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Breakdown of Fermi's Golden Rule in Exciton-Photon Interaction

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According to Fermi's golden rule, the radiative decay rate of excitons in a thin film becomes higher with increasing film thickness because of the increment of the interaction volume between excitons and photons. However, for a thick film, the decay rate is inversely proportional to the film thickness, because the excitons behave as polaritons and the decay time is proportional to the time of flight. This contradiction reflects a breakdown of Fermi's golden rule in the exciton-photon interaction. We have revealed the breakdown condition by a rigorous calculation method that connects the two radiative decay schemes.

KEYWORDS: Fermi's golden rule, exciton-photon interaction, radiative decay, exciton superradiance, polariton, group velocity

According to Fermi's golden rule, the transition rate from one state to another is proportional to the coupling strength. However, this scenario is broken if coupling is relatively strong. In the case of the radiative decay process of excitons in a confined system, the decay rate increases together with the crystal size because of the increment of the interaction volume.[1–4] This is called exciton superradiance, and is usually limited by the coherence volume of excitons governed by dephasing processes. However, there should be a fundamental limitation owing to the breakdown of Fermi's golden rule, because the radiative decay rate should vanish in an infinite system. Actually, for a thick film, where the exciton-polariton picture is applicable, the decay rate should be inversely proportional to the thickness, in contrast to the exciton superradiance, because the decay time should be proportional to the time of flight (thickness divided by group velocity). This crossover from the exciton superradiance to the polariton scheme explicitly reflects the breakdown of Fermi's golden rule in the exciton-photon interaction. This means that, in the polariton scheme, a photon created by electron-hole recombination is reabsorbed in a film with sufficiently large thickness, and the exciton and photon behave as a polariton. On the other hand, in the superradiance scheme, the photon can go outside of the film without reabsorption because of the small film thickness, and then the radiative decay obeys Fermi's golden rule. Although this crossover has been theoretically discussed in the pioneering work by Knoester[5] and also in other works,[6–8] there remains the fundamental task of elucidating the exact crossover condition in order to achieve comprehensive understanding in the entire size region, particularly at a large thickness greater

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than the light wavelength, where the long wavelength approximation is invalid and the spatial structures of the exciton center-of-mass motion and radiation field must be strictly considered.

From the experimental side, a short decay time of about 100 fs has recently been observed in the degenerate four-wave mixing in a CuCl film with a thickness of 187 nm,[9] where there are few impurities and defects and the exciton center-of-mass motion has good coherence throughout the whole sample. Interestingly, this decay process is significantly faster than the usual dephasing process of CuCl excitons.[10,11] This means that the size enhancement of the radiative decay rate is not limited by the dephasing processes. Therefore, nowadays, the exciton superradiance approaching the crossover is no longer just a conceptual effect, but has become an experimental reality. For future experiments, investigating the crossover problem is definitely important. The purpose of this letter is to present the crossover condition elucidated by means of a rigorous calculation method and an intuitive analysis of polariton modes in finite-sized crystals.

We adopt a material in which the translational symmetry is broken in the z direction, and discuss the radiative decay of s-polarized excitons whose center-of-mass is confined in a finite region. We consider a background system with the dielectric function $\varepsilon_{\rm bg}(z,\omega)$, and a resonant contribution from excitons inducing a current density $J(z,\omega)$. The Maxwell wave equation for the vector potential $A(z,\omega)$ is represented as

$$\left[(\partial^2/\partial z^2) + q^2(z,\omega)\right] A(z,\omega) = -\mu_0 J(z,\omega), \tag{1}$$

where $q^2(z,\omega) = \varepsilon_{\rm bg}(z,\omega)\omega^2/c^2 - {k_\parallel}^2$, and $k_\parallel$ is the in-plane wave number. We can rewrite this equation as

$$A(z,\omega) = A_0(z,\omega) - \mu_0 \int {\rm d}z\ G(z,z',\omega)\ J(z',\omega), \tag{2}$$

where $A_0(z,\omega)$ is the homogeneous solution of eq. (1), and $G(z,z',\omega)$ is the Green function satisfying

$$\left[(\partial^2/\partial z^2) + q^2(z,\omega)\right] G(z,z',\omega) = \delta(z-z'). \tag{3}$$

