Stochastic models of exciton transport: The Haken-Strobl model

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Exciton dephasing in crystals due to the phonon scattering is studied within the framework of the stochastic Haken-Strobl model. The model corresponds to the extremely fast-modulation limit and is applicable to triplet excitons in molecular crystals. The model describes the crossover from the coherent (band) short-time exciton dynamics to incoherent diffusive motion on the long time scale. An efficient method for the determination of the moments of the exciton displacement is developed. Analytic expressions for the mean-square displacement tensor and for the fourth-order moment of exciton displacement on a three-dimensional lattice with inversion symmetry are derived. Solution of the model for arbitrary initial conditions is obtained. The equilibrium state of the system corresponds to the uniform population of the states in the exciton band. The equilibration time scale coincides with the time scale on which the crossover between coherent and diffusive motion occurs. It is given approximately by the inverse amplitude of the second-order correlation function of the stochastic modulation. Physical assumptions underlying the model and the range of its applicability are discussed.

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I. INTRODUCTION

Experimental data on the temperature dependence of the photoconductivity in naphthalene crystals [1–3] and on the line shape and mobility of excitons in molecular crystals [4–10] show that neither the band mechanism, nor the hopping mechanism (diffusion), can describe the transport of electrons and excitons in molecular crystals. These two mechanisms are in a certain sense complementary. The band mechanism applies at short times, while the hopping mechanism is realized on longer time intervals. The actual time scale, on which the crossover between the two mechanisms occurs, coincides with the time scale on which the phase of the wave function of an exciton (electron) is destroyed. This phase destruction (dephasing) originates from scattering on impurities and/or lattice imperfections or on photons. In ideal crystals scattering on phonons is the only mechanism. The dephasing time scale depends on the exciton- (electron-) phonon coupling strength and on the thermal population of the phonon states. At low temperatures the phonon modes are frozen, hence the scattering cross section of the exciton (electron) is small. In this limit the motion is quasicoherent and can be described by the band mechanism. On the other hand, at high temperatures the scattering cross section is large and the exciton mean free path is of the order of a lattice constant. According to the Ioffe-Regel criterion the exciton (electron) motion in this limit is diffusive. In an intermediate temperature regime both mechanisms are required for the adequate description of the transport. Models which allow simultaneous description of both the coherent (band) and the incoherent (diffusive) motion of the exciton are therefore of considerable interest. The microscopic small polaron model [11] which has been widely used for electrons [12] and excitons [13–17] in molecular crystals is a well-known example of such a model.

An alternative approach is based on phenomenological stochastic models [18–21]. These models may be viewed as the finite exciton bandwidth generalizations of the Anderson-Kubo [22,23] stochastic model in the line-shape theory. Within these models the incoherent exciton scattering is described by stochastic modulation of the matrix elements of the resonant interaction. The latter is responsible for the exciton delocalization and the coherent transport. The effect of the exciton-phonon coupling is reduced within the stochastic models to the loss of coherence (dephasing). This limitation is severe, since it ignores important physical effects, such as the phonon sidebands of excitonic transitions and the exciton self-trapping [24]. On the other hand, the models have the important advantage of being analytically solvable [18,19,25–30].

In this paper the general three-dimensional (3D) Haken-Strobl model with inversion symmetry is studied. The model corresponds to the extremely fast modulation limit, and predicts a Lorentzian line shape for the phononless exciton band. The physical condition for the applicability of the model is that the exciton bandwidth is small compared to both the thermal energy and the phonon bandwidth. This condition is satisfied for the lowest triplet excitons in molecular crystals. In fact the Haken-Strobl model has been useful for the description of line shapes in optical absorption and luminescence spectra [5–7], as well as ESR [4] and NMR [31] spectra of the lowest triplet excitons in molecular crystals.

The paper is organized as follows. In Sec. II the formalism is outlined together with physical assumptions underlying the model. A derivation of the stochastic Liouville equation is presented in Sec. III. It is employed in Sec. IV to obtain analytic expressions for the first two nonvanishing moments of the exciton displacement within the 3D Haken-Strobl model with inversion symmetry. An alternative nonlocal time formalism based

on the generalized master equation is studied in Sec. V. The expressions for the moments are used to determine the memory functions. In Sec. VI a proof is presented for the absence of energy dissipation within the model. The phase mixing is shown to be the only effect of scattering. The Nyquist theorem allows one to establish the relationship between the absence of energy dissipation and the vanishing exciton mobility. Solution of the model for arbitrary initial conditions is obtained in Sec. VII. It is shown that the equilibrium state corresponds to uniform population of the exciton band. Finally, Sec. VIII contains a brief summary of the results together with an analysis of the model's limitations and its range of applicability.

II. THE MODEL

A. Formalism

The Haken-Strobl model is described by the Hamiltonian [18,19]

$$\hat{H}(t)\equiv\hat{H}_0+\hat{V}(t) = \sum_{R_i,R_j}\{h(R_i,R_j)+v(R_i,R_j;t)\}\hat{a}^{\dagger}_{R_i}\hat{a}_{R_j}, \tag{2.1}$$

where $\hat{a}^{\dagger}_{R_i}$ and $\hat{a}_{R_i}$ are the exciton creation (annihilation) operators on lattice site with coordinate R_i, and the summation is over the lattice sites. The first term in the Hamiltonian accounts for the coherent exciton transfer with

$$h(R_i,R_j)\equiv\langle\psi(r-R_i)|\hat{H}_0|\psi(r-R_j)\rangle$$

being the matrix element of the resonant interaction between the wave functions localized on the ith and jth lattice site, respectively. The incoherent exciton scattering by the phonons is modeled by the stochastic potential, $v(R_i,R_j;t)$, which describes the modulation of the resonant matrix elements. The stochastic potential is assumed to be a Gaussian Markovian process with vanishing correlation time (fast modulation limit). It is therefore completely characterized by the first two correlation functions

$$\langle v(R_i,R_j;t)\rangle=0 \tag{2.2}$$

and

$$\langle v(R_i,R_j;t)v(R_k,R_l;t)\rangle = 2g(R_i,R_j)\delta(t-t')\{\delta^{R_k}_{R_i}\delta^{R_l}_{R_j}+\delta^{R_l}_{R_i}\delta^{R_k}_{R_j}-\delta^{R_j}_{R_i}\delta^{R_l}_{R_k}\delta^{R_k}_{R_i}\}. \tag{2.3}$$

The angle brackets denote the averaging over the states of the thermal bath and $\delta^{R_j}_{R_i}\equiv\delta(R_i-R_j)$. In the following we shall assume that the lattice has an inversion center. From the translation and the inversion symmetry of the lattice it follows that $h(R_i,R_j)=h(|R_i-R_j|)$ and $g(R_i,R_j)=g(|R_i-R_j|)$.

The problem is simplified by the use of the momentum (Bloch) representation. In this representation the Hamiltonian is recast in the form

$$\hat{H}(t)=\int d^3q\,\varepsilon(q)\hat{a}^{\dagger}_q\hat{a}_q+\int d^3q_1\int d^3q_2\tilde{v}(q_1,q_2;t)\hat{a}^{\dagger}_{q_1}\hat{a}_{q_2}, \tag{2.4}$$

where

$$\varepsilon(q)\equiv\sum_{R_i}h(R_i)\exp(-iqR_i) \tag{2.5}$$

and

$$\tilde{v}(q_1,q_2;t)\equiv\frac{1}{(2\pi)^3}\sum_{R_i,R_j}v(R_i,R_j;t)\times\exp\{i(q_1R_i-q_2R_j)\}. \tag{2.6}$$

Integration in Eq. (2.4) is over the states in the first Brillouin zone. The formulas above have been written for the particular case of a simple cubic lattice (lattice constant is set equal to unity). Extension of these formulas for arbitrary centrosymmetric lattices is straightforward.

B. Assumptions and approximations

The physical assumptions underlying the Haken-Strobl model can be summarized as follows.

(a) *Single-particle approximation.* The exciton-exciton interaction is neglected within the model. This assumption limits the range of applicability of the model to small excitation concentrations (low laser intensities). On the other hand, it makes the quantum statistical effects irrelevant, so that the model is also applicable for electrons.

(b) *Fast modulation limit.* The vanishing correlation time assumption [see Eq. (2.3)] implies that the exciton bandwidth is much smaller than the phonon bandwidth [13,14]. This condition is satisfied for triplet excitons in molecular crystals.

