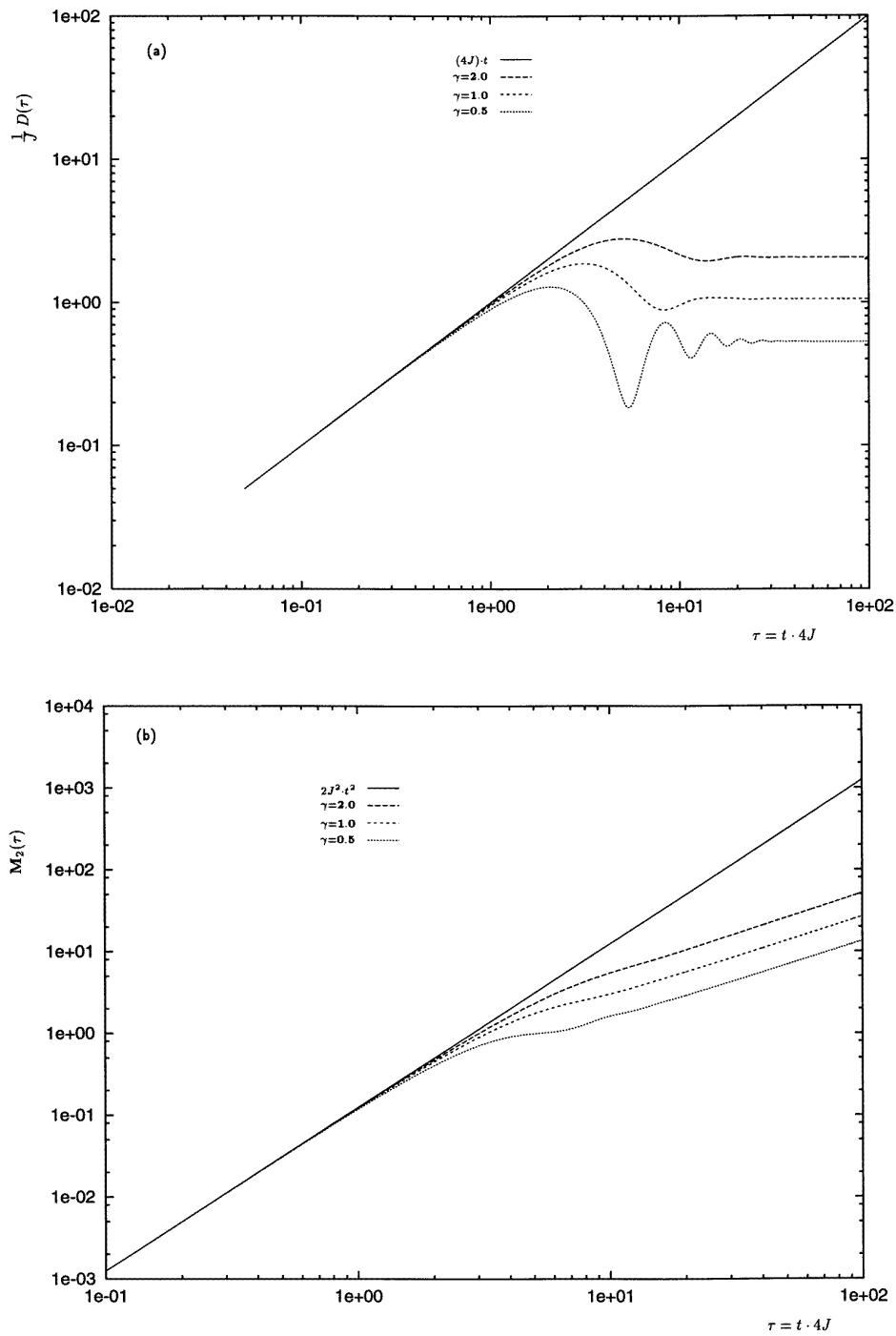


Figure 2. (a) FSSE: the diffusion function $D(\tau)$ resulting from the memories of figure 1. The solid line refers to coherent propagation without coupling to a bath ($D(t) = 4J^2t = J\tau$). (b) FSSE: the time evolution of the second moment resulting from the memories and diffusion functions of figures 1 and 2(a). For short times we observe coherent propagation ($\sim 2J^2t^2$) and for long times diffusive transport ($\sim Dt$).

