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Relaxation of the free energy landscape and temperature modulation spectroscopy

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ABSTRACT

The free energy landscape (FEL) depends on temperature by its definition and the FEL is reorganized with time delay when the temperature is modulated. We investigate how the relaxation of the FEL manifests itself in physical properties. Exploiting a simple two-level model for the dielectric relaxation, we first show that the relaxation of the FEL produces time dependence of the relaxation time of the dielectric response. Then we discuss the relaxation of dielectric susceptibility when the temperature is suddenly increased/decreased and show that the susceptibility relaxes to the equilibrium value with the same relaxation time as the FEL in the long time limit. In order to show the general feature of the temperature modulation spectroscopy, we consider the dynamics of an order parameter of the Landau model which has a delayed response to the temperature modulation with relaxation time. When the temperature is modulated sinusoidally, we show that there appear second order responses at the sum and the difference of the frequencies of the external field and the temperature modulation and that the relaxation time of the FEL can be deduced from these two responses.

1. Introduction

The free energy landscape (FEL) approach is robust in explaining various physical properties of non-equilibrium systems such as the cooling rate dependence of the entropy and specific heat and the time–temperature-transformation diagram of the crystallization time of super-cooled liquids. The FEL theory is a generalization of the Landau theory of phase transition to non-equilibrium systems which show a clear distinction between slow and fast dynamics, where atomic configurations play the role of the order parameters in the Landau theory. The FEL theory can explain various properties of super-cooled liquids and singularities related to glass transition in a unified framework [1,2].

The important feature of the FEL is in the fact that it depends on temperature, which is a clear contrast to the potential energy landscape introduced by Goldstein [3]. Therefore, the FEL responds to temperature modulations and the response must manifest itself in physical properties of the system described by the FEL. There have been several works which observed response of systems to temperature modulation. Hecksher et al. [4] reported the relaxation of dielectric susceptibility when the temperature was increased/decreased suddenly. Harada et al. [5] investigated the dielectric response when the temperature is modulated sinusoidally, and argued that the experimental results can be explained by introducing a time dependence of the α-relaxation time. In fact, we have shown that a delay in the response of the FEL to a sinusoidal temperature modulation produces the dielectric susceptibility showing significant dependence on the relaxation time of the FEL under the crossover temperature [2].

In this paper, we first discuss in Section 2 the dielectric relaxation when a step temperature modulation is applied. We exploit a simple two level model for the dielectric relaxation and show that the delayed response of the FEL gives rise to the time-dependent relaxation time. In Section 3, we investigate the dynamics of an order parameter which is governed by the Landau free energy with a dissipation term, and show that (1) a relaxation time shows time dependence when the temperature is changed suddenly, and (2) there appear second order responses at the sum and the difference of the frequencies of the external field and the temperature modulation when the temperature is modulated sinusoidally, and that the relaxation time of the FEL can be deduced from these two responses. Section 4 is devoted to conclusion.

2. Dielectric relaxation under a temperature jump

2.1. Dielectric relaxation

As a model system, we consider a set of dipoles each of which takes independently one of two opposite directions denoted by $\sigma = 1$ and $\sigma = -1$ in the external electric field $E(t)$. We denote by $p(\sigma, t)$ the probability that a dipole is in state σ at time t. Then, the polarization $P(t)$ is given by $P(t) = \mu[p(+1, t) - p(-1, t)]$, where μ is the electric

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dipole moment of a dipole. We assume that probability $p(\sigma,t)$ obeys a master equation

$$\frac{\partial p(\sigma,t)}{\partial t} = w_{-\sigma,\sigma}p(-\sigma,t) - w_{\sigma,-\sigma}p(\sigma,t) \tag{1}$$

where $w_{\sigma,\sigma'}$ is the transition rate of the dipole from state σ to σ′. We assume that a barrier exists between two states and employ.