(c) *Macroscopic population of phonon states.* The phonons are treated within the model as a thermal bath which modulates the resonant interaction. The effect of an exciton on the phonon bath is neglected. This assumption implies macroscopic population of the phonon modes, which holds above the Debye temperature.

(d) *Continuous phonon spectrum.* Replacement of the phonon bath by a stochastic Gaussian field is valid if the spectrum is continuous.

(e) *Weak exciton-phonon coupling.* The model implicitly assumes that the exciton-phonon coupling is weak. The actual criterion of the weakness is that the formation of bound exciton-phonon states is impossible [16,17]. The only physical effect of the coupling under this condition is incoherent scattering, which results in narrowing of the phononless exciton band and in dephasing. This assumption constitutes a severe limitation since it precludes the use of the Haken-Strobl model to describe such physical effects as exciton self-trapping [24] and the phonon sidebands of the excitonic transition.

(f) *Statistical independence of fluctuations.* The fluctuations of the different matrix elements of the Hamiltonian are assumed to be statistically independent [see Eq. (2.3)]. This assumption is not justified if the exciton is scattered

on the acoustic phonons. However, it is valid if the scattering on the intramolecular modes dominates [14].

(g) *Narrow exciton band.* The states within the exciton band are assumed to be uniformly populated. Formal proof of this treatment can be found in Sec. IV. It is physically equivalent to the assumption that the exciton bandwidth is small compared with the thermal energy $\Delta\varepsilon \ll kT$. The latter condition holds for the lowest triplet excitons in molecular crystals for temperatures above ~ 20 K.

Having thus specified the model we turn to the analysis of the exciton dynamics. The latter can be studied from the time evolution of the density matrix. Two formally equivalent approaches can be used for this purpose. The first one, based on the stochastic Liouville equation [32,33], will be employed in the following section. The alternative approach based on the generalized master equation [34–36] will be discussed in Sec. V.

III. STOCHASTIC LIOUVILLE EQUATION

Our starting point will be the quantum-mechanical equation of motion for the density matrix ($\hbar=1$):

$$\dot{\rho}(k,k';t)=-i[\varepsilon(k)-\varepsilon(k')]\rho(k,k';t) -i\int d^3q[\bar{v}(k,q;t)\rho(q,k';t) -\bar{v}(q,k';t)\rho(k,q;t)]. \quad (3.1)$$

Evaluation of the observables, however, requires the knowledge of the coarse-grained density matrix, $\langle\rho(k,k';t)\rangle$. Averaging of Eq. (3.1) over the states of the phonon bath results in the stochastic Liouville equation (SLE) for the coarse-grained density matrix [28,30]

$$\langle\dot{\rho}(k,k';t)\rangle=-\{\Gamma+i[\varepsilon(k)-\varepsilon(k')]\}\langle\rho(k,k';t)\rangle +\frac{1}{(2\pi)^3}\int d^3q\ \mathcal{G}(k+q/2;k'+q/2) \times\langle\rho(k+q,k'+q;t)\rangle, \quad (3.2)$$

where the following notations have been introduced:

$$\mathcal{G}(q,q')\equiv -2g(0)+2\sum_{R_i} g(R_i) \times\{\cos[(q+q')R_i]+\cos[(q-q')R_i]\} \quad (3.3)$$

and

$$\Gamma\equiv 2\sum_{R_i} g(R_i). \quad (3.4)$$

For subsequent use the SLE, Eq. (3.2), will be rewritten in an equivalent form. We introduce the variables $s\equiv(k+k')/2$ and $u\equiv(k-k')/2$ and recast the coarse-grained density matrix in the form

$$\langle\rho(k,k';t)\rangle=F(u,s;t)\exp(-\Gamma t). \quad (3.5)$$

Using the periodicity of the function $F(u,s;t)$

$$F(u,s+2\pi;t)=F(u,s;t),$$

Eq. (3.2) can be recast in the form

$$\dot{F}(u,s;t)=P(u,s)F(u,s;t) +\frac{1}{(2\pi)^3}\left\{Q(u)\int d^3q\ F(u,q;t) +\int d^3q\ R(s,q)F(u,q;t)\right\} \quad (3.6)$$

with

$$P(u,s)\equiv 2i\sum_{R_i} h(R_i)\sin(uR_i)\sin(sR_i), \quad (3.7)$$

$$Q(u)\equiv 2\sum_{R_i} g(R_i)\cos(2uR_i), \quad (3.8)$$

and

$$R(s,q)\equiv 2\sum_{R_i\neq 0} g(R_i)\cos[(s+q)R_i]. \quad (3.9)$$

Laplace transformation of SLE, Eq. (3.6), with respect to the time variable

$$\phi(u,s;p)\equiv\int_0^\infty dt\ \exp(-pt)F(u,s;t)$$

leads to

$$p\phi(u,s;p)=F(u,s;0)+P(u,s)\phi(u,s;p) +\frac{1}{(2\pi)^3}\{Q(u)\int d^3q\ \phi(u,q;p) +\int d^3q\ R(s;q)\phi(u,q;p)\}. \quad (3.10)$$

The function $F(u,s;0)$ is the coarse-grained density matrix at the initial time ($t=0$). We shall assume that an exciton is initially localized at the lattice origin ($R_i=0$). This assumption is formally equivalent to

$$F(u,s;0)=\frac{1}{(2\pi)^3}. \quad (3.11)$$

This completes the definition of the model. Below the SLE, Eq. (3.10) will be employed for the calculation of the momentum of the displacement of an exciton.

IV. MOMENTS OF DISPLACEMENT

In this section a method for finding the moments of the exciton displacement within the Haken-Strobl model is developed. For illustration, explicit results for the first two nonvanishing moments are obtained (odd order moments of the displacement vanish identically due to the inversion symmetry). These moments provide the information about the exciton dynamics in the whole time domain. In particular, they exhibit the crossover from the coherent short-time motion to diffusive motion on the longer time scale. An important advantage of the Haken-Strobl model is that in certain cases exact analytic expressions for the moments can be obtained. Thus Schwarzer and Haken [25] and Reineker [26] derived an expression for the mean-square displacement (MSD) for the one-dimensional (1D) model with nearest-neighbor interactions (see also [29]). Their result has been extended to include non-nearest-neighbor interactions in [27] and [30]. Below we derive an expression for the MSD tensor

for the general 3D Haken-Strobl model with inversion symmetry. The approach has an advantage compared with those used previously in that it can be employed to evaluate the higher-order moments of the displacement.

A. Mean-square displacement tensor

Our starting point will be the expression for the MSD tensor in terms of the coarse-grained density matrix:

$$\langle r^2_{\nu\lambda}(t)\rangle = -\int d^3k \frac{\partial^2\langle\rho(k,k';t)\rangle}{\partial k'_\nu \partial k'_\lambda}\bigg|_{k'=k} \tag{4.1}$$

with k'_ν denoting the projection of the vector k' on the νth axis. Using Eq. (3.5) we can recast Eq. (4.1) in the form

$$\langle r^2_{\nu\lambda}(t)\rangle = -\frac{1}{8\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} dp \exp[(p-\Gamma)t] \times \int d^3s\, \phi''_{\nu\lambda}(0,s;p) \tag{4.2}$$

where the shorthand notation

$$\phi''_{\nu\lambda}(0,s;p) \equiv \frac{\partial^2\phi(u,s;p)}{\partial u_\nu \partial u_\lambda}\bigg|_{u=0}$$

has been introduced. The problem is reduced to evaluation of the integrals

$$Z_{\nu\lambda}(p) \equiv \int d^3s\, \phi''_{\nu\lambda}(0;s,p).$$

This can be done using the Laplace transformation of the stochastic Liouville equation, Eq. (3.10).