which relates the imaginary part $\sigma_K''(\omega)$ (compare equation (39)) to the spectral function

$$J_K(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \langle \mathcal{L}_I \mathcal{L}_0 A_K \mathcal{L}_I \mathcal{L}_0 A_K(t) \rangle_T e^{i\omega t} \quad (83)$$

which is defined as the Fourier transform of the real-time correlation function. Neglecting terms of order higher than V^2 allows us to perform the thermal expectation values in (83) with H_0 . Comparing the result with equation (32) we get

$$s''(\omega) = -\pi \frac{\sinh(\beta\omega/2)}{\beta\omega/2} \exp(\beta\omega/2) \{f_1(\omega) + f_2(\omega)\} \quad (84)$$

with

$$f_1(\omega) = \frac{1}{N+1} \sum_{k,q} |V_q|^2 (n_q + 1) (v_k - v_{k+q})^2 \frac{e^{-\beta\epsilon_k}}{Z_0} \delta[\omega - (\epsilon_{k+q} - \epsilon_k - \Omega_q)] \quad (85)$$

$$f_2(\omega) = \frac{1}{N+1} \sum_{k,q} |V_q|^2 n_q (v_k - v_{k+q})^2 \frac{e^{-\beta\epsilon_k}}{Z_0} \delta[\omega - (\epsilon_{k+q} - \epsilon_k + \Omega_q)]. \quad (86)$$

The factors $e^{-\beta\epsilon_k}/Z_0$ are due to the excitonic expectation values

$$\langle c_k^\dagger c_k \rangle_T^{(0)} = \frac{e^{-\beta\epsilon_k}}{Z_0} \quad Z_0 = \sum_k e^{-\beta\epsilon_k} \quad (87)$$

of a single particle in thermal equilibrium. Performing the k -sum we obtain

$$s''(\omega) = \frac{1}{Z_0} \frac{V^2}{\alpha} \frac{\sinh(\beta\omega/2)}{\beta\omega/2} \{s^+(\omega) + s^-(\omega)\} \quad (88)$$

with

$$s^\pm(\omega) = -\frac{1}{\pi} \int_{\substack{q \in [0, \pi] \\ |u_q^\pm| < 1}} dq \sin^2 q \left[\cosh\left(\frac{1}{2}\gamma \cos \frac{q}{2} \sqrt{1 - (u_q^\pm)^2}\right) / \sinh\left(\frac{1}{2}\alpha\gamma \sin \frac{q}{2}\right) \right] \\ \times \sqrt{1 - (u_q^\pm)^2} \quad (89)$$

and abbreviations u_q^\pm defined in (71).

6. Broad excitonic bandwidths ($\alpha < 1$)

In this section we want to present the numerical results for a large exciton bandwidth. Figure 1 displays the time evolution of the memory function for different temperatures $\gamma = 4J/T$ in the case where the exciton bandwidth exceeds the phonon bandwidth by a factor 2 ($\alpha = 0.5$) and a coupling constant $\delta = 0.01$. The excitation type is that of a FSSE (section 5). A sharp oscillatory decay is seen with the ‘decay rate’ increasing with increasing temperature.

Figure 2(a) displays the diffusion function resulting from the memories of figure 1, and in figure 2(b) the time evolution of the second moment is depicted on a double-logarithmic scale. In both pictures the solid line represents the coherent motion without coupling to the bath. It is observed that for small times the motion of the excitons is determined by this limit, but within some typical coherence time τ_c the diffusion function saturates at a constant value (the diffusion constant). This results in a linear time dependence of the second moment, which can be seen in figure 2(b). Inspecting figure 2, we notice that both the coherence time and the diffusion constant decrease with increasing temperature (γ smaller). Since coherent motion refers to a constant, non-decaying memory, this corresponds

to the increasing decay rate of the memories with increasing temperature (see figure 1). The physical reason for this behaviour is the increase of the scattering probabilities for excitons due to the Bose occupation of the phonon states (compare equation (67)).

We do not present the corresponding pictures for a TSE since they show a similar behaviour. Indeed, they are completely identical in the high-temperature region. For low temperatures the qualitative behaviour remains the same, i.e. complete decay, but memories of a TSE display an even faster decay than those of a FSSE. Possible reasons will be discussed at the end of this section.