On the other hand, from the exciton-photon interaction

$$\hat{H}_{\rm int} = -\int {\rm d}z\ \hat{A}(z)\ J(z), \tag{4}$$

the expectation value $A = \langle \hat{A} \rangle$ of the vector potential is given in the same form as eq. (2) according to the linear response theory. Therefore, the retarded correlation function of $\hat{A}$ in the background system corresponds to the Green function satisfying eq. (3), as discussed in ref. 12:

$$\mu_0 G(z,z',\omega) = \frac{1}{{\rm i}\hbar} \int_0^\infty {\rm d}t\ \exp({\rm i}\omega t)\, \langle [\hat{A}(z,t), \hat{A}(z',0)] \rangle\ . \tag{5}$$

Furthermore, it is also identical to the time-ordered correlation function of $\hat{A}$ under the ro-

tating wave approximation (RWA), which can be considered as a good approximation in our calculation, because both the frequency shift and the radiative decay rate reach only $3 \sim 4$ % of the bare exciton frequency even at maximum. Therefore, the correlation function of $\hat{A}$ in the background system can be obtained by finding the Green function satisfying eq. (3), which is already known for general multilayer systems.[13)]

Next, we discuss the time-ordered correlation functions of excitons. For simplicity, we consider only one relative exciton motion with eigenfrequency $\omega_{\rm T}$, and denote the center-of-mass motion by index m. The excitonic current density is quantized as $\hat{J}(z) = \mathcal{J} \sum_m g_m(z)\ \hat{b}_m +$ H.c., where $\hat{b}_m$ is the annihilation operator of an exciton in state m, and $g_m(z)$ is its center-of-mass wavefunction. The absolute value of the coefficient $\mathcal{J}$ can be estimated by the longitudinal-transverse (LT) splitting energy as $\hbar\omega_{\rm LT} = |\mathcal{J}|^2/\varepsilon_{\rm bg}\varepsilon_0{\omega_{\rm T}}^2$. From the interaction Hamiltonian (4), we obtain the self-energy tensor of excitons as

$$\Sigma_{m,m'}(\omega) = \varepsilon_{\rm bg}\omega_{\rm LT}(\omega_{\rm T}/c)^2 \times \int_{-\infty}^{\infty} {\rm d}z{\rm d}z'\ g_m^*(z)\ G(z,z',\omega)\ g_{m'}(z'), \tag{6}$$

and the time-ordered correlation function tensor of excitons is derived as the inverse of the matrix whose elements are given as $(\omega - \Omega_m)\delta_{m,m'} - \Sigma_{m,m'}(\omega)$, where Ω_m is the bare exciton frequency including the center-of-mass kinetic energy of state m. The resonance frequency $\omega_{\rm res}$ and the radiative decay rate γ of exciton-photon coupled modes are, respectively, obtained from the real and imaginary parts of poles $\{\omega_{\rm res} - {\rm i}\gamma\}$ of the exciton correlation function tensor.

Compared with a previous work by Björk et al.,[6)] our calculation method correctly provides the crossover thickness of the two radiative decay schemes, because, through eq. (6), we consider the retarded interaction between different exciton states, which is essential for the strong exciton-photon coupling at the crossover thickness. Although this interaction was also considered in refs. 7 and 8, the crossover condition has not been completely clarified.