From the definition of the functions $P(u,s)$ and $Q(u)$, Eqs. (3.3) and (3.4), it follows that

$$P(0,s) = P''_{\nu\lambda}(0,s) = Q'_\nu(0) = 0, \tag{4.3}$$

$$Q(0) = 2\sum_{R_i} g(R_i) \equiv \Gamma, \tag{4.4}$$

$$P'_\nu(0,s) = 2i\sum_{R_i} h(R_i) R_i^\nu \sin(sR_i), \tag{4.5}$$

$$Q''_{\nu\lambda}(0) = -8\sum_{R_i} g(R_i) R_i^\nu R_i^\lambda \tag{4.6}$$

with R_i^ν being the projection of the lattice vector R_i on the ν axis. Differentiation of the SLE, Eq. (3.10), with account of Eqs. (4.3)–(4.6) leads to

$$p\phi''_{\nu\lambda}(0,s;p) = P'_\nu(0,s)\phi'_\lambda(0,s;p) + P'_\lambda(0,s)\phi'_\nu(0,s;p) + \frac{1}{(2\pi)^3}\left\{Q(0)Z_{\nu\lambda}(p) + Q''_{\nu\lambda}(0)X(p) + \int d^3q\, R(s,q)\phi''_{\nu\lambda}(0,q;p)\right\}. \tag{4.7}$$

Integration of Eq. (4.7) with the use of the relation $\int d^3s\, R(s,q) = 0$ gives

$$(p-\Gamma)Z_{\nu\lambda}(p) = Q''_{\nu\lambda}(0)X(p) + 2i\sum_{R_i} h(R_i) \times [R_i^\nu B_\lambda(R_i;p) + R_i^\lambda B_\nu(R_i;p)], \tag{4.8}$$

where the following notations have been introduced:

$$X(p) \equiv \int d^3s\, \phi(0,s;p), \tag{4.9}$$

$$B_\nu(R_i;p) \equiv \int d^3s \sin(sR_i)\phi'_\nu(0,s;p). \tag{4.10}$$

Straightforward analysis of the SLE, Eq. (3.10), for the diagonal elements of the coarse-grained density matrix ($u=0$) shows that

$$X(p) = \frac{1}{(p-\Gamma)} \tag{4.11}$$

and

$$\phi(0,s;p) = \frac{1}{(2\pi)^3}\frac{1}{(p-\Gamma)}. \tag{4.12}$$

The physical implication of this result is that the diagonal elements of the coarse-grained density matrix for the localized initial conditions are both time and momentum independent:

$$\langle\rho(k,k;t)\rangle = \frac{1}{(2\pi)^3}. \tag{4.13}$$

In other words, the exciton remains uniformly spread over the band. Differentiation of Eq. (3.10) gives

$$p\phi'_\nu(0,s;p) = P'_\nu(0,s)\phi(0,s;p) + \frac{1}{(2\pi)^3}\left\{\Gamma\int d^3q\, \phi'_\nu(0,q;p) + \int d^3q\, R(s,q)\phi'_\nu(0,q,p)\right\}. \tag{4.14}$$

It follows from Eq. (4.14) that

$$\int d^3s\, \phi'_\nu(0,s;p) = 0.$$

Furthermore

$$B_\nu(R_i;p) = \frac{2ih(R_i)R_i^\nu}{(p-\Gamma)[p+2g(R_i)]}. \tag{4.15}$$

In the derivation of Eq. (4.15) the inversion symmetry of the lattice has been used together with the relations

$$\int d^3q \sin(qR_i)\sin(qR_j) = \frac{(2\pi)^3}{2}\{\delta(R_i-R_j)-\delta(R_i+R_j)\}, \tag{4.16}$$

$$\int d^3q \sin(q,R_i)\cos(qR_j) = 0. \tag{4.17}$$

Substitution of Eqs. (4.6), (4.11), and (4.15) into Eq. (4.8) results in

$$Z_{\nu\lambda}(p)=-\frac{8}{(p-\Gamma)^2}\sum_{R_i}\left\{g(R_i)+\frac{[h(R_i)]^2}{[p+2g(R_i)]}\right\}R_i^{\nu}R_i^{\lambda}. \tag{4.18}$$

Substitution of this result into Eq. (4.2) leads to the final expression for the MSD tensor

$$\langle r^2_{\nu\lambda}(t)\rangle=2t\sum_{R_i}\left\{g(R_i)+\frac{[h(R_i)]^2}{\Gamma+2g(R_i)}\right\}R_i^{\nu}R_i^{\lambda}+2\sum_{R_i}\frac{[h(R_i)]^2R_i^{\nu}R_i^{\lambda}}{[\Gamma+2g(R_i)]^2}\times(\exp\{-[\Gamma+2g(R_i)]t\}-1). \tag{4.19}$$

In the one-dimensional case this expression coincides with the result derived in [27,30].

On the short time scale ($\Gamma t \ll 1$) it follows from Eq. (4.19) that

$$\langle r^2_{\nu\lambda}(t)\rangle\simeq t^2\sum_{R_i}[h(R_i)]^2R_i^{\nu}R_i^{\lambda}. \tag{4.20}$$

The exciton motion in this limit is coherent and can be described by the band mechanism. On the long time scale ($\Gamma t \gg 1$) the expression for the MSD tensor, Eq. (4.10), reduces to

$$\langle r^2_{\nu\lambda}(t)\rangle\simeq 2t\sum_{R_i}\left\{g(R_i)+\frac{[h(R_i)]^2}{\Gamma+2g(R_i)}\right\}R_i^{\nu}R_i^{\lambda}. \tag{4.21}$$

The exciton dynamics on this time scale is diffusive. The diffusion tensor is given by

$$D_{\nu\lambda}=\sum_{R_i}\left\{g(R_i)+\frac{[h(R_i)]^2}{\Gamma+2g(R_i)}\right\}R_i^{\nu}R_i^{\lambda} \tag{4.22}$$

in accordance with the result obtained in [37]. It follows that Eq. (4.19) describes the crossover between the coherent short-time dynamics and the diffusive motion on the long time scale.

B. Fourth-order moment

The method can be employed to obtain the higher-order moments of the displacement. The expression of the fourth-order moment is derived in Appendix A. The final result can be recast in the form

$$\langle\hat{r}^{\,4}_{\mu\nu\lambda\sigma}(p)\rangle=\Upsilon^{(1)}_{\mu\nu\lambda\sigma}(p)+\Upsilon^{(2)}_{\mu\nu\lambda\sigma}(p)+\Upsilon^{(3)}_{\mu\nu\lambda\sigma}(p), \tag{4.23}$$

where

$$\Upsilon^{(1)}_{\mu\nu\lambda\sigma}(p)\equiv\frac{2}{p^2}\sum_{R_i}\left\{g(R_i)+\frac{[h(R_i)]^2}{[p+\Gamma+2g(R_i)]}\right\}\times R_i^{\mu}R_i^{\nu}R_i^{\lambda}R_i^{\sigma}, \tag{4.24}$$

$$\Upsilon^{(2)}_{\mu\nu\lambda\sigma}(p)=2p\{\langle\hat{r}^{\,2}_{\mu\nu}(p)\rangle\langle\hat{r}^{\,2}_{\lambda\sigma}(p)\rangle+\langle\hat{r}^{\,2}_{\mu\lambda}(p)\rangle\langle\hat{r}^{\,2}_{\nu\sigma}(p)\rangle+\langle\hat{r}^{\,2}_{\mu\sigma}(p)\rangle\langle\hat{r}^{\,2}_{\nu\lambda}(p)\rangle\} \tag{4.25}$$

and

$$\Upsilon^{(3)}_{\mu\nu\lambda\sigma}(p)\equiv-\frac{1}{p^2}\sum_{R_i}\frac{h(R_i)}{[p+\Gamma+2g(R_i)]}\times\sum_{R_j}^{(\neq -R_i)}\frac{h(R_j)}{[p+\Gamma-2g(|R_i+R_j|)]}\times\sum_{R_k}\frac{h(R_k)h(|R_i+R_j+R_k|)}{[p+\Gamma+2g(|R_i+R_j+R_k|)]}\Xi_{\mu\nu\lambda\sigma}. \tag{4.26}$$

In these formulas $\langle\hat{r}^{\,2}_{\mu\nu}(p)\rangle$ is the Laplace transform of the mean-square displacement tensor

$$\langle\hat{r}^{\,2}_{\mu\nu}(p)\rangle=\frac{2}{p^2}\sum_{R_i}\left\{g(R_i)+\frac{[h(R_i)]^2}{[p+\Gamma+2g(R_i)]}\right\}R_i^{\mu}R_i^{\nu}. \tag{4.27}$$

The symmetric fourth-rank tensor $\Xi_{\mu\nu\lambda\sigma}$ is defined as

$$\Xi_{\mu\nu\lambda\sigma}=\xi_{\mu}^{\nu\lambda\sigma}+\xi_{\nu}^{\mu\lambda\sigma}+\xi_{\lambda}^{\mu\nu\sigma}+\xi_{\sigma}^{\mu\nu\lambda} \tag{4.28}$$

and

$$\xi_{\mu}^{\nu\lambda\sigma}\equiv R_i^{\mu}[(R_i^{\nu}+R_j^{\nu}+R_k^{\nu})(R_j^{\sigma}R_k^{\lambda}+R_j^{\lambda}R_k^{\sigma})+(R_i^{\lambda}+R_j^{\lambda}+R_k^{\lambda})(R_j^{\nu}R_k^{\sigma}+R_j^{\sigma}R_k^{\nu})+(R_i^{\sigma}+R_j^{\sigma}+R_k^{\sigma})(R_j^{\nu}R_k^{\lambda}+R_j^{\lambda}R_k^{\nu})]. \tag{4.29}$$

Straightforward inverse Laplace transformation of Eqs. (4.24)–(4.26) gives the final result for the fourth-order moment of the displacement tensor, $\langle r^4_{\mu\nu\lambda\sigma}(t)\rangle$.