$$w_{\mp\sigma,\pm\sigma} = w_0 \exp\left[-\frac{\Delta U \pm \sigma\mu E(t)}{k_B T}\right] \tag{2}$$

where ΔU is the barrier height between two states, $w_0$is the attempt frequency which serves as the scale of $(\text{time})^{-1}$, and k_B is the Boltzmann constant and T is the temperature. Note that the transition rate satisfies the detailed balance so that the probability distribution approaches the equilibrium value after infinitely long time. It is easy to show that the polarization obeys

$$\frac{\partial P(t)}{\partial t} = 2W\left[\mu\,\sinh\left(\frac{\mu E}{k_B T}\right) - \cosh\left(\frac{\mu E}{k_B T}\right)\mathrm{P(t)}\right] \tag{3}$$

where $W = w_0 \exp\left[-\frac{\Delta U}{k_B T}\right]$ [6]. Assuming the weak external electric field, we solve this equation by perturbation method in which the polarization is expanded as

$$P(t) = P_0(t) + P_1(t) + \cdots \tag{4}$$

It is straightforward to show that the leading two terms obey the following equations:

$$\frac{\partial P_0(t)}{\partial t} = -2WP_0(t) \tag{5a}$$

$$\frac{\partial P_1(t)}{\partial t} = -2W\left[P_1(t) - \frac{\mu^2 E(t)}{k_B T}\right] \tag{5b}$$

Now, in order to include effects of the delay in response of the FEL to temperature modulations, we assume that W depends on time. One may assume that either the barrier height ΔU or the temperature T shows a delayed response [7]. In order to make mathematical analysis simple, we assume here, without loss of the essential features, that parameter W has a simple time dependence.

$$W \equiv W(t) = w_0 \exp\{-[A_1 + (A_0 - A_1)e^{-t/\tau_F}\ ]\} \tag{6}$$

when the temperature of the heat bath is changed at time $t = 0$. Namely, the parameter W changes from e^{-A_0} at $t = 0$ to e^{-A_1} at $t = \infty$ due to the change in the temperature of the heat bath, and τ_F may be regarded as the relaxation time of the FEL.

2.2. Time dependence of the relaxation time

It is straightforward to solve Eq. (5a). We find that

$$P_0(t) = P_0(0)\exp\left[-2\int_0^t W(t')dt'\right] \tag{7}$$

and, therefore, the dielectric relaxation is given by

$$P_0(t) = P_0(0)e^{\varphi(t)} \tag{8}$$

with

$$\varphi(\mathrm{t}) = \exp[-2w_0\tau_F e^{-A_1}\{E_i(-\alpha) - E_i(-\beta)\}] \tag{9}$$

where $\alpha = (A_0 - A_1)e^{-t/\tau_F}$ and $\beta = A_0 - A_1$ and $\mathrm{E}_i(-x) = -\int_x^\infty \frac{e^{-t}}{t}dt$ is the integrated exponential function. Note that Eq. (9) satisfies the correct limits $\varphi(\mathrm{t}{\sim}0) = -2w_0e^{-A_0}t$ and $\varphi(t{\sim}\infty) = -2w_0e^{-A_1}t$. Eq. (8) indicates that the relaxation time of the polarization depends on time. In fact, we can define the relaxation time τ_P by $\tau_P = -[d\ln P_0(t)/dt]^{-1}$, and thus τ_P is given by

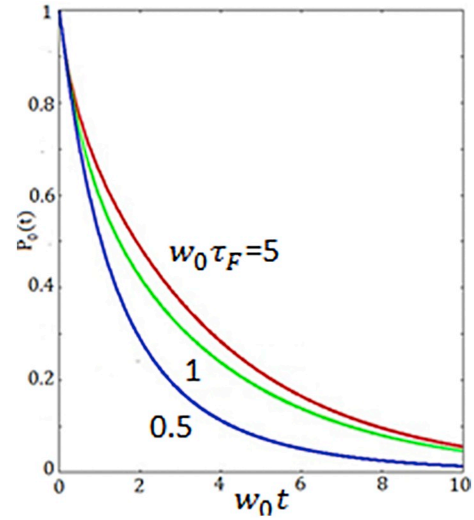

Fig. 1. The relaxation of the polarization for $w_0\tau_F = 5,\ 1,\ 0.5$, when $A_0 = 1$, $A_1 = 2$.

$$\tau_P = \frac{1}{2W(t)} \tag{10}$$

Fig. 1 shows the relaxation of the polarization for three different values of the relaxation time of the FEL. We show in Fig. 2 the time dependence of the relaxation time of the polarization.