In the calculation, we assume a CuCl film with thickness d, and the background dielectric constant $\varepsilon_{\rm bg} = {n_{\rm bg}}^2 = 5.59$ both inside and outside of the film. The wavefunctions of the exciton center-of-mass motion are sinusoidal functions whose amplitudes are zero at the interfaces: $g_m(z) = \sqrt{2/d}\sin(k_m z)$, $k_m = m\pi/d$, $m = 1, 2, \ldots$ and $k_\parallel = 0$. The exciton translational mass is $m_{\rm ex} = 2.3m_0$, where m_0 is the free electron mass. The bare exciton frequencies are given as $\hbar\omega_{\rm T} = 3.2022$ eV and $\Omega_m = \omega_{\rm T} + \hbar{k_m}^2/2m_{\rm ex}$. The LT splitting energy is $\hbar\omega_{\rm LT} = 5.7$ meV.

Figure 1 shows a thickness dependence of the radiative decay rate γ in a CuCl film. The decay rate of the lowest mode increases with the thickness until about 80 nm, half the light wavelength with frequency $\omega_{\rm T}$ in CuCl, but subsequently, it reversely decreases, as discussed in previous works.[5,7,14)] This is because the exciton-photon coupling is maximized under phase matching where the exciton and radiation fields have the same spatial structure. In this

manner, the decay rate of the higher center-of-mass motion state is maximized at each phase-matching thickness satisfying $k_m \simeq n_{\rm bg}\omega_{\rm T}/c$, and the maximum value gradually increases owing to the exciton superradiance,[6,8,15] as seen in Fig. 1. However, although no dephasing processes are considered in the calculation, we find that the exciton superradiance is broken at thicknesses over about 2 μm. Furthermore, the behavior becomes discontinuous at the peak, and the peak value cannot be found by this numerical calculation.

For the analysis of this breakdown condition, we calculate the exciton-photon coupled modes by another method. First, we consider that the complex frequency $\omega_{\rm res} - {\rm i}\gamma$ satisfies the dispersion relation (under RWA)

$$\frac{c^2\tilde{k}^2}{(\omega_{\rm res} - {\rm i}\gamma)^2} = \varepsilon_{\rm bg} + \frac{\varepsilon_{\rm bg}\omega_{\rm LT}}{\omega_{\rm T} - (\omega_{\rm res} - {\rm i}\gamma)} \tag{7}$$

with a complex wave number $\tilde{k}$. Here, for simplicity, we do not consider the exciton center-of-mass kinetic energy. Next, we consider that $\omega_{\rm res} - {\rm i}\gamma$ and $\tilde{k}$ also satisfy the self-sustaining condition

$$r^2 \exp({\rm i}2\tilde{k}d) = 1, \tag{8}$$

where $r = (\tilde{k}-\tilde{k}_{\rm out})/(\tilde{k}+\tilde{k}_{\rm out})$ is the reflection coefficient at the interfaces and $\tilde{k}_{\rm out} = n_{\rm bg}(\omega_{\rm res} - {\rm i}\gamma)/c$ is the complex wave number outside of the film. Equation (8) means that there is neither amplitude decay nor phase shift even after a round trip inside the film. By simultaneously solving eqs. (7) and (8), we obtain infinite sets of $\{\omega_{\rm res} - {\rm i}\gamma, \tilde{k}\}$. For large thicknesses over about 1 μm, we verify that half of the sets have almost the same values of $\{\omega_{\rm res} - {\rm i}\gamma\}$ as calculated by the correlation function method, and the other half represents the photon-like coupled modes, which cannot be numerically calculated as poles of the exciton correlation function. On the other hand, in order to obtain exactly the same values for small thickness, we must consider Pekar's additional boundary condition (ABC)[16] under the self-sustaining condition (8), because we assume exciton center-of-mass wavefunctions with amplitudes of zero at the interfaces. However, the exciton center-of-mass motion is not essential for the breakdown condition, because the breakdown occurs at a relatively large thickness. Furthermore, the qualitative behavior is not modified even for small thickness where the ABC is required.

