Response theory for nonresonant hole burning: Stochastic dynamics

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Response theory for nonresonant hole burning: Stochastic dynamics

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Abstract. – The time signals relevant for nonresonant spectral hole burning, a pump-wait-probe method designed to investigate slow relaxation, are calculated. The step-response function following the application of a high-amplitude ac field (pump) and an intermediate waiting period is shown to be the sum of the equilibrium-integrated response and a modification due to the preparation via ac irradiation. Both components are calculated for a class of stochastic dipole reorientation models. The results indicate that the method can be used for a clearcut distinction of homogeneously and heterogeneously broadened susceptibilities as they occur in the slow primary relaxation of supercooled liquids and other disordered materials. This is because only in the heterogeneous case is a frequency-selective modification of the response possible.

Disordered materials such as glasses, spin-glasses, disordered crystals and proteins exhibit nonexponential relaxation behavior on macroscopic time scales [1]. In the past decade several experimental techniques have been invented in order to investigate the detailed nature of the nonexponential primary response particularly of amorphous polymers and supercooled liquids [1–3]. These techniques allow to specifically select a (slow) sub-ensemble and afterwards monitor its relaxation. They have shown the existence of *dynamic* heterogeneities [4]. In accord with the definition given in ref. [5], a response or relaxation function is termed dynamic heterogeneous if it is possible to specifically address effectively slow, intermediate or fast contributions of the ensemble-averaged function. Otherwise, the relaxation will be termed homogeneous.

Recently, the technique of nonresonant spectral hole burning (NHB) has been developed and applied to study the primary relaxation of supercooled liquids on the time scale of seconds [6]. In the meantime, NHB has also been used to investigate the slow relaxation of disordered crystals [7], amorphous ion-conductors [8] and spin-glasses [9]. The interpretation of the results has mainly been guided by the fact that via the application of a large-amplitude ac field of frequency Ω (10^{-2} Hz–10^2 Hz) the sample absorbs energy of an amount proportional to the imaginary part of the susceptibility evaluated at the pump frequency Ω [10]. It was assumed that a frequency-selective modification of the spectrum should be feasible only if the

response is given by a heterogeneous superposition of entities relaxing at different rates. However, the results of a recent numerical investigation of the application of NHB to a solvable glass-model [11] suggest that this view may have to be revised. Beyond phenomenological interpretations a deeper understanding of a pump-wait-probe experiment like NHB can be expected from a thorough analytical analysis, which, however, has not been presented up to date.

It is the purpose of this letter to provide a sound response theory for NHB. The experimental protocol of NHB consists of the following procedure [6]. First, a large-amplitude ac pump field $E_\mathrm{P} \sin{(\Omega \tau)}$ is applied to a sample in thermal equilibrium for a time $t_\mathrm{p} = n(2\pi/\Omega), n = 1, 2, 3, \ldots$. After this pump period the system is left in zero field for a waiting time t_w before the step response is monitored via the application of a small-amplitude dc field E_S at time $t = 0$.

In contrast to ordinary nonlinear response theory, I calculate the linear response of a variable $S(t)$ to the static field E_S *but* with a disturbed initial state of the system prior to the application of E_S. This initial state is calculated in order $\mathcal{O}(E_\mathrm{P}^2)$. Correspondingly, the response reads as $R^*(E_\mathrm{S}, E_\mathrm{P}, t, t_\mathrm{w}, t_\mathrm{p}) = R(E_\mathrm{S}, t) + \Delta R(E_\mathrm{S}, E_\mathrm{P}, t, t_\mathrm{w}, t_\mathrm{p})$, where $R(E_\mathrm{S}, t)$ denotes the equilibrium integrated response. The "modification" $\Delta R(E_\mathrm{S}, E_\mathrm{P}, t, t_\mathrm{w}, t_\mathrm{p})$ originates from the deviations from thermal equilibrium at time $t = 0$ and consists of two terms of order $\mathcal{O}(E_\mathrm{P})$ and $\mathcal{O}(E_\mathrm{P}^2)$, respectively. A subtraction of the signals following the application of a positive and a negative dc field E_S along with the addition of the signals obtained for a positive and a negative pump allow to extract the relevant terms in $\mathcal{O}(E_\mathrm{S}), \mathcal{O}(E_\mathrm{P}^2)$. This corresponds to the phase cycle employed in experiments [6]. The final result reads as