In conclusion, the time-dependent relaxation time [5] may be accounted by the delayed response of the FEL to the temperature jump.

2.3. Relaxation of the susceptibility

When a sinusoidal external electric field $E(t) = E_0\cos\omega t = \mathrm{Re}\,E_0e^{i\omega t}$ is applied, the response of the system is measured from the first order term $P_1(t)$ determined by Eq. (5b) within the linear response regime. It is straightforward to obtain

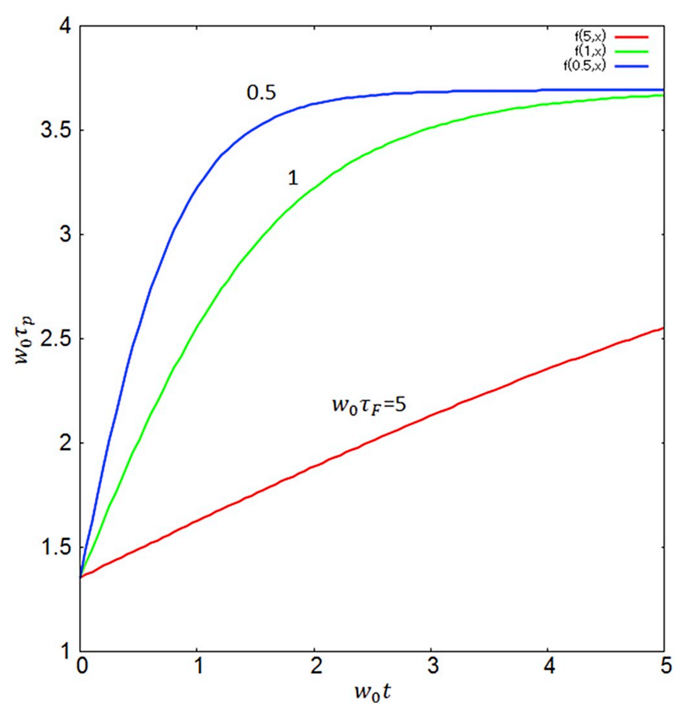

Fig. 2. The time dependence of the relaxation time for $w_0\tau_F = 5,\ 1,\ 0.5$, when $A_0 = 1$, $A_1 = 2$.

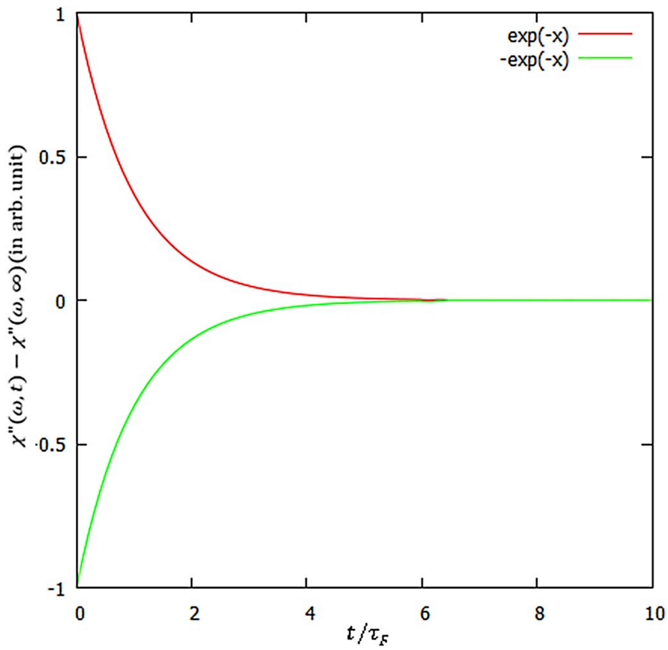

Fig. 3. The relaxation of the susceptibility at a given frequency. (a) $A_1 > A_0$ (b) $A_1 < A_0$.

