Transient grating spectroscopy of exciton sound waves in dense exciton fluids

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A dynamic description is developed for the motion of an exciton fluid at high exciton density. Coherent oscillatory modes of the exciton density are predicted provided the exciton–phonon coupling is sufficiently small. The physical mechanism is similar to that of sound waves in an ordinary gas. A method to probe these motions using transient grating with strong pump fields is proposed. The grating recurrence time is estimated to be about 100 ps for typical molecular crystals. Exciton Bose condensation could also be probed using the same technique.

1. Introduction

Most studies of exciton transport have focused on low density of excitons created by relatively weak electromagnetic fields. An extensive literature exists on this subject, particularly on whether exciton motion is coherent (free particle like) or incoherent (diffusive) [1,2]. The most likely physical scenario seems to be that for very short times excitons move coherently and the motion becomes incoherent due to scattering by phonons and impurities. The problem in settling this question is firstly that coherent exciton motion was never observed, and secondly theoretical analysis suggests that for a situation in which coherent motion should be observable, polariton related effects become important. Various estimates for the exciton–phonon interaction time t_{phon} differ by an order of magnitude [3].

Intense electromagnetic fields can create excitons at high density. Many new physical phenomena then appear resulting from exciton–exciton interactions. The simplest, exciton annihilation, is the most common in molecular crystals with Frenkel excitons, and is usually treated using kinetic schemes. This process appears even at moderate intensity and often complicates the measurement of radiative decay of excitons. It has been suggested that at high density excitons undergo Bose condensation [4,5].

We develop here a dynamical description for an *exciton gas at high density*, that includes collisions between excitons. At high exciton density we found that a new phenomenon may occur: deviations from a uniform exciton density may disappear and reappear later. The physical mechanism is analogous to that of sound waves in an ordinary gas. Pushing this analogy, a number of interesting observations can be made. The sound velocity is proportional to the thermal velocity of the particles, and, to first order, independent of density. We propose that a four wave mixing experiment, transient grating, can directly probe these exciton sound waves. Combining the time at which the grating first vanishes with the grating wavelength, the thermal exciton velocity can be directly extracted. This together with the exciton diffusion coefficient enables in principle a reliable measurement of the phonon scattering time t_{phon}.

The theory proposed here can be extended to a phenomenological treatment of the transient grating dynamics of a Bose condensed phase [4,5]. This is important as the major problem for observing the Bose condensation is to find a clear signature, which the transient grating may provide.

2. Kinetic model

In order to describe the dynamics of a dense exciton fluid we use an approach based on the Boltz-

mann equation. We start by considering the one exciton phase space density $f(r, v, t)$, the probability density of finding an exciton with velocity v at position r. This probability is the Wigner transform of the binary exciton variable $\langle B^{\dagger}_{r+s/2} B_{r-s/2} \rangle$ [6]. For simplicity we do not include polarization-dependent effects here. We consider four different physical mechanisms for the time evolution of this density.

(1) Lifetime. This, in the time domain, will just be an additional prefactor multiplying the final signal. We will not consider it here, based on the observation that the time scale under consideration is generally shorter or at least of similar order of magnitude as the exciton lifetime.

(2) Free, coherent (unperturbed) exciton motion. If we have only free exciton motion then obviously we have

$$f(r, v, t) = f(r - vt, v, t) . \tag{1}$$

Here we have treated r and v as classical, continuous variables. This will be a good approximation as long as we are probing relatively slow and long wavelength effects. We also assume that the excitons have a certain isotropic effective mass.

(3) Impurity and phonon scattering. Due to scattering by impurities and phonons $f(r, v, t)$ will change. In the BGK [7] or strong collision model an exciton with initial velocity v is assumed to be scattered to an arbitrary final velocity v' with a probability proportional to the thermal velocity distribution. The temperature of this distribution is the temperature of the phonons which equals the crystal temperature.

