Nonlinear response and its behavior in transient and stationary processes

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Transient responses and stationary processes with alternating fields are treated in the nonlinear regime in order to clarify their relations in the time and frequency domains. It is shown that a frequency-domain experiment in which a weak ac field is superimposed on a strong biasing dc field corresponds to the transient process of a strong constant biasing field with the sudden application of weak constant field. Furthermore, it is found that the Fourier-Laplace transform of the second-order nonlinear transient rise process corresponds to the amplitude for the ω component of the stationary experiment with coupled dc and ac fields with the angular frequency ω. For a simple ac input, we demonstrated how the stationary nonlinear response may conveniently be calculated with the help of the theory of random walk. Also, interrelations among the rise, decay, and rapidly reversing transients are clarified.

INTRODUCTION

In a previous paper, Morita[1] has shown how the nonlinear response by an external perturbation may be calculated once the conditional probability of the unperturbed system is given. The main purpose of the present paper is to apply this theory to investigation of the behavior of transient and stationary processes. This enables us to relate nonlinear response in the time domain to that in the frequency domain arising from the transient and stationary processes, respectively. We shall consider a transient process in which a constant perturbation p is applied for sufficiently long time for a system to reach equilibrium, then at time $t=0$ another constant perturbation, with different strength p_0, is suddenly switched on. This general case includes the transient rise, decay, and rapidly reversing processes often used in Kerr effect relaxation experiments.[2] Generally we shall show that the experimental result for the rapidly reversing field can be produced from the results for the rise and decay processes if we confine ourselves to second-order nonlinear terms, while if we take into account more than the third-order terms, the experiment with the rapidly reversing field provides information which is not inherent to the rise and decay processes. Also treated is the stationary nonlinear response induced by alternating fields.

It will be shown how the stationary response due to an alternating field $p(t)=p_0\cos(\omega t)$ may be calculated with the help of the concept of random walk. This approach is certainly more convenient than the existing one,[3] and we shall see clearly how complicated the final expression becomes particularly for higher-order nonlinear terms. Hence we shall restrict ourselves to second-order nonlinear terms by considering the stationary case where $p(t)=A\cos(\omega_1 t)+B\cos(\omega_2 t)$, and show that the amplitude of the ω_1 or ω_2 components gives the Fourier-Laplace transform of the rise transient.

As a new result, it will be shown that higher-order nonlinear terms can be calculated and summed to obtain the stationary distribution function for the case where $p(t)=p_1+p^*\cos(\omega t)$ assuming $(p^*/p_1)\ll 1$. It will be seen that the Fourier-Laplace transform of the transient distribution function for the special case where $p=p_1+p_0$ leads to the above stationary distribution function and this situation gives information missing in the conventional techniques for the rise, decay, and rapidly reversing fields. From this general consideration, we will be able to see explicitly that frequency domain experiments of Block and Hayes[4] correspond not to the rise transient through linear response theory as speculated by Ullman,[5] but to this transient process. This point will be considered extensively in Discussion.

THEORY

In accordance with the previous formulation, by that of Morita,[1] we write the time-evolution equation as given by

$$\frac{\partial f(x,t)}{\partial t}=[\hat{D}_0(x)+\epsilon p(t)\hat{D}_1(x)]f(x,t) , \tag{1}$$

where $f(x,t)$ is the distribution function of a system whose natural or unperturbed motion is described by the operator $\hat{D}_0(x)$, whereas the perturbed operator is represented by $\hat{D}_1(x)$, x stands for a set of variables other than time t for expressing $f(x,t)$, and $p(t)$ is a function of t indicating the time dependence of the perturbation. It should be noted that the perturbation term is assumed to consist of the product of a function $p(t)$ and the operator $\hat{D}_1(x)$ by separating variables t and x. The formal solution for $f(x,t)$ in Eq. (1) can conveniently be expressed using the transition probability density $g(x,x',t,t')$ which satisfies

$$\frac{\partial g(x,x',t,t')}{\partial t}=\hat{D}_0 g(x,x',t,t')$$

and $g(x,x',t,t')=\delta(x-x')$ at $t=t'$, where $\delta(x)$ is the Dirac delta function. The final result is given by

$$f_j(x,t)=\mathbf{g}\int_{t\ge t_1\ge\cdots\ge t_j\ge 0}\int\cdots\int \mathbf{D}(t-t_1)\mathbf{D}(t_1-t_2)\cdots\mathbf{D}(t_{j-2}-t_{j-1})\mathbf{f}(t_{j-1}-t_j)\times p(t_1)p(t_2)\cdots p(t_j)dt_1dt_2\cdots dt_j\ , \tag{2}$$

where we have written

$$f(x,t)=f_0(x)+\epsilon f_1(x,t)+\epsilon^2 f_2(x,t)+\cdots\ , \tag{3}$$

and introduced a set of orthnormal functions $g_n(x)$'s satisfying the following eigen equation:

$$\hat{D}_0(x)g_n(x)=-\lambda_n g_n(x)\ , \tag{4}$$

with $n=1,2,3,\ldots$. In Eq. (3), $f_0(x)$ is the equilibrium distribution function without the perturbation, ϵ is the small parameter, and $-\lambda_n$ in Eq. (4) is the eigenvalue. It was shown that in Eq. (2),

$$[\mathbf{D}(t)]_{ij}=\int\int g_i^*(x)g(x,x',t)\hat{D}_1(x')g_j(x')dx\,dx'\ , \tag{5}$$

and

$$[\mathbf{f}(t)]_i=\int\int g_i^*(x)g(x,x',t)\hat{D}_1(x')f_0(x')dx\,dx'\ , \tag{6}$$

where $[\mathbf{D}(t)]_{ij}$ and $[\mathbf{f}(t)]_i$ are elements of the square matrix $D(t)$ and the column matrix $f(t)$, respectively, which are related to the correlation functions determined once $g(x,x',t,t')$ is known as seen from Eqs. (5) and (6).

We shall consider the transient process where a constant field $p(t)=p$ has been applied for sufficiently long time to reach the equilibrium state for $t<0$, and at $t=0$ another constant field $p(t)=p_0$ is suddenly switched on. In this case, we have to find $F(x,s)$ which satisfies

$$[s-\hat{D}_0(x)-p_0\hat{D}_1(x)]\tilde{F}(x,s)=f_{\mathrm{eq}}(x,p)\ , \tag{7}$$

where

$$\tilde{F}(x,s)=\int_0^\infty f(x,t)e^{-st}dt=\mathscr{L}(f(x,t))\ ,$$

and $f_{\mathrm{eq}}(x,p)$ represents the equilibrium distribution function in the presence of the field p. It follows from Eq. (7) that

$$\begin{aligned}\tilde{F}(x,s)=&\frac{f_0(x)}{s}+\frac{p^2}{p_0}\frac{\mathbf{g}}{s}[\mathbf{E}-p\tilde{\mathbf{D}}(0)]^{-1}\tilde{\mathbf{f}}(0)\\&+(p_0-p)\frac{\mathbf{g}}{s}[\mathbf{E}-p_0\tilde{\mathbf{D}}(s)]^{-1}\tilde{\mathbf{f}}(s)\\&+p\left[1-\frac{p}{p_0}\right]\mathbf{g}\frac{1}{s}[\mathbf{E}-p_0\tilde{\mathbf{D}}(s)]^{-1}\\&\times[\mathbf{E}-p\tilde{\mathbf{D}}(0)]^{-1}\tilde{\mathbf{f}}(0)\ .\end{aligned} \tag{8}$$

This equation immediately gives interesting results. When $p=p_0$, it leads to $f_{\mathrm{eq}}(x,p)$ as required, while when $p_0=0$ (corresponding to the decay transient) we have

$$\tilde{F}^{(d)}=\frac{f_0(x)}{s}-p\frac{\mathbf{g}}{s}\tilde{\mathbf{f}}(s)+p\frac{\mathbf{g}}{s}[\mathbf{E}-p\tilde{\mathbf{D}}(s)][\mathbf{E}-p\tilde{\mathbf{D}}(0)]^{-1}\tilde{\mathbf{f}}(0)\ . \tag{9}$$

In the case $p=0$ (corresponding to the rise transient) we find that

$$\tilde{F}^{(r)}=\frac{f_0(x)}{s}+p_0\frac{\mathbf{g}}{s}[\mathbf{E}-p_0\tilde{\mathbf{D}}(s)]^{-1}\tilde{\mathbf{f}}(s)\ . \tag{10}$$

And for the rapidly reversing field where $p_0=-p$, we obtain

$$\begin{aligned}\tilde{F}^{(\mathrm{rev})}=&\frac{f_0(x)}{s}-p\frac{\mathbf{g}}{s}[\mathbf{E}-p\tilde{\mathbf{D}}(0)]^{-1}\tilde{\mathbf{f}}(0)\\&-2p\frac{\mathbf{g}}{s}[\mathbf{E}+p\tilde{\mathbf{D}}(s)]^{-1}\tilde{\mathbf{f}}(s)\\&+2p\frac{\mathbf{g}}{s}[\mathbf{E}+p\tilde{\mathbf{D}}(s)]^{-1}[\mathbf{E}-p\tilde{\mathbf{D}}(0)]^{-1}\tilde{\mathbf{f}}(0)\ .\end{aligned} \tag{11}$$