Figure 2 shows the dispersion relation and frequency dependence of γ at film thicknesses of 1.6, 2, and 3 μm. The poles of the exciton correlation functions are plotted with symbols, and the solutions of eqs. (7) and (8) for given real k are plotted with lines. Here, in the latter calculation, we do not consider the k-selection rule of the self-sustaining condition to show the continuous k-dependence. At the thickness of 1.6 μm, where the exciton superradiance is maintained, eqs. (7) and (8) have two solutions: one has an exciton-like frequency with small γ, and the other has a photon-like frequency with large γ. Because of the relatively weak exciton-photon coupling, these exciton- and photon-like modes are slightly modified from the bare

exciton and photon states, respectively. The exciton superradiance is obtained for exciton-like modes under the phase-matching condition $k = n_{\rm bg}\omega_{\rm T}/c$. However, with increasing thickness, γ values of the two modes become close to each other, and $\omega_{\rm res}$ values split to upper and lower branches, as seen at the thickness of 3 μm, because of the strong exciton-photon coupling. After that, γ of both branches decreases inversely proportional to the thickness, as first pointed out by Knoester.[5] This is the suppression mechanism of the exciton superradiance discussed by Björk et al.[6] and also by Agranovich et al.[7] While this crossover from exciton-/photon-like to polariton modes just reflects the breakdown of Fermi's golden rule in the exciton-photon interaction, there remains the task of elucidating the breakdown condition.

To analyze the breakdown condition, we consider the effective thickness of the exciton-photon coupled mode as the inverse of the wave number uncertainty:

$$d_{\rm eff} \equiv -({\rm Im}[\tilde{k}])^{-1} = (\ln|r|^2/2)^{-1}d. \tag{9}$$

This expression is obtained from eq. (8), and it provides $\gamma = v_{\rm g}/d_{\rm eff}$ in the polariton scheme, where $v_{\rm g}$ is the group velocity of polaritons. This relation was first indicated by Agranovich et al.,[7] and also verified with eq. (7) in our calculation. However, it is not applicable in general, particularly in the superradiance scheme, where the concept of polariton propagation is not suitable. In Fig. 3, we plot the frequency dependence of an apparent propagation speed $\gamma d_{\rm eff}$ (effective thickness divided by radiative decay time) with continuously changing thickness. The solid lines are the calculated poles of the exciton correlation function, and $d_{\rm eff} = -({\rm Im}[\tilde{k}])^{-1}$ is obtained from eq. (7) for each $\omega_{\rm res} - {\rm i}\gamma$. On the other hand, the dotted lines are calculated by simultaneously solving eqs. (7) and (8). A slight deviation between solid and dotted lines is caused by the exciton center-of-mass kinetic energy. The dashed lines represent $v_{\rm g}$ of polaritons.

As seen in Fig. 3(b), $\gamma d_{\rm eff}$ agrees with $v_{\rm g}$ of polaritons except in the superradiance situation ($\omega_{\rm res} \simeq \omega_{\rm T}$). On the other hand, under the phase-matching condition $k = n_{\rm bg}\omega_{\rm T}/c$, the real part of eq. (7) can be approximated as

$$\gamma^2 - (c/n_{\rm bg}){d_{\rm eff}}^{-1}\gamma + \omega_{\rm T}\omega_{\rm LT}/2 = 0. \tag{10}$$

When the film is sufficiently thinner than the breakdown thickness, we obtain the two solutions of this equation: $\gamma = (n_{\rm bg}\omega_{\rm T}\omega_{\rm LT}/2c)d_{\rm eff}$ for the exciton-like (superradiant) mode and $\gamma = (c/n_{\rm bg})/d_{\rm eff}$ for the photon-like mode. The propagation speed of the latter is equal to the speed of light $c/n_{\rm bg}$ in the background medium, as seen in Fig. 3(a), because of the weak exciton-photon coupling. On the other hand, $\gamma d_{\rm eff}$ of the superradiant mode grows with increasing thickness, and as seen in Fig. 3(a), the crossover from exciton-/photon-like to polariton modes occurs when $\gamma d_{\rm eff}$ reaches $c/2n_{\rm bg}$, which is the group velocity of polaritons under the phase-matching condition $k = n_{\rm bg}\omega_{\rm T}/c$. This breakdown condition $\gamma d_{\rm eff} = c/2n_{\rm bg}$ is obtained as the degenerate solution of eq. (10), and it means that the exciton and photon behave as a polariton