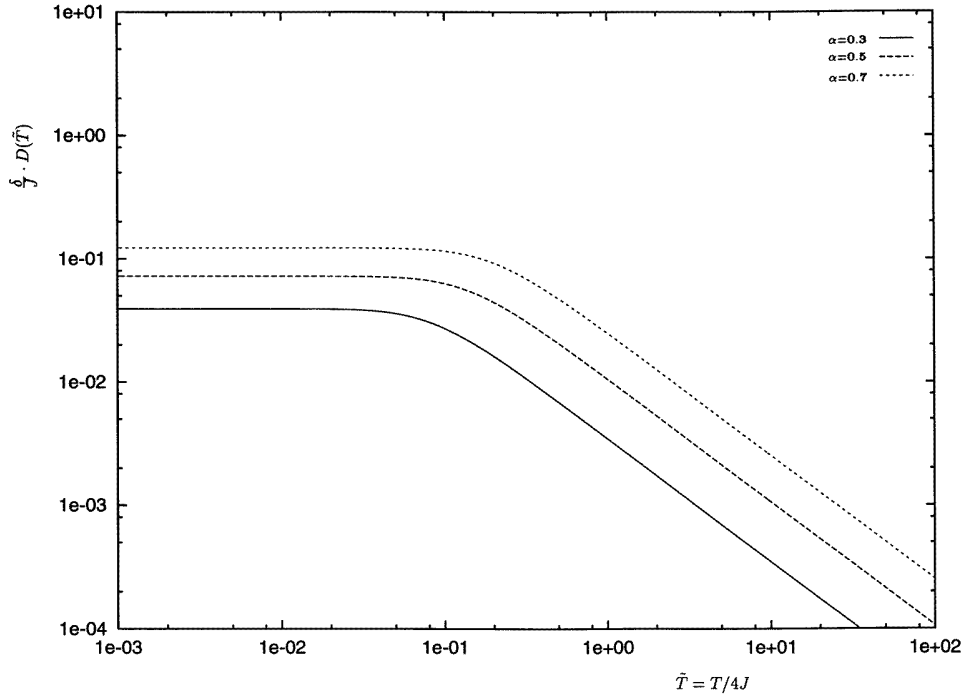


Figure 3. FSSE: the temperature-dependent diffusion constant. For low temperatures the diffusion constant saturates to a constant value and for high temperatures it becomes $\sim 1/T$. Bandwidth parameter: $\alpha = 0.3$ (solid line); $\alpha = 0.5$ (dashed line); and $\alpha = 0.7$ (dotted line).

In figure 3 we have drawn the temperature-dependent diffusion constant for a FSSE (section 4). The bandwidth parameters have been chosen as $\alpha = 0.3$ (solid line), $\alpha = 0.5$ (dashed line) and $\alpha = 0.7$ (dotted line). The finite value of the diffusion constant for $T \rightarrow 0$ is due to the characteristics of the one-dimensional acoustic mode density ($\rho(\omega = 0) = \text{constant}$). We observe a relatively sharp transition between an almost constant value at low temperatures ($\tilde{T} \leq 10^{-1}$) to a decay $\sim 1/T$ at higher temperatures ($\tilde{T} \geq 10^{-1}$).

Figure 4 compares the diffusion constant resulting from a FSSE with that of a TSE. The two approaches are completely identical in the high-temperature region whereas for low temperatures the ‘thermal’ diffusion constant turns out to be smaller. There are two possible reasons for this strange behaviour. First, we are not able to calculate the static susceptibility $\tilde{\chi}$ exactly, which was possible in the case of a FSSE. Since the contribution of the higher-order terms in the Goldberger–Adams expansion of the density matrix is increasing with decreasing temperature, the results for low temperatures have to be studied more carefully.

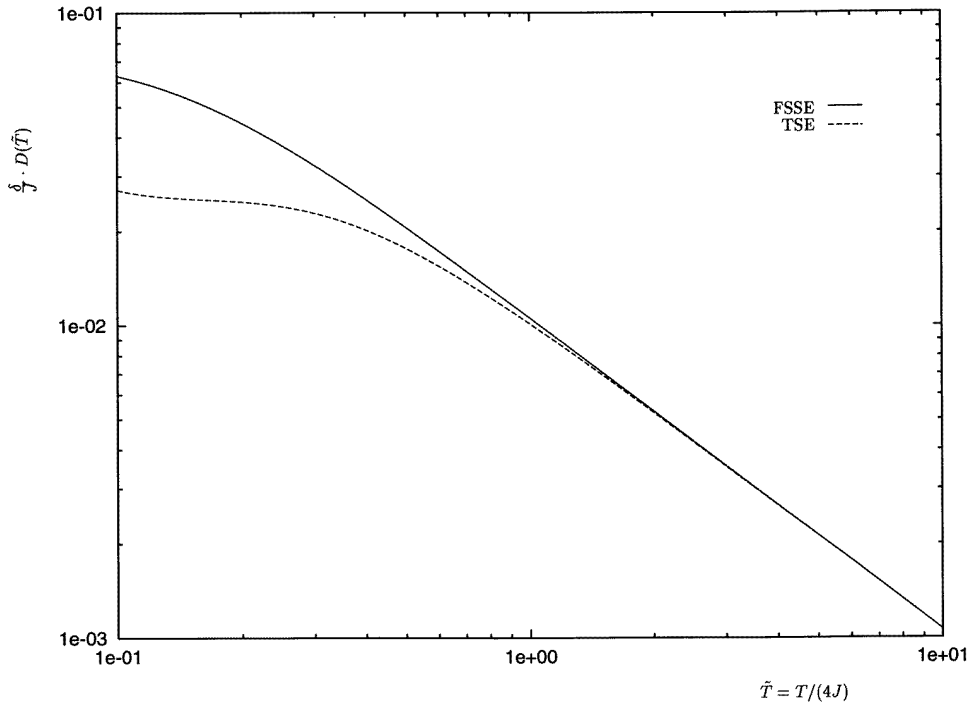


Figure 4. The temperature-dependent diffusion constant for a FSSE (solid line) and a TSE (dashed line). Bandwidth parameter: $\alpha = 0.5$.