Combining the last two effects we find the time evolution

$$\frac{\mathrm{d}}{\mathrm{d}t} f(r, v, t) = -v \nabla f(r, v, t) + \lambda \left[\left(f_{\mathrm{m}}(v) \int \mathrm{d}v' f(r, v', t) \right) - f(r, v, t) \right], \tag{2}$$

where f_{m} is the thermal (Maxwell) velocity distribution,

$$f_{\mathrm{m}}(v) = \left(\frac{m}{2\pi k_{\mathrm{B}} T} \right)^{d/2} \exp(-mv^2/2k_{\mathrm{B}}T) , \tag{3}$$

in d dimensions. Here, as in the remainder, we need to consider only one dimension, the dimension along which the grating is created. In eq. (2) λ is the exciton–phonon scattering rate. This model is quite close to a model studied by Knoester and Mukamel [6]. The collision term in eq. (2) is such that the total number of excitons is conserved, that is

$$\frac{\mathrm{d}}{\mathrm{d}t} \int \mathrm{d}v \, f(r, v, t) = 0 . \tag{4}$$

(4) At high densities collisions between excitons become important. We assume that these collisions conserve total momentum but not energy. Furthermore we assume that f is close to equilibrium and that deviations are relatively small, so that the exciton–exciton collision rate does not depend on the density of excitons at a certain position. These assumptions greatly simplify the calculation while we still retain the most interesting physics; the sound-like waves. A collision term that conserves both the exciton number and exciton momentum is the BGK like term

$$\mu \left\{ \left[f_{\mathrm{m}}(v) \int \mathrm{d}v' \left(1 + \frac{m}{k_{\mathrm{B}} T} v v' \right) f(r, v', t) \right] - f(r, v, t) \right\}, \tag{5}$$

where μ is the collision rate. It is proportional to the exciton density. Momentum conservation of this collision term can easily be shown by studying an equation similar to eq. (4).

3. Solution of the BGK-like model

We now perform a Fourier transform with respect to the positions, and a Fourier (Laplace) transforming with respect to the time variable

$$\tilde{A}(k, \omega) = \int \mathrm{d}r \int_0^{\infty} \mathrm{d}t \exp[-\mathrm{i}(kr + \omega t)] A(r, t) , \tag{6}$$

to arrive at the kinetic equation

$$(i\omega - ivk + \lambda + \mu)\tilde{f}(k, v, \omega)$$
$$= (\lambda + \mu) f_m(v) \int dv' \, \tilde{f}(k, v', \omega)$$
$$+ \mu v f_m(v) \int dv' \, \frac{k_B T}{m} v' \tilde{f}(k, v', \omega)$$
$$+ f(k, v, t=0), \qquad (7)$$

where as in the remainder, v is the component of $\boldsymbol{v}$ along k, as this is the only relevant component. We assume the initial condition for $f(k, v, t=0) = \exp(ikr) f_m(v)$. The solution to eq. (7) is the BGK form

$$f(k, v, \omega) = \frac{A(k, \omega) + vB(k, \omega)}{i\omega - ivk + \lambda + \mu} f_m(v) , \qquad (8)$$

where A and B are determined by the initial condition, and can be found by a simple calculation. We obtain

$$n(k, \omega) \equiv \int dv \, f(k, v, \omega)$$
$$= \frac{\xi_0(1 - \mu\xi_2) + \mu\xi_1^2}{[1 - (\lambda + \mu)\xi_0](1 - \mu\xi_2) - (\lambda + \mu)\mu\xi_1^2} , \qquad (9)$$

with

$$\xi_n = \int_{-\infty}^{\infty} dv \, v^n \frac{f_m(v)}{i\omega - ikv + \lambda + \mu} . \qquad (10)$$

In terms of the plasma dispersion function

$$Z(z) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dt \frac{\exp(-t^2)}{t - z} . \qquad (11)$$

We have

$$\xi_0 = \frac{-i}{k} \left(\frac{m}{2k_B T} \right)^{1/2} Z\left(\left(\frac{m}{2k_B T} \right)^{1/2} \frac{i(\lambda + \mu) - \omega}{k} \right) , \qquad (12)$$

$$\xi_1 = \frac{i}{k} + \frac{\omega - i(\lambda + \mu)}{k} \xi_0 , \qquad (13)$$

$$\xi_2 = \frac{\omega - i(\lambda + \mu)}{k} \xi_1 . \qquad (14)$$

Standard representations exist for the plasma dispersion function [8], which can be evaluated using numerical techniques. Eq. (9) has to be numerically Fourier transformed in order to find the time-domain response.