when the apparent propagation speed $\gamma d_{\rm eff}$ reaches the group velocity $v_{\rm g}$ of polaritons. In other words, the superradiant excitons do not appear to propagate beyond the group velocity of polaritons. After the breakdown, $\omega_{\rm res}$ splits into upper and lower branches, and gradually saturate to bulk polariton frequency satisfying $\gamma d_{\rm eff} = v_{\rm g}$.

It is worth noting that the breakdown condition may be applied to the general situation, because it is simply derived from dispersion relation (7), which includes no information outside of the excitonic medium. Actually, we also verified the breakdown condition in another situation: CuCl film in vacuum. Figure 4 shows the thickness dependence of $\gamma d_{\rm eff}$. As a result of multiple reflection inside the film, the size enhancement of γ becomes more rapid and the crossover thickness becomes smaller compared with that in Fig. 1. However, we find that the breakdown also occurs when $\gamma d_{\rm eff}$ reaches $c/2n_{\rm bg}$.

We calculate the resonance frequency and radiative decay rate of exciton-photon coupled modes in a film with finite thickness. The calculation is based on the exciton correlation function tensor renormalizing the exciton-photon interaction. We demonstrate that the exciton superradiance (Fermi's golden rule) is broken at thicknesses exceeding a particular length. To analyze the breakdown condition, we use another calculation method based on the dispersion relation and the self-sustaining condition. Although this method reproduces the strict values only for large thickness, it can provide the photon-like modes, which cannot be calculated by the correlation function method. From the dispersion relation consisting of a complex frequency and wave number, we derive the breakdown condition as $\gamma d_{\rm eff} = c/2n_{\rm bg}$, which may be a general condition for the breakdown of Fermi's golden rule in the exciton-photon interaction.

Acknowledgments

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Fig. 1. Thickness dependence of radiative decay rates of exciton-photon coupled modes in CuCl film.

Fig. 2. (a) Dispersion relation and (b) frequency dependence of γ. The lines are solutions of eqs. (7) and (8) without considering the k-selection rule. The symbols are plots of values calculated by the exciton correlation function method.

Fig. 3. (Color online) Frequency dependence of apparent propagation speed $\gamma d_{\rm eff}$ (a) in linear scale and (b) in log scale. The red solid lines are calculated by the correlation function method, and the blue dotted lines are calculated by simultaneously solving eqs. (7) and (8). The green dashed lines represent $v_{\rm g}$ of polaritons.

Fig. 4. Thickness dependence of apparent propagation speed $\gamma d_{\rm eff}$ for a CuCl film in vacuum.