Second, there exists an intrinsic temperature dependence in the concept of a TSE. It has been shown [4] that for high temperatures a TSE results in a deviation of the local occupation numbers which is strongly localized at the single site of the excitation, comparable with the situation for a FSSE. With decreasing temperature, the excitation becomes broader and broader which means that the influence of large-wavelength exciton modes with vanishing group velocity is increasing. This could also be the reason for the different results at low temperatures.

7. Small excitonic bandwidths ($\alpha > 1$)

In the previous section the connection between a (complete) decay of the memory and the transition to diffusive transport has been established for systems with broad exciton bands. Figure 5 displays the time evolution of the memories in the case of a small excitonic bandwidth ($\alpha = \Omega_D/(4J) = 2.0$). A completely different qualitative behaviour, i.e. incomplete decay, is observed. Physically this is due to the specific model, since there exists no scattering process in second order fulfilling both the energy and momentum conservation laws ($\epsilon_{k+q} - \epsilon_k \pm \Omega_q \neq 0$).

Figure 6 shows the time dependence of the diffusion function resulting from the memories depicted in figure 5. The solid line represents the coherent limit which equals the short-time behaviour of the other curves. Contrary to the case of a broad exciton band, the non-decaying part of the memory results in a diffusion function increasing linearly with

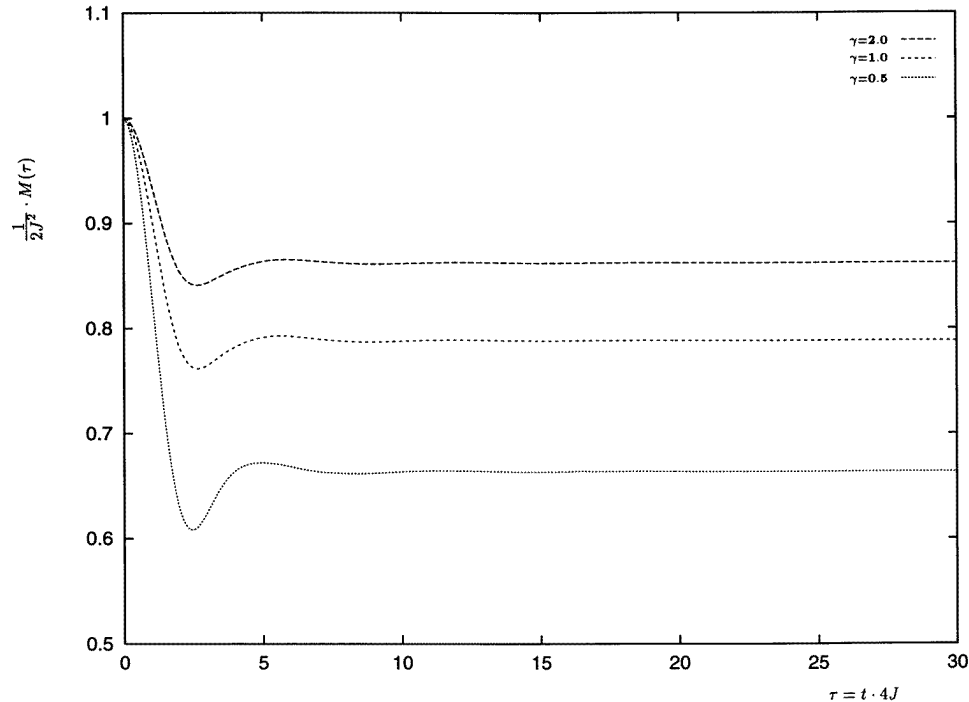


Figure 5. FSSE: the K^2 -term of the memory function $((1/4J^2) \lim_{K \rightarrow 0} (\partial^2/\partial K^2) M_K(\tau), \tau = 4Jt)$ for three different temperatures ($\gamma = 0.5, 1.0, 2.0$) in the case of a small exciton band ($\alpha = \Omega_D/(4J) = 2.0, \delta = 0.1$). In contrast to figure 1, the decay here is incomplete with a finite asymptotic value depending on the temperature.

time ($\sim t$) also in the long-time regime. The pre-factor is somewhat reduced compared with the uncoupled situation due to exciton renormalization which means partial ‘dressing’ of the excitons with a phonon cloud. It is observed that increasing the temperature (γ smaller) is tantamount to a smaller value of the non-decaying memory, i.e. a smaller increase of the diffusion function. Again this is due to the Bose occupation of the phonon states.

All of the pictures correspond to a system with a FSSE. As far as the TSE is concerned, we refer to the remarks of the previous section.