$$R^*(t, t_\mathrm{w}, t_\mathrm{p}) = R(t) + \Delta R(t, t_\mathrm{w}, t_\mathrm{p}), \tag{1}$$

with $R(t) = (1/2)(R(E_\mathrm{S}, t) - R(-E_\mathrm{S}, t)) \equiv R(E_\mathrm{S}, t)$ and

$$\Delta R(t, t_\mathrm{w}, t_\mathrm{p}) = \mathcal{N} \int_0^t \mathrm{d}\tau \, \mathrm{Tr} \left\{ S(0) e^{-i\mathcal{L}(t-\tau)} \left[-i\mathcal{L}_1(E_\mathrm{S}) \right] e^{-i\mathcal{L}(\tau + t_\mathrm{w})} \Delta\rho_2(t_\mathrm{p}) \right\}. \tag{2}$$

Here, $\mathcal{L}$ is the Liouvillian, $\mathcal{L}_1(E_\mathrm{S})$ the first-order perturbation due to the dc field and $\mathcal{N}$ is a constant. $\Delta\rho_2(t_\mathrm{p})$ denotes the $\mathcal{O}(E_\mathrm{P}^2)$ deviation from thermal equilibrium of the density matrix directly after the pump. This results from two terms, $\mathcal{L}_1(E_\mathrm{P})$ and $\mathcal{L}_2(E_\mathrm{P})$ of respective order $\mathcal{O}(E_\mathrm{P})$ and $\mathcal{O}(E_\mathrm{P}^2)$ [12]. It is evident from eq. (2) that a nonvanishing $\Delta R(t, t_\mathrm{w}, t_\mathrm{p})$ results only because the system has been driven out of equilibrium prior to the linear response experiment and eq. (1) shows that the modified response is just the sum of the ordinary linear response and the modification. Therefore, in the NHB experiments the linear response starting from a modified inital state (in $\mathcal{O}(E_\mathrm{P}^2)$) is monitored as opposed to ordinary nonlinear (dielectric) experiments.

In order to be able to further discuss the implications of eqs. (1), (2), in the following I will consider explicit models of stochastic dynamics without inertial terms. This is a reasonable assumption for the slow relaxation processes of interest in the present context. The results obtained so far can be used directly for the corresponding Fokker-Planck (FP) or master equation (ME) obeyed by the conditional probability $P(\boldsymbol{x}, t)$, where $\boldsymbol{x}(t)$ denotes the stochastic process under consideration [13, 14]. For a FP equation, the nonlinear response theory can be formulated in general terms [15]. In this case the resulting expressions are particularly simple because higher-order terms like $\mathcal{L}_2(E)$ vanish.

If a ME is considered instead the situation can be quite different. The procedure of calculating the response as for a FP equation can be utilized only if the transition probabilities in the ME are chosen in such a way that a Kramers-Moyal expansion [13] is possible. If,

however, the "jump length" in the transition probabilities is large, the question how to couple the transition probabilities to the field arises. This can be understood most easily with the following argument. Denote the transition probability for an $x_i \to x_k$ transition without externally applied fields by $\kappa_{k,i}(t) = \kappa(x_k, x_i; t)$, the time-dependent probability distribution $p_i(t) = P(x_i, t)$ and the equilibrium probability by $p_i^{\mathrm{eq}} = p_i(t \to \infty)$ in a discrete notation. From ordinary statistical mechanics the change in the $p_i^{\mathrm{eq}} \propto e^{-\beta \epsilon_i}$, with $\beta = 1/(k_{\mathrm{B}} T)$ (k_{B} is the Boltzmann constant) and ϵ_i the energy, is known. If the field E couples to a function $M(\boldsymbol{x})$, these are just given by $p_i^{\mathrm{eq}}(E) = p_i^{\mathrm{eq}} \exp[\beta M(x_i) E]$. How to change the $\kappa_{k,i}(t)$ when an external field is applied is however not easily determined in the general case. The only restriction is that detailed balance has to be obeyed and this will be used in all what follows. The most general form for the $\kappa_{i,k}(E,t)$ therefore is