4. Approximate solution

Following Kamgar Parsi and Cohen [7] we now obtain an approximate analytical solution which is complimentary to the exact solution presented earlier and provides a good insight on the occurrence of the exciton-sound waves. For high wavevector k the exciton density decays rapidly and hence the motion is coherent so that

$$n(k, t) = \exp[-(k_B T/2m) k^2 t^2] . \qquad (15)$$

We would like to derive an (approximate) solution which will hold for small wavevectors. This can conveniently be found by making a polynomial assumption for $f(k, v, t)$, that is we assume that at all times

$$f(k, v, t) = \left[c_1(t) + c_2(t) \left(\frac{m}{k_B T} \right)^{1/2} v \right.$$
$$\left. + c_3(t) \frac{1}{\sqrt{2}} \left(\frac{m}{k_B T} v^2 - 1 \right) \right] f_m(v) . \qquad (16)$$

We are most interested in the exciton density $c_1(t) = n(k, t)$. Under this polynomial assumption the time evolution equation transposes to

$$\frac{d}{dt} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = -L \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} , \qquad (17)$$

with the time evolution matrix

$$L = \begin{pmatrix} 0 & -ik\left(\frac{k_B T}{m}\right)^{1/2} & 0 \\ -ik\left(\frac{k_B T}{m}\right)^{1/2} & \lambda & -ik\left(\frac{2k_B T}{m}\right)^{1/2} \\ 0 & -ik\left(\frac{2k_B T}{m}\right)^{1/2} & \lambda + \mu \end{pmatrix} . \qquad (18)$$

For the time dependence of the exciton density we find

$$n(k, t) = \sum_{i=1}^{3} a_i \exp(-\gamma_i t) , \qquad (19)$$

where γ_i are the eigenvalues of L, and the a_i are determined by the initial conditions. If the eigenvalues of L have imaginary parts, oscillatory behavior of $n(k, t)$ may be present.

5. Application to transient grating

In a classic experiment Rose, Righini and Fayer (RRF) [9] measured the exciton diffusion coefficient of anthracene in a transient grating experiment [10]. In the transient grating setup we first apply a pair of time-coincident resonant strong pulses with wavevectors k_1, k_2 that sets up an exciton grating with wavevector $k_G = k_1 - k_2$. Some time later, a weak off resonant probe pulse with wavevector k_3 is applied that is diffracted by the remnant of the grating of the first pulse to produce a signal with wavevector $k_s = k_3 + k_G$. The intensity of the diffracted signal is proportional to $S(t) = |n(k_G, t)|^2$. With respect to the issue raised here, it is important to note that RRF observed a diffusive behavior. We assume that the first pulse generates a certain exciton density (population) $n(r)$. The main assumption is that after the creation of the grating coherences between different excited molecules are not important. Then we can use the theory of the previous sections.

In fig. 1 we compare the exact solution to the approximate solution as well as the free flight result, eq. (15). We found that for $k < \mu$ the 3×3 matrix of section 4 gives a fair approximation and that for $k > \mu$ eq. (15) gives a fair approximation to the exact solution.