8. Results and discussion

We have calculated the time evolution of the second moment of the exciton probability density for a one-dimensional molecular crystal model with a linear coupling to acoustic phonons. Using Mori formalism and assuming a small exciton–phonon coupling, the frequency-dependent second-order memory function has been evaluated up to second order in the coupling constant ($\sim V^2$). Due to the symmetry of these functions the resulting time dependency of both the memory function and the second moment are fully time-reversal symmetric.

In our results the characteristics of the dispersion relations of the two uncoupled subsystems are crucial. The memory functions, for example, turn out to decay in the case of a broad exciton band, whereas for a small exciton bandwidth this decay remains

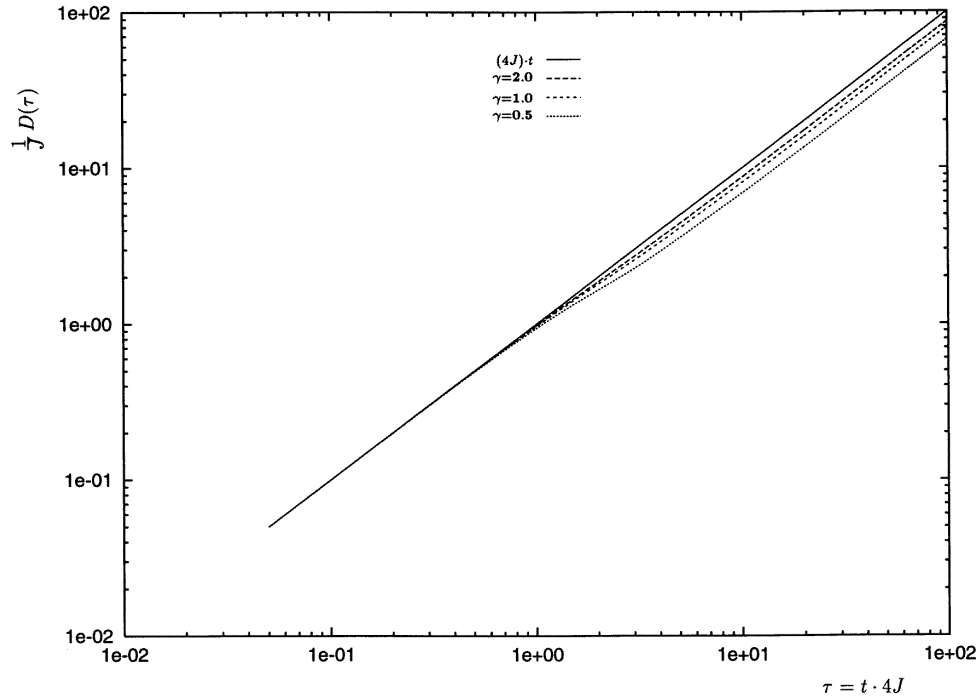


Figure 6. FSSE: the time evolution of the diffusion function for the memory functions of figure 5. The solid line displays the coherent limit without coupling to the bath. The diffusion function is proportional to the first power of the time. For long times the pre-factor is somewhat reduced due to renormalization effects.

incomplete and a finite constant value of the memory exists.

In the case of a broad exciton band the decay results in a diffusive transport with the second moment of the exciton probability density being proportional to the first power of t for long times. The diffusion constant falls off proportionally to $1/T$ for high temperatures whereas the behaviour for low temperatures depends on the specific choice of the excitation. In the case of a FSSE (compare section 4) the diffusion constant reaches a constant value as $T \rightarrow 0$, whereas for a TSE the diffusion constant tends to zero. We ascribe this second behaviour to the intrinsic temperature dependence of the TSE approach, i.e. the increasing width of the initial exciton occupation probability with decreasing temperature. The monotonic decrease in the high-temperature regime for both types of excitation is due to our choice of a diagonal coupling only. An inclusion of phonon-induced exciton transfer between different sites would yield a second transport mechanism with a quite different temperature dependence.

Since a constant memory refers to coherent motion, we are, on the other hand, not able to find diffusive transport in systems with narrow exciton bands. To achieve diffusivity either anharmonic terms in the phonon system or nonlinear exciton-phonon coupling would be necessary. In real systems the coupling to acoustic phonons is most important in the low-temperature regime when the scattering with optical phonons becomes ineffective due to the Bose occupation. For this situation we deduce that the coherence-destroying process has to be of fourth order at least. This means that for small values of the exciton-phonon

coupling and a small exciton bandwidth transport will remain coherent for very long times as far as the exciton–phonon coupling is concerned. On the other hand this means that the transport process is almost completely controlled by disorder effects. The inclusion of these effects within the presented formalism seems possible and will be given elsewhere.

Another generalization of our results would be the extension to higher-dimensional systems. This procedure is straightforward and requires only an increasing amount of numerical effort. Our future work will be concerned with the inclusion of transitive (non-diagonal) coupling and also with the non-perturbative approaches based on unitary transformations or mode-coupling theories for example. Since our result is exact in a perturbative sense, it is well suited for checking results, which are received in a non-perturbative manner.