$$\kappa_{i,k}(E,t) = \kappa_{i,k}(t) e^{\beta E \Psi_{i,k}}, \quad \text{where} \quad \Psi_{i,k} = \alpha M(x_i) - (1-\alpha) M(x_k), \tag{3}$$

with α denoting a real number. The perturbation series for the ME follows from eq. (2) if one substitutes $(-i\mathcal{L})$ by the master operator $\mathcal{W}$ and the perturbation $(-i\mathcal{L}_n)$ by a corresponding $\mathcal{V}^{(n)}$ in $\mathcal{O}(E^n)$. The matrix elements of $\mathcal{W}$ and $\mathcal{V}^{(n)}$ are given by

$$(\mathcal{W})_{i,k} = \kappa_{i,k}(t) - \delta_{i,k} \sum_l \kappa_{l,k}(t),$$

$$(\mathcal{V}^{(n)})_{i,k} = \frac{1}{n!} [\beta E(t)]^n \left\{ \kappa_{i,k}(t) \Psi_{i,k}^n - \delta_{i,k} \sum_l \kappa_{l,k}(t) \Psi_{l,k}^n \right\}. \tag{4}$$

The constant α is determined by calculating the long time limit of the $p_k(E,t)$ as these have to coincide with $p_k^{\mathrm{eq}}(E)$ in the presence of external fields. For example, for a ME that obeys a Kramers-Moyal expansion, one has $\alpha = 1/2$ [13].

To fix the notation, in the following I will consider the reorientations of rigid molecules with a permanent dipole moment μ. Thus $S(t)$ in eq. (2) is identified with $\mu(t)$, the stochastic process $\boldsymbol{x}(t)$ with the orientation $w(t) = (\phi(t), \theta(t), \psi(t))$ in terms of Euler angles and $M(w_i) = \mu_i = \mu \cos \theta_i$. For simplicity, correlations due to the dipolar coupling of distinct molecules and local field corrections are neglected throughout. A simple way to model molecular reorientations is to assume that they occur in a completely random way. This is usually termed as a "random jump model" [16]. In this model the transition probabilites for a change in orientation from $w_i \to w_k$ are independent of w_i, w_k and are given by $\kappa_{k,i} = \Gamma/N \; \forall i, k = 1, \ldots, N$. (If reorientations on a sphere are considered, $N = 8\pi^2$.) The equilibrium probabilities are $p_i^{\mathrm{eq}} = 1/N$ and therefore the choice of α is not determined *a priori*.

In the following, I will consider a slight modification of this random jump model, for which the corresponding ME can still easily be solved analytically. This model is defined by the choice

$$\kappa_{k,i}(t) = p_k^{\mathrm{eq}} \Gamma(t), \tag{5}$$

which depends only on the final orientation of the transition. From this fact it is evident that for this model $\alpha = 1$. Additionally, a time-dependent rate $\Gamma(t)$ is considered because this will be used in the later discussion. A simple choice yielding a nonexponentially decaying response is

$$\Gamma(t) = b t^{b-1} / \tau, \quad b \in [0,1], \tag{6}$$

which reduces to a time-independent rate τ^{-1} for $b = 1$. Though the considered model is very simple minded, it still shows the characteristic features of any stochastic model. In models with more complex (time independent) $\kappa_{k,i}$ several rates λ_m will occur as the eigenvalues of the master operator $\mathcal{W}$. The mean decay rate in such more sophisticated models can be defined by $(1/N)\sum_m \lambda_m = (1/N)\sum_i \kappa_{i,i}$. As this just equals τ^{-1} for $b = 1$, cf. eq. (6), the simple model on average also reveals the features of more realistic ones. Furthermore, if only two orientations are considered, $N = 2$, the time-honoured double-well potential (DWP) model with an asymmetry $(\epsilon_1 - \epsilon_2)$ [17] is recovered.