Finally for the case where $p_0=p+p^*$ with assuming $(p^*/p)\ll 1$, we find by neglecting terms higher than the second order in p^*,

$$\begin{aligned}\tilde{F}^{(b)}=&\frac{f_0(x)}{s}+p\frac{\mathbf{g}}{s}[\mathbf{E}-p\tilde{\mathbf{D}}(0)]^{-1}\tilde{\mathbf{f}}(0)\\&+p^*\frac{\mathbf{g}}{s}\{[\mathbf{E}-p\tilde{\mathbf{D}}(s)]^{-1}\tilde{\mathbf{f}}(s)\\&-[\mathbf{E}-p\tilde{\mathbf{D}}(0)]^{-1}\tilde{\mathbf{f}}(0)\\&+[\mathbf{E}-p\tilde{\mathbf{D}}(s)]^{-1}[\mathbf{E}-p\tilde{\mathbf{D}}(0)]^{-1}\tilde{\mathbf{f}}(0)\}\ .\end{aligned} \tag{12}$$

At this stage, we consider the stationary process with alternating fields. We first treat the case where $p(t)=p_0\cos(\omega t)$. To this end, we should calculate $f_j(x,t)$ in accordance with Eq. (2) in the limit of $t\to\infty$ which corresponds to $f_j^{(\infty)}(x,t)$ in the stationary state where all transient effects are removed. For the calculation of the product $p(t_1)p(t_2)\ldots p(t_j)$ in Eq. (2), we use the relation $p(t)=(p_0/2)[\exp(i\omega t)+\exp(-i\omega t)]$. Letting $a_m=1$ or -1, where $1\le m\le j$, we find

$$p(t_1)p(t_2)\cdots p(t_j)=(p_0/2)^j\sum\exp\left[i\omega\sum_{m=1}^{j}a_m t_m\right]\ , \tag{13}$$

where the first summation $\sum$ on the right-hand side of Eq. (13) must be carried out over all possible 2^j combinations of $a_1, a_2, \ldots, a_j$. Equation (13) can be further written setting $a_1=1$ giving

$$p(t_1)p(t_2)\cdots p(t_j)$$
$$=(p_0/2)^j\left\{\left[\sum{}'\exp\left[i\omega\sum_{m=1}^{j}a_m t_m\right]\right]+\text{c.c.}\right\} \qquad (14\text{a})$$
$$=p_0(p_0/2)^{j-1}\sum{}'\cos\left[\omega\sum_{m=1}^{j}a_m t_m\right], \qquad (14\text{b})$$

where c.c. represents the complex conjugate of the preceeding term. Now the first summation $\sum'$ in Eqs. (14a) and (14b) should be taken over all possible 2^{j-1} combinations of $a_2, a_3, \ldots, a_j$ fixing $a_1=1$. In calculating $f_j^{(\infty)}(t)$, we find it convenient to use Eq. (14a) rather than Eq. (14b). Therefore we can write

$$\tilde{F}_j(x,s)=\mathscr{L}\left[\int\int_{t\ge t_1\ge\cdots\ge t_j\ge 0}\cdots\int \mathbf{D}(t-t_1)[\mathbf{D}(t_1-t_2)e^{i\omega b_1(t_1-t_2)}][\mathbf{D}(t_2-t_3)e^{i\omega b_2(t_2-t_3)}]\cdots\right.$$
$$\left.\times[\mathbf{D}(t_{j-2}-t_{j-1})e^{i\omega b_{j-2}(t_{j-2}-t_{j-1})}][f(t_{j-1}-t_j)e^{i\omega b_{j-1}(t_{j-1}-t_j)}]e^{i\omega b_j t_j}dt_1dt_2\cdots dt_j\right]$$
$$=\tilde{\mathbf{D}}(s)\tilde{\mathbf{D}}(s-i\omega b_1)\tilde{\mathbf{D}}(s-i\omega b_2)\cdots\tilde{\mathbf{D}}(s-i\omega b_{j-2})\tilde{\mathbf{f}}(s-i\omega b_{j-1})(s-i\omega b_j)^{-1}, \qquad (15)$$

where $b_m=a_1+a_2+\ldots,+a_m$. It follows from Eq. (15) by assuming only the simple pole in $(s-i\omega b_{j-1})^{-1}$ contributes to $f_j^{(\infty)}(x,t)$ in the stationary limit that

$$f_j^{(\infty)}(x,t)=\frac{p_0^j}{2^{j-1}}\mathbf{g}\sum{}'[\mathcal{X}_j'(b_j)\cos(\omega b_j t)-\mathcal{X}_j''(b_j)\sin(\omega b_j t)], \qquad (16)$$

where

$$\mathcal{X}_j(b_j)=\mathcal{X}_j'(b_j)-\mathcal{X}_j''(b_j)$$
$$=\int_0^\infty\int_0^\infty\cdots\int_0^\infty \mathbf{D}(t_1)\mathbf{D}(t_2)\cdots\mathbf{f}(t_j)\exp\{-i\omega[b_jt_1+(b_j-b_1)t_2+\cdots+(b_j-b_{j-1})t_j]\}dt_1dt_2\cdots dt_j. \qquad (17)$$