Appendix A

The normalized second moment is given by (see equation (23))

$$M_2(t) = - \lim_{K \rightarrow 0} \left\{ \frac{(\partial^2/\partial K^2)w_K(t)}{w_K(t)} \right\} \quad (A1)$$

where $w_K(t)$ are the Fourier-transformed occupation probabilities

$$w_K(t) = \frac{1}{\sqrt{N+1}} \sum_m w_m(t) e^{-iKm}. \quad (A2)$$

Using the Mori equation (18) the Laplace transform of equation (A2) may be written as

$$w_K(z) = \frac{1}{\sqrt{N+1}} \frac{\chi_K}{z + \mathcal{M}_K(z)\chi_K^{-1}}. \quad (A3)$$

Due to the inversion symmetry of the model Hamiltonian the series expansion in powers of K of all Fourier-transformed functions contains only even powers in K and we deduce that

$$\lim_{K \rightarrow 0} \chi_K \propto K^0 \quad (A4)$$

$$\lim_{K \rightarrow 0} \mathcal{M}_K(z) \propto K^2. \quad (A5)$$

Inserting equations (A4) and (A5) into equation (A2) we are able to write

$$w_K(z) = \frac{1}{\sqrt{N+1}} \frac{\chi_K}{z} \left(\frac{1}{1 + \mathcal{M}_K(z)/(z\chi_K)} \right) = \frac{1}{\sqrt{N+1}} \frac{\chi_K}{z} \left(1 - \frac{\mathcal{M}_K(z)}{z\chi_K} + O(K^4) \right) \quad (A6)$$

and thus

$$M_2(z) = - \lim_{K \rightarrow 0} \left\{ \frac{1}{z} \frac{(\partial^2/\partial K^2)\chi_K}{\chi_K} - \frac{1}{z^2} \frac{(\partial^2/\partial K^2)\mathcal{M}_K(z)}{\chi_K} \right\}. \quad (A7)$$

The first term in equation (A7) represents $M_2(t = 0)$ whereas the second one determines the time evolution (see equation (25)), which is what we wanted to prove.

Appendix B

The second part of the memory function in equation (56) is given by

$$\mathcal{M}_K^{(2)}(z) = \frac{(A_K | \mathcal{L}_I R(z) \mathcal{L}_0 A_K)}{1 + i(A_K | R(z) \mathcal{L}_0 A_K)} \quad (B1)$$

with

$$R(z) = \frac{1}{z - i(\mathcal{L}_0 + \mathcal{L}_I)} = R_0(z) + R_0(z)i\mathcal{L}_I R_0(z) + O(\mathcal{L}_I^2) \quad (\text{B2})$$

and the unperturbed resolvent

$$R_0(z) = \frac{1}{z - i\mathcal{L}_0}. \quad (\text{B3})$$

Inserting equation (B2) into the numerator of equation (B1) we obtain

$$\mathcal{M}_K^{(2)}(z) = \frac{(A_K | \mathcal{L}_I R_0(z) \mathcal{L}_0 A_K) + (A_K | \mathcal{L}_I R_0(z) i \mathcal{L}_I R_0(z) \mathcal{L}_0 A_K)}{1 + i(A_K | R(z) \mathcal{L}_0 A_K)}. \quad (\text{B4})$$

The first term in equation (B4) vanishes due to the single-boson creation and annihilation operators in \mathcal{L}_I :

$$(A_K | \mathcal{L}_I R_0(z) \mathcal{L}_0 A_K) = 0 \quad (\text{B5})$$

and in the second term we use the series expansion of the resolvent

$$R_0(z) = \frac{1}{z} \sum_{\nu=0}^{\infty} \left(\frac{i\mathcal{L}_0}{z} \right)^{\nu} \quad (\text{B6})$$

to arrive at

$$\mathcal{M}_K^{(2)}(z) = \left(A_K \left| \mathcal{L}_I R_0(z) i \mathcal{L}_I \sum_{\nu=1}^{\infty} \left(\frac{i\mathcal{L}_0}{z} \right)^{\nu} A_K \right) \right. / 1 + i(A_K | R(z) \mathcal{L}_0 A_K). \quad (\text{B7})$$

We do not have to calculate the full K -dependence of equation (B7) but to extract the leading term of order K^2 . Using

$$\lim_{K \rightarrow 0} \mathcal{L}_0^{\nu} A_K \propto K^{\nu} \quad (\text{B8})$$

we notice that we have to keep only the first two terms in the sum of equation (B7):

$$\mathcal{M}_K^{(2)}(z) = \frac{(i/z)(A_K | \mathcal{L}_I R_0(z) \mathcal{L}_I \mathcal{L}_0 A_K) - (1/z^2)(A_K | \mathcal{L}_I R_0(z) \mathcal{L}_I \mathcal{L}_0^2 A_K)}{1 + i(A_K | R(z) \mathcal{L}_0 A_K)}. \quad (\text{B9})$$