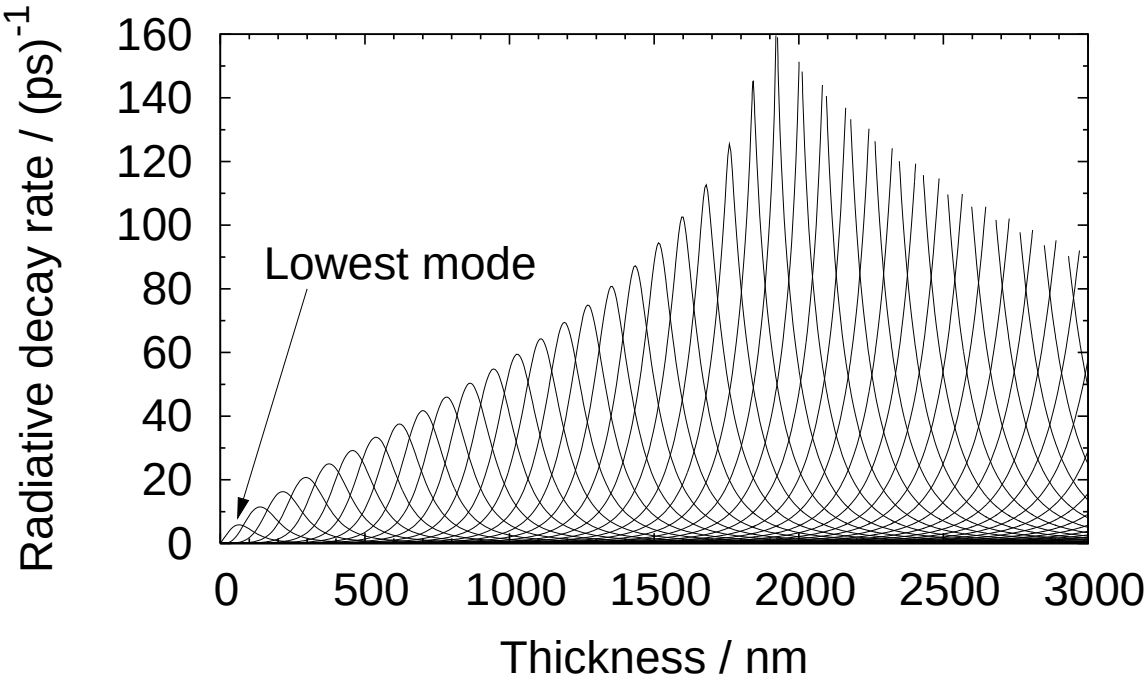
Radiative decay rate / (ps)-1
160
140
120
100
80
60
40
20
0
Lowest mode
0
500
1000
1500
2000
2500
3000
Thickness / nm

Fig. 1.

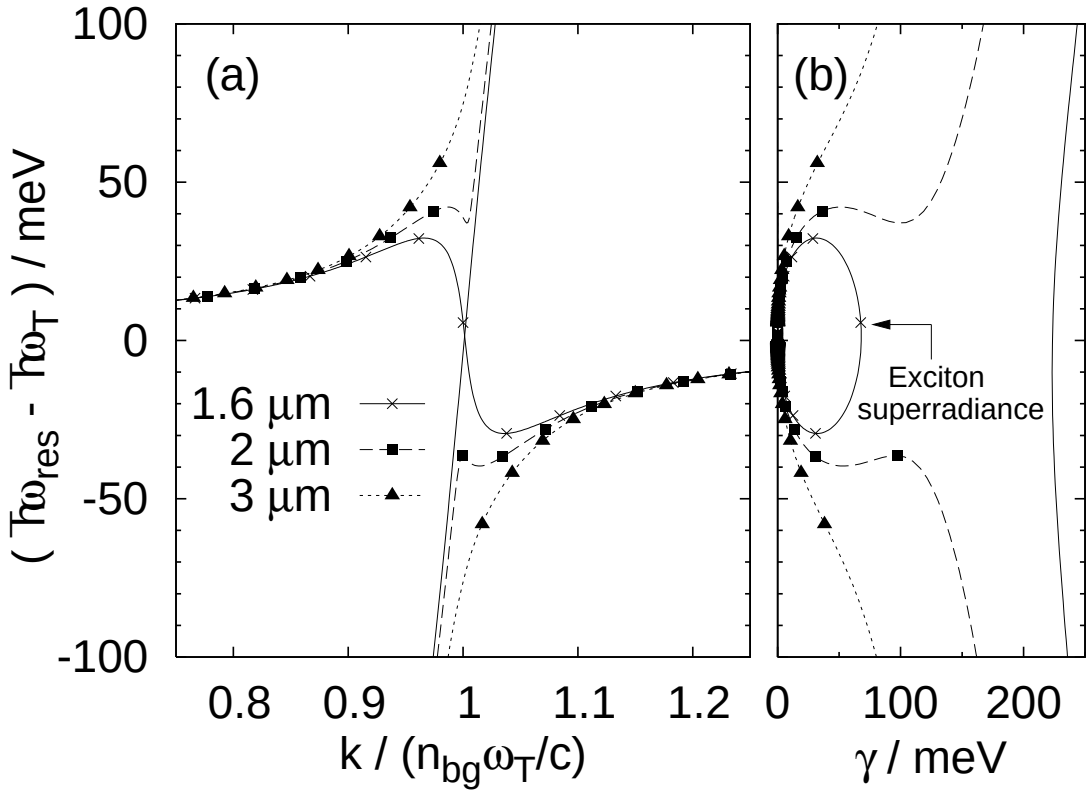
(a)
(b)
100
50
0
-50
-100
(ħω_res - ħω_T) / meV
1.6 μm
2 μm
3 μm
Exciton
superradiance
0.8
0.9
1
1.1
1.2
0
100
200
k / (n_bg ω_T/c)
γ / meV