V. GENERALIZED MASTER EQUATION

The analysis in the preceding section has been based upon the stochastic Liouville equation, which is local in time. An alternative approach is based upon the generalized master equation (GME) [34–36]. The latter has been applied to the Haken-Strobl model by Kenkre [38–40] and by Reineker and Kühne [41–44]. The relationship between the two approaches has been established in [39]. Reineker and Kühne have derived an explicit expression for the memory functions for the one-dimensional model in the first Born approximation [41], as well as an exact expression for these functions in the nearest-neighbor approximation [44]. Below we shall derive the expression for the memory functions starting from the result for the MSD tensor, Eq. (4.4), and will show that the result is equivalent to that obtained in the first Born approximation.

The GME can be written in the site representation in the following form:

$$\dot{\sigma}_i(t)=\sum_{R_i}\int_0^t d\tau\{W(R_i,R_j;t-\tau)\sigma_j(\tau)-W(R_j,R_i;t-\tau)\sigma_i(\tau)\}, \tag{5.1}$$

where $\sigma_i(t)\equiv\langle\rho(R_i,R_i;t)\rangle$ is the diagonal element of the coarse-grained density matrix. It gives the probability

that the exciton is localized on the ith site of the lattice at time t. The memory functions $W(R_i,R_j;\tau)$ represent the transition rate from the jth to the ith site of the lattice during the time interval τ. The translation and inversion symmetry of the lattice imply that $W(R_i,R_j;\tau)=W(|R_i-R_j|;\tau)$. It is more convenient to work with the Laplace transform of the GME:

$$p\hat{\sigma}_i(p)-\sigma_i(0)=\sum_{R_j}\hat{W}(|R_i-R_j|;p)[\hat{\sigma}_j(p)-\hat{\sigma}_i(p)]. \tag{5.2}$$

Multiplication of Eq. (5.2) by $R_j^\nu R_j^\lambda$ and summation over the vectors of the lattice leads to

$$p\langle\hat{r}^{\,2}_{\nu\lambda}(p)\rangle=\sum_{R_i,R_j}(R_i^\nu R_i^\lambda-R_j^\nu R_j^\lambda)\hat{W}(|R_i-R_j|;p)\hat{\sigma}_j(p). \tag{5.3}$$

For the lattice with inversion symmetry, if R_i and R_j are the symmetry vectors of the lattice so are the vectors R_i+R_j and R_i-R_j. The use of the identity

$$(R_i^\nu R_i^\lambda-R_j^\nu R_j^\lambda)=\tfrac{1}{2}\{(R_i^\nu-R_j^\nu)(R_i^\lambda+R_j^\lambda)+(R_i^\nu+R_j^\nu)(R_i^\lambda-R_j^\lambda)\}$$

together with simple transformation of the double sum over the vectors of the lattice gives the following relation between the MSD tensor and the memory functions:

$$\langle\hat{r}^{\,2}_{\nu\lambda}(p)\rangle=\frac{1}{p^2}\sum_{R_i}\hat{W}(R_i;p)R_i^\nu R_i^\lambda. \tag{5.4}$$

In the derivation the inversion symmetry of the memory functions $\hat{W}(-R_i;p)=\hat{W}(R_i;p)$ has been employed. Substitution of the explicit expression for the MSD tensor into Eq. (5.4) results in

$$\hat{W}(R_i;p)=2g(R_i)+\frac{2[h(R_i)]^2}{p+\Gamma+2g(R_i)} \tag{5.5}$$

or

$$W(R_i;t)=4g(R_i)\delta(t)+2[h(R_i)]^2\exp\{-[\Gamma+2g(R_i)]t\}. \tag{5.6}$$

In the one-dimensional case Eq. (5.6) reduces to the result of Reineker and Kühne [41] derived within the first Born approximation using the Nakajima-Zwanzig projection technique [34,35]. The fact that the memory functions, Eq. (5.6), correspond to the first Born approximation is clear from their structure. Indeed, the expression includes only contributions from direct transitions between the lattice sites (multiple transitions are neglected). A natural question arises; Why is the expression for the memory functions derived from the *exact* expression for the MSD tensor, only an approximate one? The reason is that in order to obtain exact memory functions one has to know the diagonal elements of the average density matrix in the site representation. This is formally equivalent to knowledge of *all* the moments of the displacement tensor and not only the second-order one. In order to clarify the above statement it is instructive to calculate the memory functions starting from the expression for the fourth-order moment of the displacement. For this purpose we introduce the moments of the memory functions:

$$\hat{w}^{\,2}_{\mu\nu}(p)\equiv\sum_{R_i}\hat{W}(R_i;p)R_i^\mu R_i^\nu, \tag{5.7}$$

$$\hat{w}^{\,4}_{\mu\nu\lambda\sigma}(p)\equiv\sum_{R_i}\hat{W}(R_i;p)R_i^\mu R_i^\nu R_i^\lambda R_i^\sigma. \tag{5.8}$$

The second- and the fourth-order moments of the memory functions are related to the moments of the displacement via

$$\hat{w}^{\,2}_{\mu\nu}(p)=p^2\langle\hat{r}^{\,2}_{\mu\nu}(p)\rangle \tag{5.9}$$

and

$$\hat{w}^{\,4}_{\mu\nu\lambda\sigma}(p)=p^2\langle\hat{r}^{\,4}_{\mu\nu\lambda\sigma}(p)\rangle-2p^3[\langle\hat{r}^{\,2}_{\mu\nu}(p)\rangle\langle\hat{r}^{\,2}_{\lambda\sigma}(p)\rangle+\langle\hat{r}^{\,2}_{\mu\lambda}(p)\rangle\langle\hat{r}^{\,2}_{\nu\sigma}(p)\rangle+\langle\hat{r}^{\,2}_{\mu\sigma}(p)\rangle\langle\hat{r}^{\,2}_{\nu\lambda}(p)\rangle]. \tag{5.10}$$

The relation between the second-order moments, Eq. (5.9), follows from Eq. (5.4). The relation between the fourth-order moments is derived similarly. Substitution of the explicit expressions for the second- and fourth-order moments, Eq. (4.27) and Eqs. (4.23)–(4.26), into Eq. (5.10) results in

$$\hat{w}^{\,4}_{\mu\nu\lambda\sigma}(p)=p^2[\Upsilon^{(1)}_{\mu\nu\lambda\sigma}(p)+\Upsilon^{(3)}_{\mu\nu\lambda\sigma}(p)]. \tag{5.11}$$

If the contribution from the term $\Upsilon^{(3)}_{\mu\nu\lambda\sigma}(p)$ is neglected the result for the memory functions coincides with that derived starting from the expressions for the MSD tensor, Eq. (5.5), which has been shown to be the first-order Born approximation. Thus all the information about the correlation effects is contained in the term $\Upsilon^{(3)}_{\mu\nu\lambda\sigma}(p)$, which describes the contribution from sequential four-step transitions. Note that this term cannot be recast in the simple form $\sum_{R_i}\hat{W}(R_i;p)R_i^\mu R_i^\nu R_i^\lambda R_i^\sigma$. Therefore it is impossible to determine the memory functions *uniquely* from the expression for $\hat{w}^{\,4}_{\mu\nu\lambda\sigma}(p)$.