This result enables us to determine $\mathcal{X}_j(b_j)$ by calculating $b_j, b_j-b_1, b_j-b_2, \ldots, b_j-b_{j-1}=a_j$. We find $b_j=j$ (1), $j-2$, (${}_1C_{j-1}$), $j-4$ (${}_2C_{j-1}$), $\ldots$, $-j+4$ (${}_{j-2}C_{j-1}=j-1$), and $-j+2$ (${}_{j-1}C_{j-1}=1$) where the number in parentheses represents the number of times that value of b_j appears. Similarly, we have $b_j-b_1=j-1$ and $-j+1$ (1), $j-3$ and $-j+3$ (${}_1C_{j-1}=j-1$), $j-5$ and $-j+5$ (${}_2C_{j-1}$), $\ldots$, $b_j-b_2=j-2$ and $-j+2$ (2), $j-4$ and $-j+4$ [$2{}_1C_{j-2}=2(j-2)$], $j-6$ and $-j+6$ ($2{}_2C_{j-2}$), $\ldots$, $b_j-b_3=j-3$ and $-j+3$ ($2^2{}_0C_{j-3}=4$), $j-5$ and $-j+5$ [$2^2_1C_{j-3}=4(j-3)$], $\ldots$, and so on. These values are listed for $j=3$, 4, 5, and 6 in Table I. We have shown schematically in Fig. 1 how values of b_j may be obtained conveniently with the help of the random walk concept where the walker starts from $a_1=1$ through all the possible paths to the final destination with values of b_j, taking forward and backward steps for $a_m=1$ and -1, respectively. It is obvious that if j is even, b_j is also even, whereas if j is odd, b_j is odd. The expression for $\mathcal{X}_j(b_j)$ must be obtained with taking account of the above considerations, leading to very complicated forms for large values of j. The case $j=2$ has been considered previously.[1]

Because of the complexity in obtaining higher-order terms for the alternating field, we confine ourselves here to calculating $f_2^{(\infty)}(x,t)$ in the case of $p(t)=A\cos(\omega_1 t)+B\cos(\omega_2 t)$. After carrying out a similar procedure to the case $p(t)=p_0\cos(\omega t)$, we find that

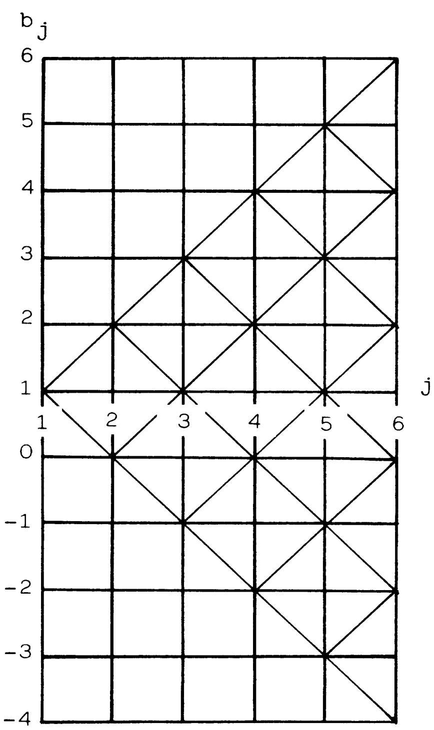

FIG. 1. Diagram showing how b_j may conveniently be obtained with the help of the random walk concept.

TABLE I. Values of $b_j, b_j-b_1, b_j-b_2, \ldots$, for $j=6$, 5, 4, and 3.

$j=6$

b_6	b_6-b_5	b_6-b_4	b_6-b_3	b_6-b_2	b_6-b_2
6	5	4	3	2	1
4	3	4	3	2	1
4	3	2	3	2	1
2	1	2	3	2	1
4	3	2	1	2	1
2	1	2	1	2	1
2	1	0	1	2	1
0	−1	0	1	2	1
4	3	2	1	0	1
2	1	2	1	0	1
2	1	0	1	0	1
0	−1	0	1	0	1
2	1	0	−1	0	1
0	−1	0	−1	0	1
0	−1	−2	−1	0	1
−2	−3	−2	−1	0	1
4	3	2	1	0	−1
2	1	2	1	0	−1
2	1	0	1	0	−1
0	−1	0	1	0	−1
2	1	0	−1	0	−1
0	−1	0	−1	0	−1
0	−1	−2	−1	0	−1
−2	−3	−2	−1	0	−1
2	1	0	−1	−2	−1
0	−1	0	−1	−2	−1
0	−1	−2	−1	−2	−1
−2	−3	−2	−1	−2	−1
0	−1	−2	−3	−2	−1
−2	−3	−2	−3	−2	−1
−2	−3	−4	−3	−2	−1
−4	−5	−4	−3	−2	−1