Fig. 2.

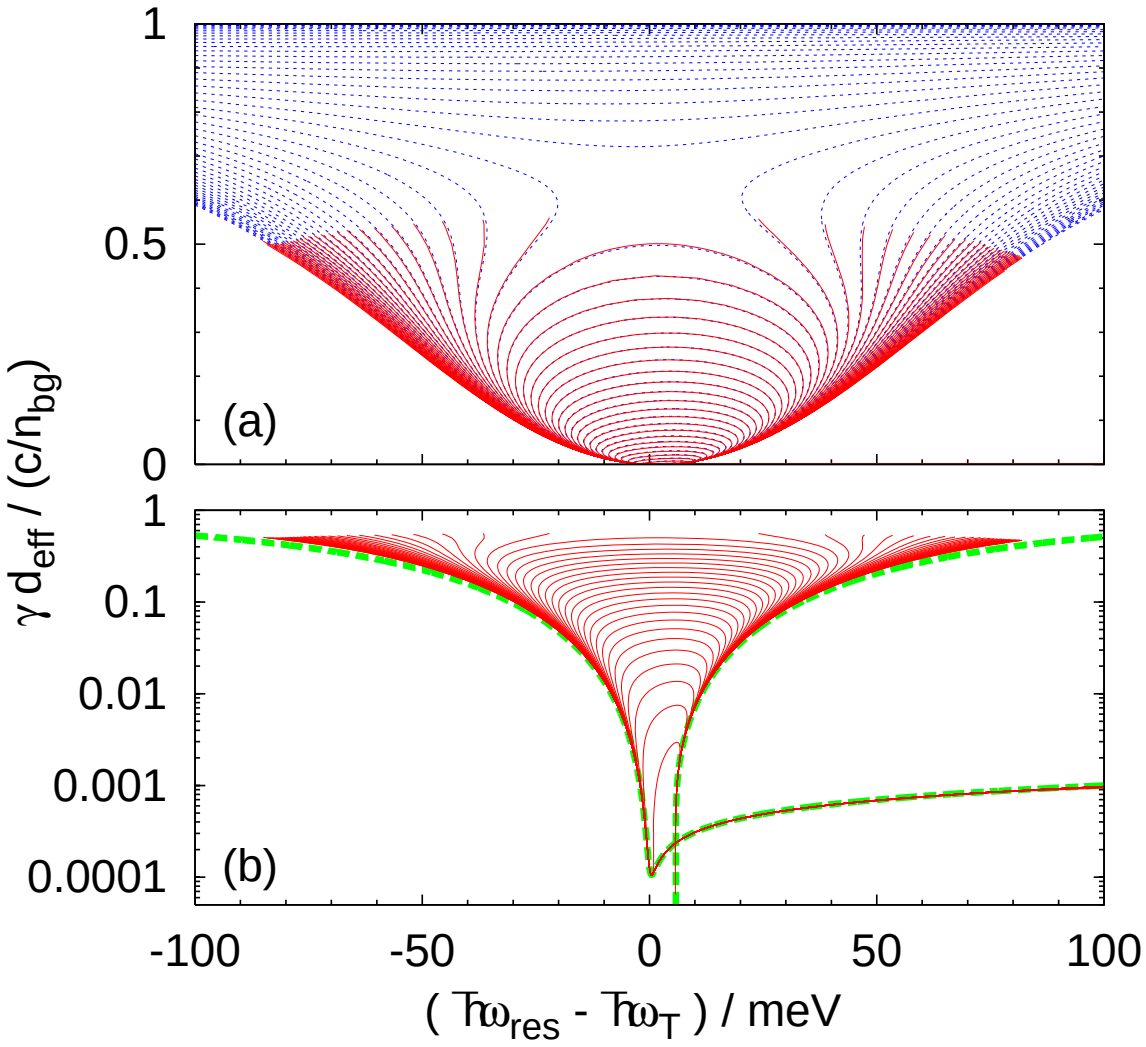
1
0.5
0
(a)
1
0.1
0.01
0.001
0.0001
(b)
γ d_eff / (c/n_bg)
-100
-50
0
50
100
(ħω_res - ħω_T) / meV