$$P_1(t) - P_1(0) = \mathrm{Re}\chi(\omega, t) E_0 e^{i\omega t} \tag{11}$$

$$\chi(\omega, t) = \int_0^t \frac{2\mu^2}{k_B T} W(t') e^{-2\int_{t'}^t W(t'')dt''} e^{i\omega(t'-t)} dt' \tag{12}$$

The short time behavior is written as

$$\chi(\omega, t) \sim \frac{2\mu^2}{k_B T}\left[W(0)t + \frac{1}{2}\{W'(0) - \{i\omega + 2W(0)\}W(0)\}t^2\right] \tag{13}$$

with $W'(0) = w_0(A_0 - A_1)e^{-A_0}/\tau_F$, and in the long time limit, it is written as

$$\chi(\omega, t) - \chi(\omega,\infty) = \frac{\mu^2}{k_B T} 2i\omega \left(\frac{1}{2w_0 e^{-A_1} - \frac{1}{\tau_F} + i\omega} - \frac{1}{2w_0 e^{-A_1} + i\omega}\right)\psi(t) \tag{14}$$

with $\psi(t) = w_0 e^{-A_1}(A_1 - A_0)\tau_F e^{-t/\tau_F}$. Namely, the susceptibility relaxes to the equilibrium value with the same relaxation time as the FEL in the long time limit. Fig. 3 shows schematically the relaxation of the susceptibility at a given frequency.

3. Effect of temperature modulation in the Landau model

3.1. Basic formalism

We consider a system whose free energy $\Phi(M)$ is given by the Landau form

$$\Phi(M) = A(T)M^2 + BM^4 - MH \; (B > 0) \tag{15}$$

where M is the order parameter and H is an external field. We assume that the dynamics of the order parameter is described by the Lagrangian equation

$$\frac{d}{dt}\frac{\partial \mathscr{L}}{\partial \dot{M}} - \frac{\partial \mathscr{L}}{\partial M} + \frac{\partial \mathscr{F}}{\partial \dot{M}} = 0 \tag{16}$$

where the Lagrangian $\mathscr{L}$ is defined by

$$\mathscr{L}(M, \dot{M}, t) = \frac{\mu}{2}\dot{M}^2 - \Phi(M) \tag{17}$$

and the dissipation term $\mathscr{F}(\dot{M})$ is given by

$$\mathscr{F}(\dot{M}) = \frac{k}{2}\dot{M}^2 \tag{18}$$

In order to investigate the delay in response of the free energy to temperature modulations, we assume $A(T) > 0$ and consider a massless case $\mu = 0$, i.e.

$$k\frac{dM}{dt} = -2A(T)M - 4BM^3 + H \tag{19}$$

3.2. Effect of a discontinuous change in temperature

We introduce the following temperature jump at $t = 0$;

$$T(t) = \begin{cases} T_0 \; (t \le 0) \\ T_1 \; (t > 0) \end{cases} \tag{20}$$

and assume that parameter $A(t) \equiv A(T(t))$ relaxes from $A_0 \equiv A(T_0)$ to $A_1 \equiv A(T_1)$ with delay as

$$A(t) = \begin{cases} A_0 \; (t \le 0) \\ A_1 + (A_0 - A_1)e^{-\frac{t}{\tau_F}} \; (t > 0) \end{cases} \tag{21}$$

We first consider the relaxation of the order parameter towards the equilibrium value M_{eq} when no external field exists. It is easy to show that $\delta M(t) \equiv M(t) - M_{eq}$ is given by

$$\delta M(t) = \delta M_0 \exp\left[-\frac{2}{k}\int_0^t A(t')dt'\right] \tag{22}$$

where we have assumed that $|\delta M(t)|$ is small. We can define the relaxation time τ_M of $\delta M(t)$ by

$$\tau_M = -\left[\frac{d \, \ln \delta M}{dt}\right]^{-1} \tag{23}$$

Fig. 4 shows the time dependence of the relaxation time τ_M. In the long time limit, τ_M approaches τ_F.