The response for the model defined by eqs. (5), (6) is now calculated according to eqs. (1), (2) using (4). The resulting normalized response is given by $\Phi(t) = e^{-t^b/\tau}$ and

$$\Delta\Phi(t, t_{\mathrm{w}}, t_{\mathrm{p}}) = -\frac{(\beta E_{\mathrm{P}})^2}{\langle\Delta\mu^2\rangle} A(\Omega, b)(t^b/\tau)e^{-t^b/\tau}e^{-t_{\mathrm{w}}^b/\tau}\,, \tag{7}$$

with $\langle\Delta\mu^2\rangle = \langle\mu^2\rangle - \langle\mu\rangle^2$, $\langle\mu^n\rangle = \sum_i p_i^{\mathrm{eq}}\mu_i^n$. The magnitude of the modification at a given pump frequency, *i.e.* the "excitation profile", is given by $(t_{\mathrm{p}} \equiv 2n\pi/\Omega)$

$$A(\Omega, b) = \langle\mu\rangle^2\langle\Delta\mu^2\rangle(b/\tau)^2 e^{-t_{\mathrm{p}}^b/\tau}\int_0^{t_{\mathrm{p}}}\mathrm{d}t_1\int_0^{t_1}\mathrm{d}t_2\,\sin(\Omega t_1)t_1^{b-1}\sin(\Omega t_2)t_2^{b-1}e^{t_2^b/\tau} +$$

$$+ \frac{1}{2}\big(\langle\mu\rangle^2\langle\mu^2\rangle - \langle\mu\rangle\langle\mu^3\rangle\big)(b/\tau)e^{-t_{\mathrm{p}}^b/\tau}\int_0^{t_{\mathrm{p}}}\mathrm{d}t_1\,\sin(\Omega t_1)^2 t_1^{b-1}e^{t_1^b/\tau}. \tag{8}$$

Equation (8) reveals one of the central results of the present calculations, namely the frequency selectivity of NHB. $A(\Omega, b)$ vanishes for large and small burn frequencies Ω. This directly implies that a nonvanishing modification of the response can only be achieved for Ω on the order of τ^{-1}. The sign of $A(\Omega, b)$ is determined by the prefactor of the second term and therefore depends on the details of the assumptions for the p_i^{eq}. Note that for a vanishing $\langle\mu\rangle = 0$ one has $A(\Omega, b) = 0$. Furthermore, for a DWP model, it is easily seen that $\langle\mu\rangle^2\langle\mu^2\rangle = \langle\mu\rangle\langle\mu^3\rangle$ and the second term of $A(\Omega, b)$ vanishes. The same holds approximately, if only small asymmetries are assumed in the general case. Therefore, in the following calculations the second term of $A(\Omega, b)$ will be neglected throughout.

A transparent expression allowing a simple interpretation for the excitation profile is obtained for the special case $b = 1$:

$$A(\Omega, 1) \simeq \frac{3}{2}\langle\mu\rangle^2\langle\Delta\mu^2\rangle\epsilon''(\Omega\tau)\epsilon''(2\Omega\tau)\big(1 - e^{-t_{\mathrm{p}}/\tau}\big). \tag{9}$$

Here, $\epsilon''(m\Omega\tau) = m\Omega\tau/(1 + m^2\Omega^2\tau^2)$. Therefore, $A(\Omega, 1)$ is determined by the absorbed energy and higher-order terms, in accord with what is expected on physical grounds [6].