In fig. 2 the eigenvalues are plotted for different values of the parameters. For $k = 0$ we always have three real modes and the grating appears diffusive (fig. 3a) The diffusion coefficient is

$$D = k_B T / m\lambda . \qquad (20)$$

For appropriate parameters we find oscillations in $n(k, t)$ and hence in the grating (fig. 3b and also fig. 1a). These parameters are in a region where the approach of section 4 gives a good approximation of the dynamics. For large k the free flight dominates and eq. (15) is accurate (fig. 1a). An interesting question is obviously: when does the signal show macroscopic coherent oscillations. For this we refer to fig. 4 where in a contour plot the minimum of $n(k, t)$ is given. Obviously for an oscillation to take place the minimum has to be negative (although the signal is proportional to $|n(k, t)|^2$).

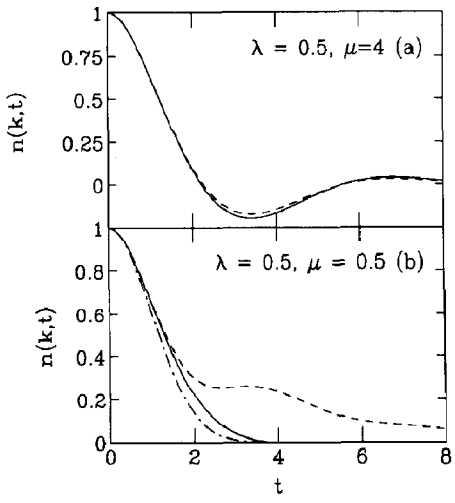

Fig. 1. (a) The Fourier transform of the exciton density as a function of time for the parameters given. The transient grating signal is proportional to $|n(k, t)|^2$. Solid line: the exact solution of section 3, dashed line: the approximate solution of section 4. The most notable feature is the oscillatory behavior which provides a sensitive probe for the exciton velocity. In this figure the time scale was expressed in unit of $(m/k_B T)^{1/2}/k$ (m effective mass, T temperature, k_B is the Boltzmann constant, and k is the wavevector of the grating). Physically reasonable values for the parameters are given in section 6, $t = 1$ corresponds to 100 ps. (b) Here the approximate solution is no longer a good approximation as the wavevector is too large. The high wavevector result eq. (15) (dot-dashed line) gives a quite reasonable approximation.

6. Discussion

The smallest achievable optical grating spacing is half the optical wavelength, hence of the order of 1 μm. According to Knoester and Mukamel [3] the exciton-like polaritons in naphtalene have a group velocity of 2×10^3 m/s. We use this value for the exciton velocity $v = (k_B T/m)^{1/2}$. The exciton diffusion coefficient of anthracene has been measured by RRF to be $1 \pm 0.2 \times 10^{-3}$ m^2/s (at 1.8 K) [9]. Combining these two numbers we find that the exciton–phonon scattering rate v^2/D for these molecular crystals is about 4×10^9 s^{-1}. According to the findings of section 5 the grating recurrence may appear if the ex-

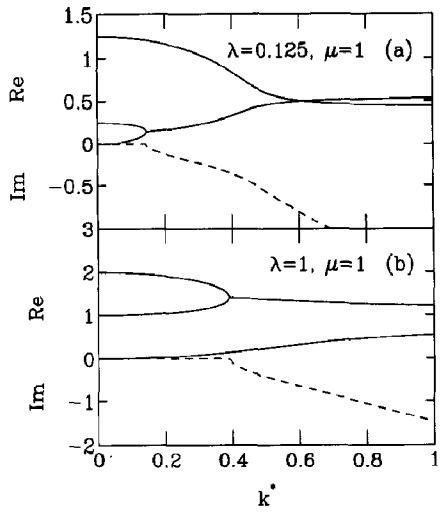

Fig. 2. (a) The eigenvalues of the matrix L in units of μ. The solid lines are the real parts and the dashed line is the imaginary part of the eigenfunctions, only the negative branch is plotted. Only when the imaginary part is nonzero can oscillations be expected. In this figure the wavevector is expressed in units of $\mu(k_BT/m)^{1/2}$. (b) shows that the branching features of (a) are not universal.