We next consider the susceptibility when an external field $H(t) = H_0 e^{i\omega_H t}$ is applied. The deviation of the order parameter $\delta M(t)$ obeys

$$k\frac{d\delta M}{dt} = -2A(t)\delta M + H_0 e^{i\omega_H t} \tag{24}$$

It is straightforward to find the solution to Eq. (24) in the form

$$\delta M(t) = \chi(\omega, t) H_0 e^{i\omega_H t} \tag{25}$$

where the time-dependent susceptibility $\chi(\omega, t)$ is given by

$$\chi(\omega, t) = \frac{1}{k}\int_0^t \exp\left[-\frac{2}{k}\int_{t'}^t A(t'')dt'' - i\omega_H(t - t')\right]dt' \tag{26}$$

For a fixed ω_H, the susceptibility decays to its equilibrium value in proportion to

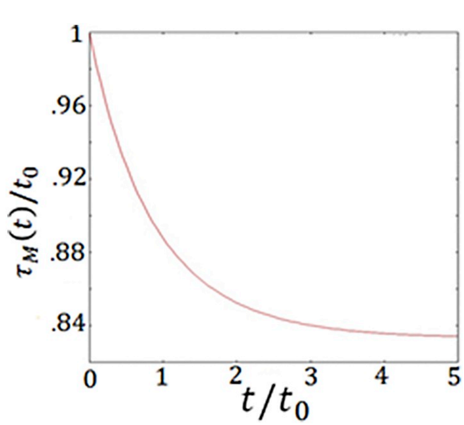

Fig. 4. The time dependence of the relaxation time. ($t_0 \equiv k/2A_0$).

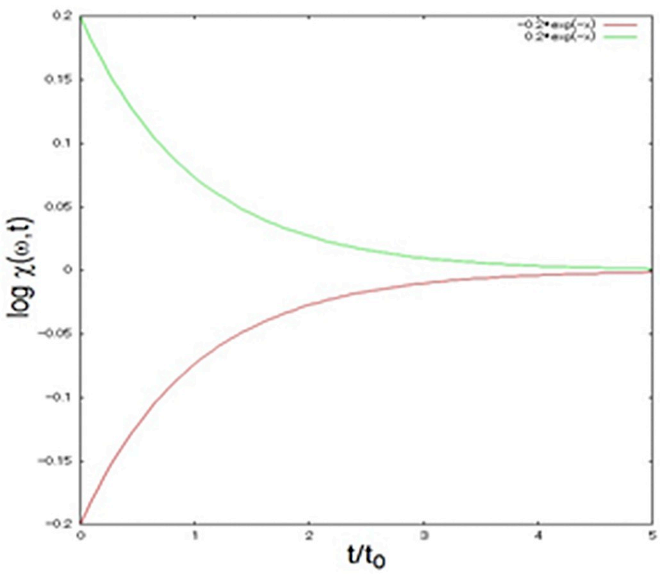

Fig. 5. The relaxation of the susceptibility. (a) $T_0 > T_1$ and (b) $T_0 < T_1$.

$$\chi(\omega, t) \propto \exp\left[\frac{2}{k}(A_0 - A_1)\tau_F e^{-\frac{t}{\tau_F}}\right] \tag{27}$$

We show in Fig. 5 the relaxation of the susceptibility for (a) $T_0 > T_1$ and (b) $T_0 < T_1$.

3.3. Effect of a sinusoidal temperature modulation

When the temperature of the heat bath is modulated sinusoidally as

$$T(\mathrm{t}) = T + \Delta T\cos(\omega_T t) \tag{28}$$

the delayed response of the free energy can be represented as the modulation of $A(t)$:

$$A(t) = \int_{-\infty}^{t} [A + \Delta A\cos(\omega_T t)]e^{-\frac{t-t'}{\tau_F}}dt' = A + \Delta A\frac{\cos(\omega_T t - \varphi)}{\sqrt{1+\tan^2\varphi}} \tag{29}$$