VI. ABSENCE OF ENERGY EXCHANGE

Up to this point we studied the loss of coherence of an exciton. We turn now to the analysis of energy exchange between the exciton and the thermal bath. Firstly it will be shown that there is no energy exchange *on the average* between the localized exciton and thermal bath within the Haken-Strobl model. We start from the general expression for the average energy of an exciton

$$\bar{E}(t)=\langle\mathrm{Tr}\{\hat{\rho}(t)\hat{H}(t)\}\rangle=\mathrm{Tr}\langle\{\hat{\rho}(t)\hat{H}(t)\}\rangle, \tag{6.1}$$

where $\hat{\rho}(t)$ and $\hat{H}(t)$ are the density operator and the Hamiltonian, and Tr denotes the trace of the matrix. In the momentum representation

$$\bar{E}(t)=\int d^3q\,\varepsilon(q)\langle\rho(q,q,t)\rangle+\int d^3q_1\int d^3q_2\langle\rho(q_1,q_2;t)\bar{v}(q_2,q_1;t)\rangle. \tag{6.2}$$

The diagonal elements of the coarse-grained density matrix are time independent [see Eq. (4.12)]. It follows that

$$\bar{E}(t)=h(0)+\int d^3q_1\int d^3q_2\langle\rho(q_1,q_2;t)\bar{v}(q_2,q_1;t)\rangle \quad (6.3)$$

with $h(0)$ being the unperturbed energy of an exciton localized on a lattice site. The second term on the right-hand side (rhs) of Eq. (6.3) gives the energy exchange between the exciton and the thermal bath. We shall demonstrate below that this term vanishes. Since $\bar{v}(Q,q;t)$ is the Gaussian stochastic field with the δ-type time correlator, one can employ the Novikov result for the calculation of the averages [45,46]

$$\langle\rho(q_1,q_2;t)\bar{v}(q_2,q_1;t)\rangle=\int d^3k_1\int d^3k_2\int_{-\infty}^{t}d\tau\langle\bar{v}(q_2,q_1;t)\bar{v}(k_1,k_2;\tau)\rangle\left\langle\frac{\delta\rho(q_1,q_2;t)}{\delta\bar{v}(k_1,k_2;\tau)}\right\rangle$$

$$=\frac{1}{2}\int d^3k_1\int d^3k_2\langle\bar{v}(q_2,q_1;t)\bar{v}(k_1,k_2;t)\rangle\left\langle\frac{\delta\rho(q_1,q_2;t)}{\delta\bar{v}(k_1,k_2;t)}\right\rangle, \quad (6.4)$$

where $\delta\rho(q_1,q_2;t)/\delta\bar{v}(k_1,k_2;\tau)$ is the functional derivative. The latter can be derived from the equation of motion for the density matrix, Eq. (3.1),

$$\frac{\delta\rho(q_1,q_2;t)}{\delta\bar{v}(k_1,k_2;t)}=-i[\delta(q_1-k_1)\rho(k_2,q_2;t)-\delta(q_2-k_2)\rho(q_1,k_1;t)]. \quad (6.5)$$

Substitution of this result into Eq. (6.4) gives

$$\langle\rho(q_1,q_2;t)\bar{v}(q_2,q_1;t)\rangle=-i\int d^3k[\langle\bar{v}(q_2,q_1;t)\bar{v}(q_1,k;t)\rangle\langle\rho(k,q_2;t)\rangle-\langle\bar{v}(q_2,q_1;t)\bar{v}(k,q_2;t)\rangle\langle\rho(q_1,k,t)\rangle]. \quad (6.6)$$

It follows that the contribution from the incoherent part of the Hamiltonian to the average energy of the exciton is equal to

$$\int d^3q_1\int d^3q_2\langle\rho(q_1;q_2;t)\bar{v}(q_2,q_1;t)\rangle=-i\int d^3q_1\int d^3q_2\int d^3k[\langle\bar{v}(q_2,q_1;t)\bar{v}(q_1,k;t)\rangle\langle\rho(k,q_2;t)\rangle$$
$$-\langle\bar{v}(q_2,q_1;t)\bar{v}(k,q_2;t)\rangle\langle\rho(q_1k;t)\rangle]. \quad (6.7)$$

But the two terms in brackets differ by a cyclic permutation of dummy integration variables. Thus the rhs of Eq. (6.7) vanishes identically proving the original statement that the averaged energy of the exciton is time independent.

Absence of energy exchange between the exciton and the thermal bath is closely related to the vanishing exciton mobility within the Haken-Strobl model [28]. The relation is based upon the Nyquist theorem, which expresses the energy dissipated (absorbed) by the quantum-mechanical system in terms of the complex admittance [47,48],

$$\Delta E=\int_{-\infty}^{\infty}d\omega\,\omega\coth(\beta\omega/2)\mathrm{Tr}\{\chi_{\nu\lambda}(\omega)+\chi_{\lambda\nu}(-\omega)\}\ . \quad (6.8)$$

Here $\beta\equiv 1/kT$ and $\chi_{\nu\lambda}(\omega)(\nu,\lambda=x,y,z)$ is the complex admittance of the system, which is proportional in our case to the mobility. It follows that

$$\Delta E=\int_{-\infty}^{\infty}d\omega\,\omega\coth(\beta\omega/2)\mathrm{Tr}\{\sigma_{\nu\lambda}(\omega)+\sigma_{\lambda\nu}(-\omega)\}. \quad (6.9)$$

Using the Onsager symmetry relations for the mobility tensor [48] we obtain

$$\Delta E=4\int_0^{\infty}d\omega\,\mathrm{Tr}\{\mathrm{Re}[\sigma_{\nu\lambda}(\omega)]\}\omega\coth(\beta\omega/2). \quad (6.10)$$

Therefore the absence of energy dissipation implies

$$\mathrm{Tr}\{\sigma_{\nu\lambda}(\omega)\}=0, \quad (6.11)$$

i.e., that the mobility in the Haken-Strobl model vanishes [28]. On the other hand, the use of the Nernst-Einstein relation [48] together with Eq. (4.22) for the diffusion tensor leads to the following result [49]:

$$\sigma_{\nu\lambda}\equiv\sigma_{\nu\lambda}(0)=\beta e\sum_{R_i}\left\{g(R_i)+\frac{[h(R_i)]^2}{\Gamma+2g(R_i)}\right\}R_i^{\nu}R_i^{\lambda}. \quad (6.12)$$

We shall discuss the apparent discrepancy between the two results in the following section.

VII. THE INITIAL CONDITION

The localized initial condition has been chosen mainly for technical reasons. Both the stochastic Liouville equation and the generalized master equation have a particularly simple form in this case. The choice of the initial condition leads, however, to two physical questions.

(1) Experimental realization. The question is: whether it is possible to "prepare" experimentally a localized exciton in an ideal crystal possessing translational symmetry?

This problem has been discussed by Aslangul Kottis [50].

(2) Uncertainty principle. The localized initial condition implies that the initial momentum of the exciton is undetermined. In other words, the exciton is initially uniformly spread over the band. This fact alone may lead to difficulties.

Indeed, the solution of the Haken-Strobl model with the localized initial condition gives a number of puzzling results.

(a) The diagonal matrix elements of the coarse-grained density matrix in the momentum representation are both time and momentum independent.

(b) The average energy of the localized exciton is time independent, and its mobility vanishes.

(c) Finally, the Nernst-Einstein relation between the mobility and the diffusion coefficient apparently does not hold [the diffusion coefficient, Eq. (4.22), is finite].

As already mentioned, the first result implies uniform population of the states in the exciton band. An interesting question is, whether this result is associated with the choice of the localized initial condition. This point can be clarified by solving the SLE with arbitrary initial conditions. For the diagonal matrix elements ($u=0$) Eq. (3.10) reduces to

$$p\phi(0,s;p)-\mu(s)=\frac{1}{(2\pi)^3}\left\{\Gamma\int d^3q\,\phi(0,q;p)+\int d^3q\,R(s,q)\phi(0,q;p)\right\}, \tag{7.1}$$

where $\mu(s)$ is the diagonal element of the initial coarse-grained density matrix: $\mu(s)\equiv F(0,s;0)$. The integral equation, Eq. (7.1), is solved in Appendix B. The final result is

$$\phi(0,s;p)=\frac{1}{(2\pi)^3}\left\{\frac{1}{(p-\Gamma)}+\sum_{R_i\neq 0}\left[\frac{a(R_i)\cos(sR_i)}{[p-2g(R_i)]}+\frac{b(R_i)\sin(sR_i)}{[p+2g(R_i)]}\right]\right\}, \tag{7.2}$$

where the summation is over the vectors of the lattice, and $a(R_i)$ and $b(R_i)$ are the Fourier expansion coefficients of the initial density matrix

$$a(R_j)\equiv\int d^3q\,\cos(qR_j)\mu(q), \tag{7.3}$$

$$b(R_j)\equiv\int d^3q\,\sin(qR_j)\mu(q). \tag{7.4}$$

The inverse Laplace transformation of Eq. (7.2) gives

$$\langle\rho(k,k;t)\rangle=\frac{1}{(2\pi)^3}+\frac{1}{(2\pi)^3}\sum_{R_i\neq 0}a(R_i)\cos(kR_i)\exp\{-[\Gamma-2g(R_i)]t\}+\frac{1}{(2\pi)^3}\sum_{R_i\neq 0}b(R_i)\sin(kR_i)\exp\{-[\Gamma+2g(R_i)]t\} \tag{7.5}$$

which is our final result for the time evolution of the diagonal elements of the coarse-grained density matrix. The initial condition enters this expression via the Fourier coefficients, $a(R_i)$ and $b(R_i)$, on the initial density matrix. The second and the third terms of the rhs of Eq. (7.5) decay in time exponentially. The physical meaning of this result is that the *equilibrium state* of the Haken-Strobl model corresponds to the uniform population of the states within the exciton band

$$\langle\rho(k,k;t)\rangle_{\rm eq}=\lim_{t\to\infty}\langle\rho(k,k;t)\rangle=(1/2\pi)^3. \tag{7.6}$$