In fig. 1 the normalized excitation profile $A(\Omega, b)/A_{\max}$ is plotted as a function of the pump frequency for $b = 1$ and $b = 0.7$ and one pump cycle. For $b = 1$, the excitation profile is considerably narrower than for $b = 0.7$ and also than the Debye susceptibility $\epsilon''(\Omega\tau)$. This means that the selection is restricted to a narrow band of frequencies. Decreasing b gives rise to broader excitation profiles.

Important features of the modification $\Delta\Phi(t, t_{\mathrm{w}}, t_{\mathrm{p}})$ given in eq. (7) are the following. i) If $\Delta\Phi(t, t_{\mathrm{w}}, t_{\mathrm{p}}) < 0$, the modified response Φ^* decays faster than the equilibrium response. In the approximation used in eq. (9) this always holds. The fact that $\Delta\Phi(t, t_{\mathrm{w}}, t_{\mathrm{p}}) \neq 0$ only for Ω on the order of τ^{-1} has already been discussed above. ii) $\Delta\Phi(t, t_{\mathrm{w}}, t_{\mathrm{p}})$ is only nonzero in a finite interval of time t, determined by b. The regime of $\Delta\Phi(t, t_{\mathrm{w}}, t_{\mathrm{p}}) \neq 0$ becomes larger with decreasing b (*i.e.* the "spectral holes" become broader). The maximum value
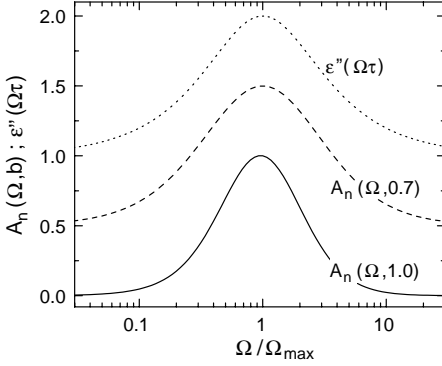
Fig. 1

Fig. 2

Fig. 1 – Normalized "excitation profile" $A_n(\Omega, b) = A(\Omega, b)/A_{max}$ *vs.* Ω/Ω_{max} for $b = 1$, $\Omega_{max}\tau = 0.736$ (full line) and $b = 0.7$, $\Omega_{max}\tau = 0.185$ (dashed line). Also shown is the imaginary part of the susceptibility, $\epsilon''(\Omega\tau)$, where τ is the relaxation time, (dotted line) for comparison. The lines for $A_n(\Omega, 0.7)$ and $\epsilon''(\Omega\tau)$ have been shifted by 0.5 and 1.0 units, respectively.
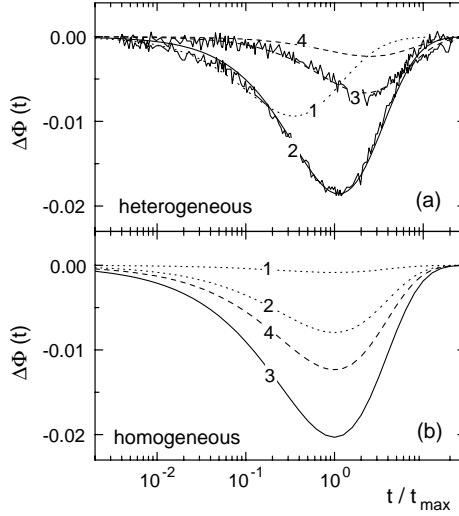
Fig. 2 – $\Delta\Phi(t)$ *vs.* rescaled time t/t_{max} for (a) a heterogeneous and (b) a homogeneous scenario for various burn frequencies Ω and $\beta^2 E_P^2/(\Delta\mu^2) = 0.18$. In both cases the equilibrium response decays as $\Phi(t) = e^{-(t/1s)^{0.7}}$. The time $t_{max} = 1.0\,s$ in case (a) and $t_{max} = 0.095\,s$ in case (b). The used frequencies are: heterogeneous scenario: $\Omega\tau = 5.0$ (1), 1.0 (2), 0.2 (3) 0.1 (4); homogeneous scenario: $\Omega\tau = 5.0$ (1), 1.0 (2), 0.1 (3), 0.05 (4); experimental data in (a) are adapted from ref. [6] and plotted in a scaled form $(\Delta\Phi(t) = -\Delta\epsilon(t)/(\epsilon(\infty) - \epsilon(0)))$. Here, $\Omega\tau = 1.02$ (2) and $\Omega\tau = 0.203$ (3).