where $\tan\varphi \equiv \omega_T\tau_F$. We solve Eq. (24) with $A(t)$ given in Eq. (29) by the perturbation method expanding δM as

$$\delta M = \delta M_0 + \delta M_1 + \delta M_2 + \cdots \tag{30}$$

Through a straightforward calculation, we find the following solutions

$$\delta M_0(t) = \delta M_0(0)e^{-\left(\frac{2A}{k}\right)t} \tag{31}$$

$$\delta M_1(t) \sim \chi_1(\omega_H)H_0 e^{i\omega_H t} \tag{32}$$

with the linear susceptibility $\chi_1(\omega_H) = \frac{k}{2A + ik\omega_H}$, and

$$\delta M_2(t) \sim [\chi_{2+}(\omega_H, \omega_T)e^{i(\omega_H+\omega_T)t} + \chi_{2-}(\omega_H, \omega_T)e^{i(\omega_H-\omega_T)t}]\Delta A\bullet H_0 \tag{33}$$

where

$$\chi_{2\pm}(\omega_H, \omega_T) = k\chi_1(\omega_H)\bullet\chi_1(\omega_H \pm \omega_T)\frac{e^{\mp i\varphi}}{\sqrt{1+tan^2\varphi}} \tag{34}$$

Namely, the second order response appears at the sum and the difference of two frequencies. Fig. 6(a) and (b) show the ω_H dependence of the real and imaginary parts of $\chi_{2+}(\omega_H,\omega_T)$, respectively, for $\omega_T t_0 = 0.2$ and $\omega_T\tau_F = 0, 1, 10, 100$.

We find that the second order susceptibilities $\chi_{2\pm}(\omega_H,\omega_T)$ satisfy the following symmetry relations:

$$\chi'_{2+}(\omega_H, \omega_\mathrm{T}) = \chi'_{2-}(-\omega_H, \omega_T) \tag{35}$$

$$\chi''_{2+}(\omega_H, \omega_T) = -\chi''_{2-}(-\omega_H, \omega_T) \tag{36}$$

Since the second order susceptibilities depend on the relaxation time of the free energy, we can deduce the relaxation time by the following method. We first define $X_\pm(\omega_H,\omega_T)$ and its real and imaginary parts by

$$X_\pm(\omega_H, \omega_T) \equiv \frac{\chi_{2\pm}(\omega_H, \omega_T)}{\chi_1(\omega_H \pm \omega_T)} = X'_\pm + iX''_\pm \tag{37}$$

Then, we can show

$$\tan 2\varphi = \frac{X''_- X'_+ - X'_- X''_+}{X'_- X'_+ + X''_- X''_+} \tag{38}$$

from which we can obtain $\tan\varphi \equiv \omega_T\tau_F$.

4. Conclusion

We have reported various effects produced by the delayed response of the free energy landscape to temperature modulations. Sudden change of the temperature induces time dependence of the relaxation time and the linear susceptibility. In the simple models we studied here, the longtime behavior of these quantities is determined by the relaxation time of the free energy landscape. Therefore, experiments reported by Hecksher et al. [4] may be explained by the relaxation of the FEL

When the temperature is modulated sinusoidally, the second order response in the dielectric susceptibility appears at the sum and the difference of frequencies of the external field and the temperature as reported by Harada et al. [5] This behavior has been explained by the FEL framework for the dielectric response [2].

We also examined effects of the delayed response of the FEL for the order parameter described by the Landau model and have shown that similar effects to the dielectric response will appear in the relaxation time and the susceptibility. It is interesting to note that we can get much information on the free energy landscape from the temperature modulation spectroscopy, since the second order response can be measured without going to the long time limit.

The Landau model studied here is robust and can be applied to many phenomena. Therefore, the present analysis will open up a new horizon in the physics of non-equilibrium systems based on the free energy landscape theory.

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Interest statements

This paper treats an important issue how one can get information on the free energy landscape (FEL), the theory on which is believed to provide unified understanding for thermodynamic and dynamic properties of non-equilibrium systems, in particular of super-cooled liquids, glass formers and glass transition as described in the review paper by T. Odagaki "Non-equilibrium statistical mechanics based on the free energy landscape and its application to glassy systems" J. Phys. Soc. Jpn. 86, 082001 (2017).