The expression for the coarse-grained density matrix, Eq. (7.5), allows us to calculate the average exciton energy for arbitrary initial conditions. In Sec. VI it was shown that the incoherent part of the Hamiltonian does not contribute to the average energy. Therefore

$$\bar{E}(t)=\int d^3q\,\varepsilon(q)\langle\rho(q,q;t)\rangle=h(0)\left\{1+\sum_{R_i\neq 0}A(R_i)\exp\{-[\Gamma-2g(R_i)]t\}\right\}. \tag{7.7}$$

Thus the average energy of the exciton tends to the equilibrium value, which coincides with the site energy, $h(0)$. The latter is reached on the time scale $\tau_r\sim 1/\Gamma$. The average momentum of the exciton can be obtained in a similar way. The common feature of all these results is that the physical observables equilibrate on the time scale $t\sim\tau_r$. Thus τ_r is the characteristic time scale of the Haken-Strobl model. First, it is the time scale on which the exciton reaches thermal equilibrium with the thermal bath. Second, it is also the time scale on which the exciton phase coherence is destroyed and its motion becomes diffusive.

Returning to the properties of the model, one can see that the first two of them are in fact associated with the choice of the initial condition. On the other hand, vanishing mobility is a characteristic feature of the Haken-Strobl model. Finally, the apparent breakdown of the Nernst-Einstein relations is associated with the fact that the model corresponds to the limit of infinite temperature ($T\to\infty$).

VIII. SUMMING UP

A. Results

Results of this work can be summarized as follows.

(1) Solution of the general 3D Haken-Strobl model

with non-nearest-neighbor interactions has been obtained for the arbitrary initial condition. The equilibrium state of the system has been shown to correspond to the uniform population of the states in the excitonic band.

(2) An efficient method of evaluation of the moments of displacement within the model has been developed. Explicit analytic expressions for the first two nonvanishing moments of displacement for the three-dimensional lattice with inversion symmetry have been derived.

(3) The expression for the fourth-order moment includes the contributions from multistep transitions. It has been shown that the inclusion of these contributions makes the simple Born approximation for the memory functions inapplicable.

(4) The energy exchange between the localized excitation and thermal bath vanishes within the model. This result is related to the vanishing exciton mobility by the Nyquist theorem.

B. Limitations and extensions

(a) Phenomenological character of the model. In the Haken-Strobl model the exciton-phonon coupling is described via the stochastic field. The correlation functions, $g(R_i,R_j)$, are introduced as phenomenological parameters. They can, however, be calculated from first principles using the small polaron theory [13–16]. This allows one to explore their temperature and pressure dependence. The results can be compared with the experimental temperature dependence of the width of the phononless excited band. If the contribution from the quadratic exciton-phonon coupling is dominant then $\Gamma(T)\simeq\Gamma(0)/\sinh^2(\hbar\omega/kT)$, with $\omega\simeq\omega_D$ being the characteristic (Debye) phonon frequency. This result is consistent with the experimental temperature dependence of the zero-phonon linewidth, $\Gamma(T)\simeq\Gamma(0)+\alpha T^2$, for triplet excitons in anthracene crystals in the temperature interval 30–100 K [5].

(b) Zero-correlation-time limit. For the validity of the zero correlation time limit the exciton bandwidth has to be much smaller than the phonon bandwidth. This conclusion is satisfied for the lowest triplet excitons in molecular crystals. The line shape of the phononless band of these excitons is Lorentzian in the temperature interval 20–100 K [5,7]. This feature is characteristic of the fats modulation limit. The situation is different for singlet excitons. The exciton bandwidth in this case is comparable to the phonon bandwidth. In order to apply the stochastic model to the singlet excitons it has to be extended to account for the finite correlation time effects. Such an extension has been suggested by Toyozawa [20] and by Sumi [21] and studied in a number of papers [51–55].

(c) The absence of energy dissipation. An important deficiency of the Haken-Strobl model is that the energy exchange between the exciton and the phonon bath is not accounted for (the model corresponds formally to the limit $T\rightarrow\infty$). Finite-temperature generalizations of the model were suggested by Lindenberg and West [56] and by Čapek [57].

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APPENDIX A

Below the expression for the fourth-order moment of the displacement within the 3D Haken-Strobl model is derived. We start from the general expression for the fourth-order moment in terms of the coarse-grained density matrix:

$$\langle\hat{r}^{\,4}_{\mu\nu\lambda\sigma}(p)\rangle=\frac{1}{16}\int d^3s\,\phi^{iv}_{\mu\nu\lambda\sigma}(0,s;p+\Gamma) \tag{A1}$$

with

$$\phi^{iv}_{\mu\nu\lambda\sigma}(0,s;p)\equiv\left.\frac{\partial^4\phi(u,s;p)}{\partial u_\mu\partial u_\nu\partial u_\lambda\partial u_\sigma}\right|_{u=0}.$$

We shall also require the Laplace transform of SLE, Eq. (3.10)

$$\begin{aligned}p\phi(u,s;p)=&\frac{1}{(2\pi)^3}+P(u,s)\phi(u,s;p)\\&+\frac{1}{(2\pi)^3}\left\{Q(u)\int d^3q\,\phi(u,q;p)\right.\\&\left.+\int d^3q\,R(s,q)\phi(u,q;p)\right\}\end{aligned} \tag{A2}$$

together with relations

$$P(0,s)=Q'_\nu(0)=P''_{\mu\nu}(0,s)=Q'''_{\mu\nu\lambda}(0)=P^{iv}_{\mu\nu\lambda\sigma}(0,s)=0, \tag{A3}$$

$$Q(0)=2\sum_{R_i}g(R_i)\equiv\Gamma, \tag{A4}$$

$$P'_\nu(0,s)=2i\sum_{R_i}h(R_i)R_i^\nu\sin(sR_i), \tag{A5}$$

$$Q''_{\nu\lambda}(0)=-8\sum_{R_i}g(R_i)R_i^\nu R_i^\lambda, \tag{A6}$$

$$P'''_{\mu\nu\lambda}(0,s)=-2i\sum_{R_i}h(R_i)R_i^\mu R_i^\nu R_i^\lambda\sin(sR_i), \tag{A7}$$

$$Q^{iv}_{\mu\nu\lambda\sigma}(0)=32\sum_{R_i}g(R_i)R_i^\mu R_i^\nu R_i^\lambda R_i^\sigma. \tag{A8}$$

Using Eq. (A2) together with Eqs. (A3)–(A8) we obtain

$$\begin{aligned}&\int d^3s\,\phi^{iv}_{\mu\nu\lambda\sigma}(0,s;p)\\&=\frac{1}{(p-\Gamma)}\{[K_\mu^{\nu\lambda\sigma}(p)+K_\nu^{\mu\lambda\sigma}(p)+K_\lambda^{\mu\nu\sigma}(p)+K_\sigma^{\mu\nu\lambda}(p)]+[L^\mu_{\nu\lambda\sigma}(p)+L^\nu_{\mu\lambda\sigma}(p)+L^\lambda_{\mu\nu\sigma}(p)+L^\sigma_{\mu\nu\lambda}(p)]\\&\quad+[Q''_{\mu\nu}(0)Z_{\lambda\sigma}(p)+Q''_{\mu\lambda}(0)Z_{\nu\sigma}(p)+Q''_{\mu\sigma}(0)Z_{\nu\lambda}(p)+Q''_{\nu\lambda}(0)Z_{\mu\sigma}(p)+Q''_{\nu\sigma}(0)Z_{\mu\lambda}(p)+Q''_{\lambda\sigma}(0)Z_{\mu\nu}(p)]\\&\quad+Q^{iv}_{\mu\nu\lambda\sigma}(0)/(p-\Gamma)\}.\end{aligned} \tag{A9}$$