of the modification is found at the time $t_{max} = (1/\tau)^{1/b}$. For a homogeneous response (a fixed value of τ) a variation of the pump frequency will only alter the overall amplitude of the modification. Therefore, it is not possible to perform a frequency-selective modification in this case. iii) The modification decreases as a function of the waiting time t_w. This re-equilibration proceeds with the same relaxation time τ. The reason for this behavior becomes evident from the form of the modified orientational distribution after the pump, $p_k^{Mod}(t_p) \sim (\mu_k - \langle\mu\rangle)p_k^{eq}$, which in turn relaxes with the dipole relaxation time τ. For more sophisticated models, other relaxation times λ_m^{-1} may occur here. The important finding is that there is no extra time scale for re-equilibration. It should be mentioned that similar results are found for a variety of stochastic models of dipole reorientation [18].

In order to further clarify the implications of the calculations, in the following I will consider specific examples. Often a stretched exponential function is used to parametrize the equilibrium response, $\Phi(t) = e^{-(t/\tau_K)^{\beta_K}}$, with β_K smaller than unity, see, *e.g.*, [1]. In a *heterogeneous* scenario, this response is viewed as originating from a distribution of τ [1] whereas $\Phi(t)$ is assumed to be intrinsically non-exponential in a *homogeneous* scenario. It is important to note that in both cases the response can be written as $\Phi(t) = \int d\tau\, g(\tau)e^{-t/\tau}$, with some distribution function $g(\tau)$. However, only in the heterogeneous scenario the distribution function $g(\tau)$ has a physical significance in the sense that it can be modified in some way, *e.g.*, by the experimental techniques cited above. In the homogeneous scenario, on the other hand,

it merely expresses a mathematical identity and a selection of a sub-ensemble is impossible.

It is instructive to compare directly the results of calculations for the two extreme scenarios for a realistically broadened susceptibility. Such a comparison of $\Delta\Phi(t)$ is shown in fig. 2 for (a) a heterogeneous and (b) a homogeneous scenario with $\Phi(t) = \exp\left[-(t/1\mathrm{s})^{0.7}\right]$. The calculations were performed in the following way. For the heterogeneous case (a) I used $b = 1$, *i.e.* $\Gamma = \Gamma(t) = 1/\tau$ in eq. (6) and a corresponding distribution of τ chosen in such a way that $\Phi(t)$ is well described by $\exp\left[-(t/1\mathrm{s})^{0.7}\right]$. The modified response is then given by a superposition $\Delta\Phi(t, t_{\mathrm{w}}, t_{\mathrm{p}}) = \int \mathrm{d}\tau\, g(\tau)\Delta\Phi(\tau, t, t_{\mathrm{w}}, t_{\mathrm{p}})$, cf. eq. (7). In the homogeneous case (b) I set $b = 0.7$, $\tau^{-b} = 1\mathrm{s}$ from which a KWW form of $\Phi(t)$ follows immediately. From the calculations for the heterogeneous case it is evident that the time at which the maximum modification shows up strongly depends on the burn frequency Ω. This demonstrates the frequency selectivity of NHB. Such a dependence is missing completely in the homogeneous case. In the heterogeneous case the maximum modification shifts towards longer times with decreasing Ω. This is because those relaxation processes with a τ yielding the maximum $A(\Omega, 1)$ (cf. eq. (9) and fig. 1) contribute most to $\Delta\Phi(t)$. The functional dependence of $\Delta\Phi_{\mathrm{max}} = \Delta\Phi(t_{\mathrm{max}}, t_{\mathrm{w}} = 0, t_{\mathrm{p}})$ upon Ω depends sensitively on the choice of the relaxation time distribution (*e.g.*, on the value of β_K). Generally, there will be a rather strong dependence for large Ω which crosses over to a Ω-independence of $\Delta\Phi_{\mathrm{max}}$ when $1/\Omega$ reaches the smallest relaxation time of the distribution. Exchange processes, which may be responsible for fluctuations of relaxation rates, may partially suppress the Ω-dependence [18].