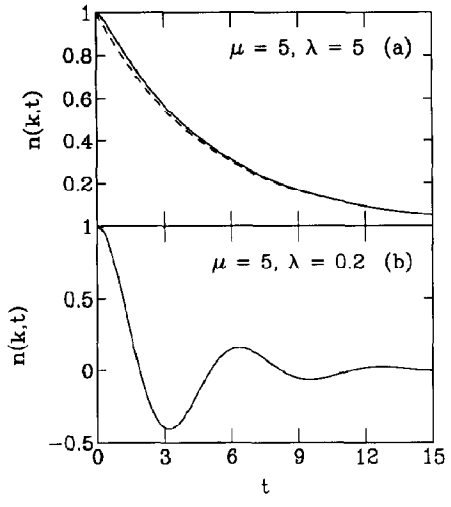

Fig. 3. (a) The time evolution at high interaction rates of the deviation from equilibrium of the exciton density. Here $k=1$ and time is expressed in units $(m/k_BT)^{1/2}/k$. Solid line: exact solution. Dashed line: a single exponential, $n(k, t)=\exp(-Dk^2t)$ where we used eq. (20) for the diffusion coefficient, for these parameters $D=0.2$. (b) For small exciton–phonon coupling we find many oscillations before the grating disappears altogether.

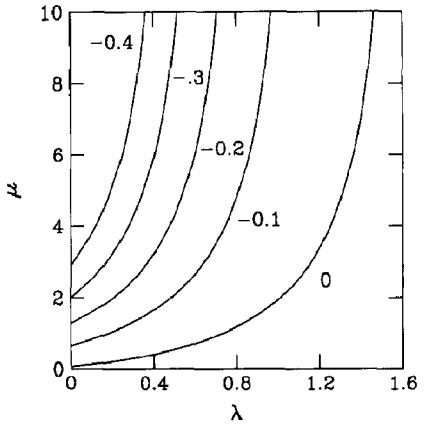

Fig. 4. Contour plot showing the minimum of $n(k, t)$ as a function of the exciton–phonon coupling λ and the exciton–exciton scattering rate μ in units $(k_BT/m)^{1/2}k$. For an average exciton velocity $v=(k_BT/m)^{1/2}$ this figure suggests that the grating recurrence can be observed whenever $\lambda<vk$ and $\mu>vk$.

citon–phonon interaction rate $\lambda<vk\approx10^{10}$ s^{-1}. A reasonable estimate for the exciton–exciton scattering rate is $\mu=nv\sigma$, where n is the exciton density and σ is the scattering cross section. This cross section will be of the order of the surface of a molecule, as an order of magnitude estimate we take $\sigma=0.1$ nm^2. The criterion $\mu>vk$ then becomes $n>5\times10^{19}$ cm^{-3}. This is achievable. A possible complication is that at these densities exciton–exciton annihilation [11] may become important in three-dimensional materials, and seems to rule out exciton-sound waves in two-dimensional structures [12]. In conclusion: observing coherent oscillations in the grating signal is in principle feasible.

The most uncertain quantity in all these estimates is the exciton thermal velocity. We are not aware of direct measurements of this quantity. However, according to Ikehara and Itoh [13] the momentum relaxation rate for transverse excitons in CuCl is of the order of 10^9 s^{-1}, and these excitons propagate over a distance of more that 20 μm. This supports the conclusion that recurrence of the grating can be realized in organic or semiconductor exciton systems.

An intriguing question is whether the transient grating provides a clean signature of a possible exciton Bose condensation, which is believed to exist under appropriate circumstances [4,5]. The formalism set up in this article is well suited for a phe-

nomenological treatment of this problem. In the theory of liquid helium neutron scattering it is found that second sound [14] – a clear signature of Bose condensation – contributes very little as there is a prefactor of (c_p/c_V-1) multiplying its contribution, which is very close to zero. We do not have information about the ratio of specific heats c_p/c_V for a Bose-condensed exciton fluid, however for an ideal Bose gas $c_p=c_V$, so observing second sound may be very difficult. However exciton–phonon couplings may make second sound visible again. Further research is needed on this interesting point.

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