$j=5$

b_5	b_5-b_4	b_5-b_5	b_5-b_2	b_5-b_1
5	4	3	2	1
3	2	3	2	1
3	2	1	2	1
1	0	1	2	1
3	2	1	0	1
1	0	1	0	1
1	0	−1	0	1
−1	−2	−1	0	1
3	2	1	0	−1
1	0	1	0	−1
1	0	−1	0	−1
−1	−2	−1	0	−1
1	0	−1	−2	−1
−1	−2	−1	−2	−1
−1	−2	−3	−2	−1
−3	−4	−3	−2	−1

$j=4$

b_4	b_4-b_3	b_4-b_2	b_4-b_1
4	3	2	1
2	1	2	1
2	1	0	1
0	−1	0	1
2	1	0	−1
0	−1	0	−1
0	−1	−2	−1
−2	−3	−2	−1

$j=3$

b_3	b_3-b_2	b_3-b_1
3	2	1
1	0	1
1	0	−1
−1	−2	−1

$$
\begin{aligned}
f_2^{(\infty)}(x,t)=\tfrac{1}{4}\mathbf{g}[&A^2\widetilde{\mathbf{D}}(2i\omega_1)\widetilde{\mathbf{f}}(i\omega_1)e^{-2i\omega_1 t}+A^2\widetilde{\mathbf{D}}(0)\widetilde{\mathbf{f}}(-i\omega_1)+B^2\widetilde{\mathbf{D}}(2i\omega_2)\widetilde{\mathbf{f}}(i\omega_2)e^{-2i\omega_2 t}+B^2\widetilde{\mathbf{D}}(0)\widetilde{\mathbf{f}}(-i\omega_2)\\
&+AB\widetilde{\mathbf{D}}(i\omega_1+i\omega_2)\widetilde{\mathbf{f}}(i\omega_2)e^{-i(\omega_1+\omega_2)t}+AB\widetilde{\mathbf{D}}(i\omega_1-i\omega_2)\widetilde{\mathbf{f}}(-i\omega_2)e^{-i(\omega_1-\omega_2)t}\\
&+AB\widetilde{\mathbf{D}}(i\omega_1+i\omega_2)\widetilde{\mathbf{f}}(i\omega_1)e^{-i(\omega_1+\omega_2)t}+AB\widetilde{\mathbf{D}}(-i\omega_1+i\omega_2)\widetilde{\mathbf{f}}(-i\omega_1)e^{-i(-\omega_1+\omega_2)t}+\text{c.c.}]\ .
\end{aligned}
\tag{18}
$$

Now, consider the two-mode case where one of the frequencies is zero, that is, $p(t)=p_1+p^*\cos(\omega t)$ assuming $(p^*/p_1)\ll 1$. It follows by neglecting terms higher than the second power of p^* and considering only terms contributing to the stationary process that

$$
\begin{aligned}
f^{(\infty)}(x,t)-f_0(x)=\mathbf{g}p_1[\mathbf{E}-p_1\widetilde{\mathbf{D}}(0)]^{-1}\widetilde{\mathbf{f}}(0)+\tfrac{1}{2}p^*\mathbf{g}(\{&[\mathbf{E}-p_1\widetilde{\mathbf{D}}(i\omega)]^{-1}[\mathbf{E}-p_1\widetilde{\mathbf{D}}(0)]^{-1}\widetilde{\mathbf{f}}(0)\\
&-[\mathbf{E}-p_1\widetilde{\mathbf{D}}(0)]^{-1}\widetilde{\mathbf{f}}(0)+[\mathbf{E}-p_1\widetilde{\mathbf{D}}(i\omega)]^{-1}\widetilde{\mathbf{f}}(i\omega)\}e^{i\omega t}+\text{c.c.})\ .
\end{aligned}
\tag{19}
$$

DISCUSSION

We discuss first the transient case, then later the stationary process. It should be noted when $p_0=p+p^*$ that we obtain information on $[E-p\widetilde{D}(s)]^{-1}[E-p\widetilde{D}(0)]^{-1}$ missing in rise, decay, and reversing processes. It is also interesting to note that for experiments with the reversing field, $\widetilde{F}(x,s)$ is connected to $[E+p\widetilde{D}(s)]^{-1}[E-p\widetilde{D}(0)]^{-1}$ which is present neither in the rise nor in the decay transients. However, if we restrict ourselves to the second-order nonlinear terms by neglecting higher-order terms, we find that

$$
\begin{aligned}
\widetilde{F}^{(\mathrm{rev})}-\frac{1}{s}f_{\mathrm{eq}}(x)
&=\left[\widetilde{F}^{(r)}_{-}-\frac{1}{s}f_{\mathrm{eq}}(x)\right]+\left[\widetilde{F}^{(r)}-\frac{1}{s}f_{\mathrm{eq}}(x)\right]\\
&\quad+2\left[\widetilde{F}^{(d)}-\frac{1}{s}f_0(x)\right]+O(p^3)\ ,
\end{aligned}
\tag{20}
$$