In Eq. (A9) the following notations have been used:

$$K_{\mu}^{\nu\lambda\sigma}(p)\equiv\int d^3s\, P'_{\mu}(0,s)\phi'''_{\nu\lambda\sigma}(0,s;p), \tag{A10}$$

$$L^{\sigma}_{\mu\nu\lambda}(p)\equiv\int d^3s\, P'''_{\mu\nu\lambda}(0,s)\phi'_{\sigma}(0,s;p), \tag{A11}$$

$$Z_{\lambda\sigma}(p)\equiv\int d^3s\, \phi''_{\lambda\sigma}(0,s;p). \tag{A12}$$

Expression for the integral $Z_{\lambda\sigma}(p)$ has been already derived [cf. Eq. (4.18)]:

$$Z_{\lambda\sigma}(p)=-\frac{8}{(p-\Gamma)^2}\sum_{R_i}\left\{g(R_i)+\frac{[h(R_i)]^2}{[p+2g(R_i)]}\right\}R_i^{\lambda}R_i^{\sigma}. \tag{A13}$$

Using Eq. (A7) $L^{\sigma}_{\mu\nu\lambda}(p)$ can be recast in the form

$$L^{\sigma}_{\mu\nu\lambda}(p)=-2i\sum_{R_i}h(R_i)R_i^{\mu}R_i^{\nu}R_i^{\lambda}\times\int d^3s\,\sin(sR_i)\phi'_{\sigma}(0,s;p). \tag{A14}$$

The integral in Eq. (A14) has been already evaluated [cf. Eq. (4.15)]

$$B_{\sigma}(R_i;p)\equiv\int d^3s\,\sin(sR_i)\phi'_{\sigma}(0,s;p)=\frac{2ih(R_i)R_i^{\sigma}}{(p-\Gamma)[p+2g(R_i)]}. \tag{A15}$$

It follows that

$$L^{\sigma}_{\mu\nu\lambda}(p)=\frac{4}{(p-\Gamma)}\sum_{R_i}\frac{[h(R_i)]^2}{[p+2g(R_i)]}R_i^{\mu}R_i^{\nu}R_i^{\lambda}R_i^{\sigma}. \tag{A16}$$

Note that the result is symmetric with respect to permutation of the indices μ,ν,λ,σ. From Eq. (A8)

$$\frac{1}{(p-\Gamma)}Q^{iv}_{\mu\nu\lambda\sigma}(0)=\frac{32}{(p-\Gamma)}\sum_{R_i}g(R_i)R_i^{\mu}R_i^{\nu}R_i^{\lambda}R_i^{\sigma}. \tag{A17}$$

Combining Eqs. (A6) and (A13) we obtain

$$Q''_{\mu\nu}(0)Z_{\lambda\sigma}(p)=\frac{64}{(p-\Gamma)^2}\sum_{R_i}g(R_i)R_i^{\mu}R_i^{\nu}\sum_{R_j}\left\{g(R_j)+\frac{[h(R_j)]^2}{[p+2g(R_j)]}\right\}R_j^{\lambda}R_j^{\sigma}. \tag{A18}$$

The other terms of this type are obtained by trivial permutation of indices. We now turn to evaluation of the integral $K_{\mu}^{\nu\lambda\sigma}(p)$. Using Eq. (A5) it can be recast in the form

$$K_{\mu}^{\nu\lambda\sigma}(p)=2i\sum_{R_i}h(R_i)R_i^{\mu}\int d^3s\,\sin(sR_i)\phi'''_{\nu\lambda\sigma}(0,s;p)\equiv 2i\sum_{R_i}h(R_i)R_i^{\mu}\Lambda_{\nu\lambda\sigma}(R_i;p). \tag{A19}$$

Straightforward manipulation of SLE, Eq. (A2), leads to

$$[p+2g(R_i)]\Lambda_{\nu\lambda\sigma}(R_i;p)=\frac{1}{(2\pi)^3(p-\Gamma)}\int d^3s\,\sin(sR_i)P'''_{\nu\lambda\sigma}(0,s)+[M_{\nu}^{\lambda\sigma}(R_i;p)+M_{\lambda}^{\nu\sigma}(R_i;p)+M_{\sigma}^{\nu\lambda}(R_i;p)], \tag{A20}$$

where

$$M_{\nu}^{\lambda\sigma}(R_i;p)\equiv\int d^3s\,\sin(sR_i)P'_{\nu}(0,s)\phi''_{\lambda\sigma}(0,s;p). \tag{A21}$$

The integral $\int d^3s\,\sin(sR_i)P'''_{\nu\lambda\sigma}(0,s)$ is readily evaluated

$$\int d^3s\,\sin(sR_i)P'''_{\nu\lambda\sigma}(0,s)=-2i(2\pi)^3h(R_i)R_i^{\nu}R_i^{\lambda}R_i^{\sigma}. \tag{A22}$$

It follows that $M_{\nu}^{\lambda\sigma}(R_i;p)$ can be recast in the form

$$M_{\nu}^{\lambda\sigma}(R_i;p)=i\sum_{R_j}h(R_j)R_j^{\nu}\times[G_{\lambda\sigma}(R_i-R_j;p)-G_{\lambda\sigma}(R_i+R_j;p)] \tag{A23}$$

with

$$G_{\lambda\sigma}(R_k;p)\equiv\int d^3s\,\cos(sR_k)\phi''_{\lambda\sigma}(0,s;p). \tag{A24}$$

Using the inversion symmetry of the lattice Eq. (A23) can be rewritten in the form

$$M_{\nu}^{\lambda\sigma}(R_i;p)=2ih(R_i)R_i^{\nu}Z_{\lambda\sigma}(p)-2i\sum_{R_j}^{(\neq -R_i)}h(R_j)R_j^{\nu}G_{\lambda\sigma}(R_i+R_j;p). \tag{A25}$$

The problem has been thus reduced to evaluation of the integrals $G_{\lambda\sigma}(R_k;p)$. Using SLE these integrals can be expressed in the form

$$G_{\lambda\sigma}(R_k,p)=\frac{1}{[p-2g(R_k)]}\{N_{\lambda\sigma}(R_k;p)+N_{\sigma\lambda}(R_k;p)\}, \tag{A26}$$

where

$$N_{\lambda\sigma}(R_k;p)\equiv\int d^3s\,\cos(sR_k)P'_{\lambda}(0,s)\phi'_{\sigma}(0,s;p). \tag{A27}$$

The integral can be recast as

$$N_{\lambda\sigma}(R_k;p)=i\sum_{R_l}h(R_l)R_l^{\lambda}\times[B_{\sigma}(R_k+R_l;p)+B_{\sigma}(R_l-R_k;p)], \tag{A28}$$

where the integral $B_{\sigma}(R_k;p)$ has been already evaluated [cf. Eq. (A15)]. As a result we obtain

$$N_{\lambda\sigma}(R_k;p)=-\frac{2}{(p-\Gamma)}\sum_{R_l}h(R_l)R_l^{\lambda}\left\{\frac{h(R_k+R_l)(R_k^{\sigma}+R_l^{\sigma})}{[p+2g(R_k+R_l)]}+\frac{h(R_l-R_k)(R_l^{\sigma}-R_k^{\sigma})}{[p+2g(R_l-R_k)]}\right\}$$

$$=-\frac{4}{(p-\Gamma)}\sum_{R_l}\frac{h(R_l)h(R_k+R_l)}{[p+2g(R_k+R_l)]}R_l^{\lambda}(R_k^{\sigma}+R_l^{\sigma}), \tag{A29}$$

where the inversion symmetry of the lattice has been employed. Substitution into Eq. (A26) leads to

$$G_{\lambda\sigma}(R_k,p)=-\frac{4}{(p-\Gamma)[p-2g(R_k)]}\sum_{R_l}\frac{h(R_l)h(R_k+R_l)}{[p+2g(R_k+R_l)]}[R_l^{\lambda}(R_k^{\sigma}+R_l^{\sigma})+R_l^{\sigma}(R_k^{\lambda}+R_l^{\lambda})] \tag{A30}$$

and from Eq. (A25)

$$M_{\nu}^{\lambda\sigma}(R_i;p)=2ih(R_i)R_i^{\nu}Z_{\lambda\sigma}(p)$$

$$+\frac{8i}{(p-\Gamma)}\sum_{R_j}^{(\neq -R_i)}\frac{h(R_j)R_j^{\nu}}{[p-2g(R_i+R_j)]}\sum_{R_l}\frac{h(R_l)h(R_k+R_l)}{[p+2g(R_k+R_l)]}[R_l^{\lambda}(R_k^{\sigma}+R_l^{\sigma})+R_l^{\sigma}(R_k^{\lambda}+R_l^{\lambda})]. \tag{A31}$$