The FEL depends on temperature by definition in contrast to the potential energy landscape which does not depend on temperature. Therefore, responses of the system against temperature modulations will directly give information on the FEL. This paper presents what one can expect from the temperature modulation theoretically for the first time.

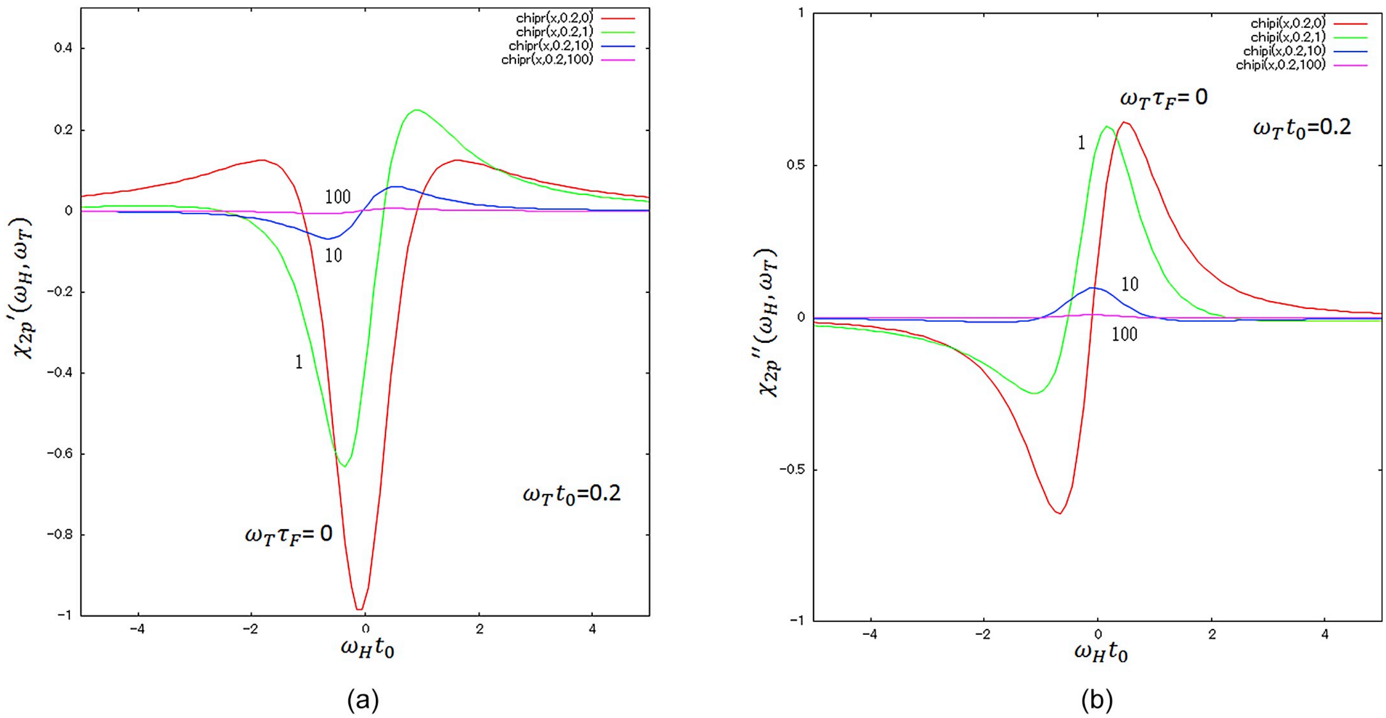

Fig. 6. The frequency (of the external field) dependence of the second order susceptibility for $\omega_T t_0 = 0.2$ and$\omega_T \tau_F = 0$, 1, 10, 100. The frequency dependence shows significant effects of τ_F. (a) The real part and (b) the imaginary part of $\chi_{2+}(\omega_H, \omega_T)$.

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