Also included fig. 2(a) are experimental data on propylene carbonate [6]. It is remarkable that all main features of the data can be described by the simple heterogeneous model. The position of the modifications and the relative amplitudes are in quantitative agreement with the data. Also the width and the asymmetry are described with high accuracy. A similar quantitative agreement is obtained for the t_{w}-dependence of experimental data on supercooled liquids [18].

So far, I have considered stochastic models for dipole reorientations. All these models show qualitatively the same features. In particular, it is found that the re-equilibration during the waiting time t_{w} takes place on the time scale of the intrinsic relaxation time (τ in the above examples). In an experiment on a relaxor ferroelectric a re-equilibration time much longer than $1/\Omega$ has been found [7]. In order to investigate the theoretical conditions for such an effect, I consider a simple "nonlinear Debye model". A physical realization of this scenario may be a system where the dynamics is dominated by domain wall depinning [19]. The polarization is assumed to relax with a correlation time $\tau_0 = \tau_\infty e^{\beta U_{\mathrm{a}}}$, where U_{a} is the activation (pinning) energy and $1/\tau_\infty$ an attempt frequency. Application of an electric field will change the activation energy roughly by an amount $U_{\mathrm{a}}(t) = U_{\mathrm{a}}(0) - cP_{\mathrm{sp}}E(t)$, where c is a constant and P_{sp} the spontaneous polarization [20], which in the simplest case is proportional the the the applied field, $P_{\mathrm{sp}} \propto E(t)$. The relaxation of the deviation from thermal equilibrium of $U_{\mathrm{a}}(t)$ is assumed to obey a linear law: $\partial_t \delta U_{\mathrm{a}}(t) + \gamma \delta U_{\mathrm{a}}(t) = c\partial_t[E(t)^2]$ (meaningful for $\gamma < 1/\tau_0$), where the rate γ may depend on the magnitude of deviation from equilibrium. This expression together with the equation for $P(t)$, $\partial_t P(t) + (1/\tau)P(t) = \chi(1/\tau)E(t)$, can be solved in $\mathcal{O}(E_{\mathrm{S}})$ and $\mathcal{O}(E_{\mathrm{P}}^2)$ for the NHB situation. Here, χ denotes the dielectric susceptibility and $\tau = \tau_0 e^{\delta U_{\mathrm{a}}(t)}$. The calculation leads to results similar to those obtained above with $\Phi(t) = e^{-t/\tau_0}$ and $\Delta\Phi(t, t_{\mathrm{w}}, t_{\mathrm{p}}) \propto e^{-\gamma t_{\mathrm{w}}}$. The important point is that in this model $1/\gamma$, and *not* τ_0 is the relevant time scale for re-equilibration.

In conclusion, I have shown that NHB can be understood as a linear response experiment starting from a nonlinearly perturbed initial state. Generally, it is always possible to separate the linear response from the effects of the pump process. For systems with stochastic dynamics the method is clearly able to discriminate between homogeonously and heterogeneously

broadened dielectric spectra. A frequency-selective modification of the response is possible only in the heterogeneous case. The re-equilibration during the waiting time is determined by the relaxation of the modified orientational distribution created during the pump period. The hole recovery does not show the appearance of a second time scale. A longer time scale for re-equilibration, if it is observed, has to be attributed to intrinsic nonequilibrium effects.

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