The first part of (B9) is proportional to K and has to be equal to zero due to inversion symmetry (which can also be proved by a direct evaluation) and the second one is of order K^2 which allows us to write (expanding the denominator for small K -values)

$$\begin{aligned} \mathcal{M}_K^{(2)}(z) &= - \lim_{K \rightarrow 0} \frac{1}{z^2} (A_K | \mathcal{L}_I R_0(z) \mathcal{L}_I \mathcal{L}_0^2 A_K) + O(K^4) \\ &= - \frac{K^2}{z^2} \frac{1}{N+1} \sum_{k,q} |V_q|^2 (v_k^2 - v_{k+q}^2) \\ &\quad \times \left\{ \frac{1}{z - i(\epsilon_{k+q} - \epsilon_k + \Omega_q)} - \frac{1}{z - i(\epsilon_{k+q} - \epsilon_k - \Omega_q)} \right\}. \end{aligned} \quad (\text{B10})$$

Calculating (B10) along the imaginary axis

$$-i\mathcal{M}_K^{(2)}(z = -iE) = m'_K(\omega) + im''_K(\omega) \quad (\text{B11})$$

we obtain for the imaginary part

$$\begin{aligned} m''_K(\omega) &= \frac{K^2}{\omega^2} \frac{1}{N+1} \sum_{k,q} |V_q|^2 (v_k^2 - v_{k+q}^2) \\ &\quad \times \{ \delta[\omega + (\epsilon_{k+q} - \epsilon_k + \Omega_q)] - \delta[\omega + (\epsilon_{k+q} - \epsilon_k - \Omega_q)] \}. \end{aligned} \quad (\text{B12})$$

Now we present the general scheme for how to evaluate a sum of type (B12), which determines also the non-vanishing parts of the memory function. First we introduce the abbreviations

$$u_q^\mp = \frac{\omega \mp \Omega_q}{4J|\sin(q/2)|} \quad (\text{B13})$$

to write the δ -functions of equation (B12) as

$$\delta[\omega \mp \Omega_q + \epsilon_{k+q} - \epsilon_k] = \frac{1}{4J|\sin(q/2)|} \delta[u_q^\mp + \sin(k + q/2)] \quad (\text{B14})$$

where we have used that

$$\epsilon_{k+q} - \epsilon_k = -2J[\cos(k + q) - \cos(k)] = 4J \sin(q/2) \sin(k + q/2) \quad (\text{B15})$$

and the property of the δ -function

$$\delta(ax) = \frac{1}{|a|} \delta(x). \quad (\text{B16})$$

Inserting equation (B14) as well as the coupling constant V_q given by equation (4) into equation (B12) yields

$$m''_K(\omega) = \frac{K^2 V^2}{\omega^2 \alpha} \frac{\pi}{N+1} \sum_q 2 \cos^2(q/2) \frac{1}{N+1} \sum_k (v_k^2 - v_{k+q}^2) \times \{\delta[u_q^+ + \sin(k + q/2)] + \delta[u_q^- + \sin(k + q/2)]\} \quad (\text{B17})$$

where the parameter α is defined in section 1 (see equations (5), (7)). Now we direct our attention to the k -sum in (B17). Introducing the new variable $k' = k + q/2$ we may write

$$\begin{aligned} & \frac{1}{N+1} \sum_{k=-\pi}^{\pi} (v_k^2 - v_{k+q}^2) \{\delta[u_q^+ + \sin(k + q/2)] + \delta[u_q^- + \sin(k + q/2)]\} \\ &= \frac{1}{N+1} \sum_{k'=-\pi+q/2}^{\pi+q/2} (v_{k'-q/2}^2 - v_{k'+q/2}^2) \{\delta[u_q^+ + \sin(k')] + \delta[u_q^- + \sin(k')]\} \end{aligned} \quad (\text{B18})$$

which on inserting

$$v_{k'-q/2}^2 - v_{k'+q/2}^2 = (4J)^2 \sin(q/2) \cos(q/2) \sin(k') \cos(k') \quad (\text{B19})$$

yields

$$\begin{aligned} & \sum_{k'=-\pi+q/2}^{\pi+q/2} (v_{k'-q/2}^2 - v_{k'+q/2}^2) \{\delta[u_q^+ + \sin(k')] + \delta[u_q^- + \sin(k')]\} \\ &= (4J)^2 \sin(q/2) \cos(q/2) \sum_{k'=-\pi+q/2}^{\pi+q/2} \sin(k') \cos(k') \\ & \quad \times \{\delta[u_q^+ + \sin(k')] + \delta[u_q^- + \sin(k')]\}. \end{aligned} \quad (\text{B20})$$

Since the function in (B20) is 2π -periodic in k' and we sum over a whole period, we may also write

$$\sum_{k'=-\pi+q/2}^{\pi+q/2} \dots = \sum_{k'=-\pi/2}^{3\pi/2} \dots = \sum_{k'=-\pi/2}^{\pi/2} \dots + \sum_{k'=\pi/2}^{3\pi/2} \dots \quad (\text{B21})$$

Substituting in the second sum $k'' = k' - \pi$ and finally $k' = -k''$ we obtain

$$m''_K(\omega) = 0 \Rightarrow m'_K(\omega) = 0 \quad (\text{B22})$$

since the second sum is just the negative of the first one.