where $\tilde{F}_{-}^{(r)}(x,s)$ is found from $\tilde{F}^{(r)}(x,s)$ by replacing p by $-p$. Hence it is seen that although the experiment with the reversing field can be produced by the rise and decay transients, if we neglect nonlinear terms higher than the third order, this result gives fresh information absent from the rise and decay processes if we take into account higher-order terms. We consider contributions arising from the permanent and induced dipole moments usually performed in treating the Kerr effect relaxation[2] by separating $\hat{D}_1(x)$ into the following two terms:

$$\hat{D}_1(x)=\hat{D}_\mu(x)+\epsilon p(t)\hat{D}_\alpha(x) , \tag{21}$$

leading to

$$\tilde{F}^{(r)}=\frac{1}{s}f_0(x)+p\frac{\mathbf{g}}{s}\tilde{\mathbf{f}}_\mu(s) +p^2\frac{\mathbf{g}}{s}[\tilde{\mathbf{f}}_\alpha(s)+\tilde{\mathbf{D}}_\mu(s)\tilde{\mathbf{f}}_\mu(s)]+O(p^3) , \tag{22}$$

$$\tilde{F}^{(d)}=\frac{1}{s}f_{\rm eq}(x) -\left[p\frac{\mathbf{g}}{s}\tilde{\mathbf{f}}_\mu(s)+p^2\frac{\mathbf{g}}{s}[\tilde{\mathbf{f}}_\alpha(s)+\tilde{\mathbf{D}}_\mu(s)\tilde{\mathbf{f}}_\mu(0)]\right]+O(p^3) , \tag{23}$$

$$\tilde{F}^{(\rm rev)}=\frac{1}{s}f_{\rm eq}(x) +2\left[-p\frac{\mathbf{g}}{s}\tilde{f}_\mu(s) +p^2\frac{\mathbf{g}}{s}[\tilde{\mathbf{D}}_\mu(s)\tilde{\mathbf{f}}_\mu(s)-\tilde{\mathbf{D}}_\mu(s)\tilde{\mathbf{f}}_\mu(0)]\right]+O(p^3) , \tag{24}$$

where matrices with subscripts μ and α are those obtained by replacing the operator $\hat{D}_1(x)$ by operators $\hat{D}_\mu(x)$ and $\hat{D}_\alpha(x)$, respectively. It should be noted that the contribution from $\hat{D}_\alpha(x)$ formally corresponds to that from $\hat{D}_1(x)$ in the linear regime except the former plays a role in the second order of p^2. In fact, if we put $\hat{D}_\mu(x)=0$, we just obtain the distribution function corresponding to that in the linear regime. For a physical variable $K(x)$ satisfying

$$\int K(x)f_0(x)dx=0$$

and

$$\boldsymbol{\kappa}\tilde{\mathbf{f}}_\mu(s)=0 ,$$

where

$$\boldsymbol{\kappa}=\int K(x)\mathbf{g}(x)dx ,$$

we find that

$$\mathscr{L}[\langle\langle K\rangle\rangle^{(r)}]=p^2\frac{\boldsymbol{\kappa}}{s}[\tilde{\mathbf{f}}_\alpha(s)+\tilde{\mathbf{D}}_\mu(s)\tilde{\mathbf{f}}_\mu(s)] , \tag{25}$$

$$\mathscr{L}[\langle\langle K\rangle\rangle^{(d)}]-\frac{1}{s}\langle\langle K\rangle\rangle_\infty^{(r)} =-p^2\frac{\boldsymbol{\kappa}}{s}[\tilde{\mathbf{f}}_\alpha(s)+\tilde{\mathbf{D}}_\mu(s)\tilde{\mathbf{f}}_\mu(0)] , \tag{26}$$

$$\mathscr{L}[\langle\langle K\rangle\rangle^{(\rm rev)}]-\frac{1}{s}\langle\langle K\rangle\rangle_\infty^{(r)} =2p^2\frac{\boldsymbol{\kappa}}{s}[\tilde{\mathbf{D}}_\mu(s)\tilde{\mathbf{f}}_\mu(s)-\tilde{\mathbf{D}}_\mu(s)\tilde{\mathbf{f}}_\mu(0)] , \tag{27}$$

where $\langle\langle K\rangle\rangle$ represents the ensemble average with the external perturbation p for the corresponding experimental condition indicated by the superscript and

$$\langle\langle K\rangle\rangle_\infty^{(r)}=\lim_{t\to\infty}\langle\langle K\rangle\rangle^{(r)} .$$