Fig. 3.

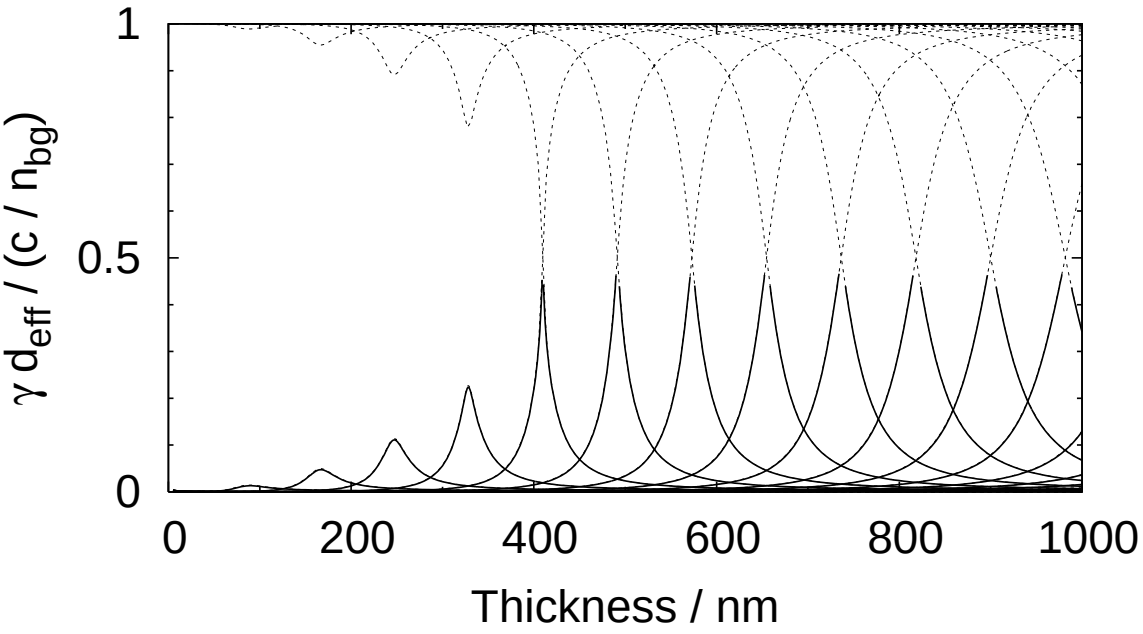

Fig. 4.