Combining Eqs. (A19) and (A20) we obtain

$$K_{\mu}^{\nu\lambda\sigma}(p)=\frac{4}{(p-\Gamma)}\sum_{R_i}\frac{[h(R_i)]^2}{[p+2g(R_i)]}R_i^{\mu}R_i^{\nu}R_i^{\lambda}R_i^{\sigma}$$

$$+\frac{32}{(p-\Gamma)^2}\sum_{R_i}\frac{[h(R_i)]^2}{[p+2g(R_i)]}\sum_{R_j}\left\{g(R_j)+\frac{[h(R_j)]^2}{[p+2g(R_j)]}\right\}[R_i^{\mu}R_i^{\nu}R_j^{\lambda}R_j^{\sigma}+R_i^{\mu}R_i^{\lambda}R_j^{\nu}R_j^{\sigma}+R_i^{\mu}R_i^{\sigma}R_j^{\nu}R_j^{\lambda}]$$

$$-\frac{16}{(p-\Gamma)}\sum_{R_i}\frac{h(R_i)}{[p+2g(R_i)]}\sum_{R_j}^{(\neq -R_i)}\frac{h(R_j)}{[p-2g(R_i+R_j)]}\sum_{R_k}\frac{h(R_k)h(R_i+R_j+R_k)}{[p+2g(R_i+R_j+R_k)]}\xi_{\mu}^{\nu\lambda\sigma}, \tag{A32}$$

where the tensor $\xi_{\mu}^{\nu\lambda\sigma}$ is defined as

$$\xi_{\mu}^{\nu\lambda\sigma}\equiv R_l^{\mu}[(R_i^{\nu}+R_j^{\nu}+R_k^{\nu})(R_j^{\sigma}R_k^{\lambda}+R_j^{\lambda}R_k^{\sigma})+(R_i^{\lambda}+R_j^{\lambda}+R_k^{\lambda})(R_j^{\nu}R_k^{\sigma}+R_j^{\sigma}R_k^{\nu})+(R_i^{\sigma}+R_j^{\sigma}+R_k^{\sigma})(R_j^{\nu}R_k^{\lambda}+R_j^{\lambda}R_k^{\nu})]. \tag{A33}$$

The first term in Eq. (A32) is symmetric with respect to permutation of the indices. Finally we obtain the following expression for the Laplace transform of the fourth-order moment of displacement:

$$\langle\hat{r}^4_{\mu\nu\lambda\sigma}(p)\rangle=\Upsilon^{(1)}_{\mu\nu\lambda\sigma}(p)+\Upsilon^{(2)}_{\mu\nu\lambda\sigma}(p)+\Upsilon^{(3)}_{\mu\nu\lambda\sigma}(p) \tag{A34}$$

with

$$\Upsilon^{(1)}_{\mu\nu\lambda\sigma}(p)=\frac{2}{p^2}\sum_{R_i}\left\{g(R_i)+\frac{[h(R_i)]^2}{[p+\Gamma+2g(R_i)]}\right\}\times R_i^{\mu}R_i^{\nu}R_i^{\lambda}R_i^{\sigma}, \tag{A35}$$

$$\Upsilon^{(2)}_{\mu\nu\lambda\sigma}(p)=2p[\langle\hat{r}^2_{\mu\nu}(p)\rangle\langle\hat{r}^2_{\lambda\sigma}(p)\rangle+\langle\hat{r}^2_{\mu\lambda}(p)\rangle\langle\hat{r}^2_{\nu\sigma}(p)\rangle+\langle\hat{r}^2_{\mu\sigma}(p)\rangle\langle\hat{r}^2_{\nu\lambda}(p)\rangle] \tag{A36}$$

and

$$\Upsilon^{(3)}_{\mu\nu\lambda\sigma}(p)=-\frac{1}{p^2}\sum_{R_i}\frac{h(R_i)}{[p+\Gamma+2g(R_i)]}\times\sum_{R_j}^{(\neq -R_i)}\frac{h(R_j)}{[p+\Gamma-2g(R_i+R_j)]}\times\sum_{R_k}\frac{h(R_k)h(R_i+R_j+R_k)}{[p+\Gamma+2g(R_i+R_j+R_k)]}\Xi_{\mu\nu\lambda\sigma} \tag{A37}$$

with $\Xi_{\mu\nu\lambda\sigma}$ being the totally symmetric fourth-rank tensor:

$$\Xi_{\mu\nu\lambda\sigma}=\xi_{\mu}^{\nu\lambda\sigma}+\xi_{\lambda}^{\mu\lambda\sigma}+\xi_{\sigma}^{\mu\nu\lambda} \tag{A38}$$

and $\xi_{\mu}^{\nu\lambda\sigma}$ defined by Eq. (A33).

APPENDIX B

Below we obtain the solution of the stochastic Liouville equation for arbitrary initial conditions. Our starting point will be Eq. (7.1) for the Laplace transform of the di-

agonal elements of the coarse-grained density matrix:

$$p\phi(0,s;p)-\mu(s)=\frac{1}{(2\pi)^3}\left\{\Gamma\int d^3q\,\phi(0,q;p)+\int d^2q\,R(s,q)\phi(0,q;p)\right\}, \tag{B1}$$

where

$$\mu(s)\equiv F(0,s;0)$$

is the normalized coarse-grained density matrix for $t=0$:

$$\int d^3s\,\mu(s)=1. \tag{B2}$$

Integration of Eq. (B1) with account that $\int d^3s\,R(s,q)=0$ leads to

$$\int d^3s\,\phi(0,s;p)=\frac{1}{(p-\Gamma)}. \tag{B3}$$

Substitution of Eq. (B3) into Eq. (B1) leads to the integral equation for the $\phi(0,s;p)$ function

$$\phi(0,s;p)-\frac{1}{(2\pi)^3 p}\int d^3q\,R(s,q)\phi(0,q;p)=\frac{1}{p}\left\{\mu(s)+\frac{1}{(2\pi)^3}\frac{\Gamma}{(p-\Gamma)}\right\}. \tag{B4}$$

Due to the oscillatory form of the kernel, $R(s,q)$, the resulting Fredholm integral equation can be solved easily. For this purpose we substitute the explicit form of $R(s,q)$ into Eq. (B4) leading to

$$\phi(0,s;p)=\frac{1}{p}\left\{\mu(s)+\frac{1}{(2\pi)^3}\frac{\Gamma}{(p-\Gamma)}\right\}+\frac{2}{(2\pi)^3 p}\sum_{R_i\neq 0}g(R_i)\cos(sR_i)\int d^3q\,\cos(qR_i)\phi(0,q;p)-\frac{2}{(2\pi)^3 p}\sum_{R_i\neq 0}g(R_i)\sin(sR_i)\int d^3q\,\sin(qR_i)\phi(0,q;p). \tag{B5}$$

Multiplication of Eq. (B5) by $\cos(sR_j)$ and integration gives

$$\int d^3s\,\cos(sR_j)\phi(0,s;p)=\frac{a(R_j)}{[p-2g(R_j)]} \tag{B6}$$

and analogously

$$\int d^3s\,\sin(sR_j)\phi(0,s;p)=\frac{b(R_j)}{[p+2g(R_j)]}. \tag{B7}$$

Here $a(R_j)$ and $b(R_j)$ are the Fourier coefficients:

$$a(R_j)\equiv\int d^3q\,\cos(qR_j)\mu(q), \tag{B8}$$

$$b(R_j)\equiv\int d^3q\,\sin(qR_j)\mu(q). \tag{B9}$$

Substitution of Eqs. (B6) and (B7) into Eq. (B5) leads to the final result for the Laplace transform of the coarse-grained density matrix:

$$\phi(0,s;p)=\frac{1}{(2\pi)^3}\left\{\frac{1}{(p-\Gamma)}+\sum_{R_i\neq 0}\left[\frac{a(R_i)\cos(sR_i)}{[p-2g(R_i)]}+\frac{b(R_i)\sin(sR_i)}{p+2g(R_i)]}\right]\right\}. \tag{B10}$$

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