Equations (25)—(27) lead to

$$\mathscr{L}[\langle\langle K\rangle\rangle^{(r)}+\langle\langle K\rangle\rangle^{(d)}-\langle\langle K\rangle\rangle_\infty^{(r)}] =p^2\frac{\boldsymbol{\kappa}}{s}\tilde{\mathbf{D}}_\mu(s)[\tilde{\mathbf{f}}_\mu(s)-\tilde{\mathbf{f}}_\mu(0)] , \tag{28}$$

from which we see that the contribution from the permanent dipole moment can be separated out, and for a pure induced dipole system where $D_\mu(t)=\mathbf{f}_\mu(t)=0$,

$$\mathscr{L}[\langle\langle K\rangle\rangle^{(r)}]=p^2\frac{\boldsymbol{\kappa}}{s}\tilde{\mathbf{f}}_\alpha(s) ,$$

and

$$\mathscr{L}[\langle\langle K\rangle\rangle^{(d)}]-\frac{1}{s}\langle\langle K\rangle\rangle_\infty^{(r)}=-p^2\frac{\boldsymbol{\kappa}}{s}\tilde{\mathbf{f}}_\alpha(s) ,$$

which give the symmetrical property that

$$\langle\langle K\rangle\rangle^{(r)}=\langle\langle K\rangle\rangle_\infty^{(r)}-\langle\langle K\rangle\rangle^{(d)} .$$

In the special case of the Kerr effect relaxation for a rigid symmetric body governed by the rotational Smoluchowski equation,[2] the normalized orientation factor $\Phi(t)=\langle\langle P_2(\cos\theta)\rangle\rangle/\langle\langle P_2(\cos\theta)\rangle\rangle_\infty$ for decay, rise, and rapidly reversing transients in the limit of infinitively low fields where θ is an angle of the symmetric axis making with the direction of an appled electric field, and $P_2(z)$ is the second Legendre polynomial has the following properties:

$$\Phi^{(d)}(t)=\exp(-6Dt) ,$$

$$\Phi^{(r)}(t)=1-\frac{3R}{2(R+1)}e^{-2Dt}+\frac{R-2}{2(R+1)}e^{-6Dt} ,$$

$$\Phi^{(\rm rev)}(t)=1-\frac{3R}{R+1}e^{-2Dt}+\frac{3R}{R+1}e^{-6Dt} ,$$

where D is the rotational diffusion constant, and $R=\mu^2/\Delta\alpha k_BT$ in which μ is the permanent dipole moment, $\Delta\alpha$ is the difference in polarizabilities along and perpendicular to the symmetric axis, k_B is the Boltzman constant, and T is the absolute temperature. Hence, we see immediately that

$$\Phi^{(\rm rev)}(t)=2[\Phi^{(d)}(t)+\Phi^{(r)}(t)]-1 .$$

In order to intepret experimental results carried out by Block and Hayes[2] who measured the stationary dielectric dispersion of poly-γ-benzyl-L-glutamate induced by an applied electric field $E(t)=E_1+E_0\cos(\omega t)$ where the strength of E_1 is much stronger than that of E_0, Ullman[5] calculated the Fourier-Laplace transform of the rise transient numerically based on the rotational Smoluchowski equation for a rigid symmetric body, and treated the dielectric dispersion in terms of linear response theory. Morita[6] found this interpretation was not correct and his final result did not agree with that obtained in accordance with the speculation of Ullman. Morita also stated that the experiment of Block and Hayes should be considered by taking not linear but nonlinear response into account. We see directly that the transient time-domain experiment for Eq. (12) corresponds to the stationary frequency-domain one for Eq. (19), thus confirming Morita's statement. This technique is particularly useful for investigating the dynamic behavior of molecules under the strain of a strong biasing external perturbation in which molecules suffer from a structural change. An immediate example is to elucidate dynamic processes of materials exhibiting

We have shown clearly how the stationary distribution function for the single alternating field may be calculated, obtaining a rather complicated final result. It can be shown that the Kramers-Kronig relations[7] which are valid in the case of linear response also holds for the real and imaginary parts of nonlinear susceptibilities, $\chi_j'(b_j)$ and $\chi_j''(b_j)$ in Eq. (17). We have investigated $f_2^{(\infty)}(x,t)$ for the double alternating fields in Eq. (18). The dc component whose frequency dependence gives information of $\mathbf{f}(t)$ was noticed by Hayakawa[8] who showed that it leads to information identical to that obtianed by dielectric dispersion based on a particular model. However, it should be noted that Hayakawa's result is not valid in general, since $D(t)$ may take out different components in $\mathbf{f}(t)$ which are not necessarily equivalent to the ones affecting dielectric dispersion. After putting $\omega_2=0$ or $\omega_1=0$ in Eq. (18), it is interesting to note that the amplitude in the ω_1 or ω_2 component is related to the Laplace transform of the sum of the rise and decay transients [cf. Eq. (15)]. Of course, this case corresponds to that in Eq. (12) when $f_2^{(\infty)}(x,t)$ is obtained. The discussion with respect to the 2ω component was made previously, and the frequency amplitude was related to the Fourier-Laplace transforms of both the rise and decay transients.[1]

The single alternating field response corresponding to the operator in Eq. (21) is given by[1]

$$\langle\langle K\rangle\rangle^{(a)}=k_0(\omega)+k_2'(\omega)\cos(2\omega t)+k_2''(\omega)\sin(2\omega t)\ , \quad (29)$$