Appendix C

Using the Goldberger–Adams expansion [3] of the density matrix (11) with respect to the interaction Hamiltonian

$$e^{\beta(H_0+H_I)} = e^{\beta H_0} \left\{ 1 - \int_0^\beta d\lambda e^{\lambda H_0} H_I e^{-\lambda H} \right\} \quad (C1)$$

we obtain to second order for the thermal expectation value for an operator A

$$\langle A \rangle_T = \left\{ \langle A \rangle_T^{(0)} - \int_0^\beta d\lambda \langle H_I(-i\lambda) A \rangle_T^{(0)} + \int_0^\beta d\lambda \int_0^\lambda d\lambda' \langle H_I(-i\lambda) H_I(-i\lambda') A \rangle_T^{(0)} \right\} \frac{Z_0}{Z} \quad (C2)$$

with

$$\frac{Z_0}{Z} = 1 - \int_0^\beta d\lambda \langle H_I(-i\lambda) \rangle_T^{(0)} + \int_0^\beta d\lambda \int_0^\lambda d\lambda' \langle H_I(-i\lambda) H_I(-i\lambda') \rangle_T^{(0)} \quad (C3)$$

and

$$H_I(-i\lambda) = e^{\lambda H_0} H_I e^{-\lambda H_0}. \quad (C4)$$

As pointed out in section 4 we need the thermal occupations

$$\langle N_k \rangle_T = \langle c_k^\dagger c_k \rangle_T \quad (C5)$$

to evaluate the static susceptibility $\tilde{\chi}_k$. The interaction Hamiltonian at the complex time $t = -i\lambda$ is given by

$$H_I(-i\lambda) = \sum_{k',q} V_q c_{k'+q}^\dagger c_{k'} \{ b_q e^{\lambda(\epsilon_{k+q} - \epsilon_k - \Omega_q)} + b_{-q}^\dagger e^{\lambda(\epsilon_{k+q} - \epsilon_k + \Omega_q)} \}. \quad (C6)$$

Inspecting equation (C6) and (C3), (C4) we notice that the first-order terms are equal to zero:

$$\langle H_I(-i\lambda) \rangle_T^{(0)} = 0 \quad (C7)$$

$$\langle H_I(-i\lambda) A \rangle_T^{(0)} = 0 \quad (C8)$$

and equation (C4) together with equation (C3) yields

$$\begin{aligned} \langle N_k \rangle_T &= \langle N_k \rangle_T^{(0)} + \int_0^\beta d\lambda \int_0^\lambda d\lambda' \langle H_I(-i\lambda) H_I(-i\lambda') N_k \rangle_T^{(0)} \\ &\quad - \langle H_I(-i\lambda) H_I(-i\lambda') \rangle_T^{(0)} \langle N_k \rangle_T^{(0)}. \end{aligned} \quad (C9)$$

Inserting (C6) into (C9) we are able to perform the λ -, λ' -integrations and we arrive at

$$\begin{aligned} \frac{\Delta N_k}{\langle N_k \rangle_T^{(0)}} &= \frac{\langle N_k \rangle_T - \langle N_k \rangle_T^{(0)}}{\langle N_k \rangle_T^{(0)}} = \sum_{k',q} |V_q|^2 (n_q + 1) A^-(k', q) \{ \delta_{k',k-q} - \langle N_{k'+q} \rangle_T^{(0)} \} \\ &\quad + \sum_{k',q} |V_q|^2 n_q A^+(k', q) \{ \delta_{k',k-q} - \langle N_{k'+q} \rangle_T^{(0)} \} \end{aligned} \quad (C10)$$

with the abbreviations

$$A^\pm(k', q) = \frac{e^{\beta \Delta^\pm(k', q)} - 1 - \beta \Delta^\pm(k', q)}{\Delta^\pm(k', q)^2} \quad (C11)$$

$$\Delta^\pm(k', q) = \epsilon_{k'+q} - \epsilon_{k'} \pm \Omega_q. \quad (C12)$$

The remaining two sums may be converted into integrals:

$$\frac{1}{N+1} \sum_{k(q)=-\pi}^{\pi} \dots \Rightarrow \int_{-\pi}^{\pi} dk (dq) \dots \quad (\text{C13})$$

which allows us to perform a numerical calculation of $\langle N_k \rangle_T$ and thus of c_2 given by equation (80).

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