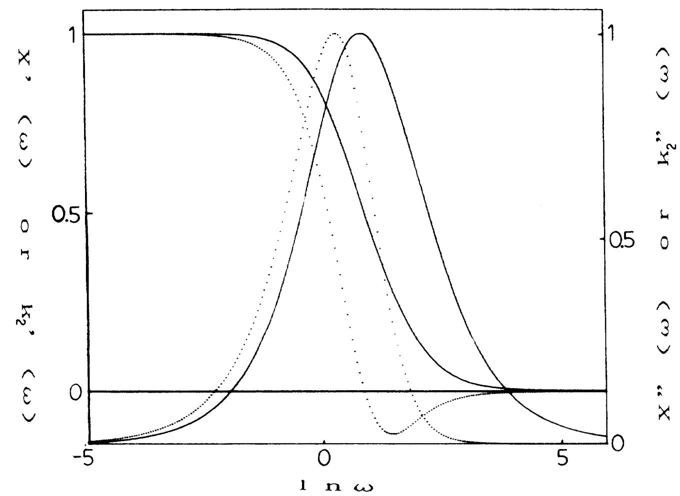

FIG. 2. Plots of normalized values of $X'(\omega)$ (solid monotonically decreasing curve), $X''(\omega)$ (solid curve with a single peak), $k_2'(\omega)$ (dotted curve with a minimum), and $k_2''(\omega)$ (dotted curve with a single peak) vs $\ln(\omega)$. Normalization has been done with respect to the corresponding maximum values, and the rotational diffusion constant D has been set to be 1.

where

$$k_0(\omega)=\tfrac{1}{2}p_0^2\boldsymbol{\kappa}\left[\int_0^\infty \mathbf{D}_\mu(t)dt\int_0^\infty \mathbf{f}_\mu(t)\cos(\omega t)dt+\int_0^\infty \tilde{\mathbf{f}}_\alpha(t)dt\right],$$

$$k_2'-ik_2''(\omega)=\tfrac{1}{2}p_0^2\boldsymbol{\kappa}[\tilde{\mathbf{D}}_\mu(2i\omega)\tilde{\mathbf{f}}_\mu(i\omega)+\tilde{\mathbf{f}}_\alpha(2i\omega)]\ .$$

It is evident from Eq. (30) that the frequency dependence of the dc component gives contribution from the permanent dipole moment. If the dc component is found to be independent of frequency, then the system is composed of molecules with induced dipoles only.

Finally, in order to see how experimental results may be in the case of $p(t)=A\cos(\omega_1 t)+B\cos(\omega_2 t)$, we consider a specific example of Kerr effect relaxation of the rigid symmetrical body in the limit of extremely weak fields. We find the stationary orientation factor $\Phi^{(\infty)}(t)$ contributing to the coefficient of AB term as given by [use Eq. (6.14) of Watanabe and Morita[2]]

$$\Phi^{(\infty)}(t)\propto AB\left[\frac{96+8(\omega_1^2+\omega_2^2-\omega_1\omega_2)-\omega_1\omega_2(\omega_1+\omega_2)^2}{(\omega_1^2+4)(\omega_2^2+4)[(\omega_1+\omega_2)^2+36]}\cos[(\omega_1+\omega_2)t]\right.$$
$$+\frac{96+8(\omega_1^2+\omega_2^2+\omega_1\omega_2)+\omega_1\omega_2(\omega_1+\omega_2)^2}{(\omega_1^2+4)(\omega_2^2+4)[(\omega_1-\omega_2)^2+36]}\cos[(\omega_1-\omega_2)t]$$
$$+\frac{2(\omega_1+\omega_2)(20+\omega_1^2+\omega_2^2+3\omega_1\omega_2)}{(\omega_1^2+4)(\omega_2^2+4)[(\omega_1+\omega_2)^2+36]}\sin[(\omega_1+\omega_2)t]$$
$$\left.+\frac{2(\omega_1-\omega_2)(20+\omega_1^2+\omega_2^2-3\omega_1\omega_2)}{(\omega_1^2+4)(\omega_2^2+4)[(\omega_1-\omega_2)^2+36]}\sin[(\omega_1-\omega_2)t]\right],$$

where the rotational diffusion constant D is set to be 1 for convenience. By putting $\omega_2=0$ and $\omega_1=\omega$ which corresponds to the case of a weak ac superimposed on a weak dc biasing fields, we have

$$\Phi^{(\infty)}(t) \propto AB[X'(\omega)\cos(\omega t)+X''(\omega)\sin(\omega t)]$$

where

$$X'(\omega)=2\frac{\omega^2+12}{(\omega^2+4)(\omega^2+36)} ,$$

and

$$X''(\omega)=\frac{\omega(\omega^2/2+10)}{(\omega^2+4)(\omega^2+36)} .$$

In Fig. 2, we show $X'(\omega)$ and $X''(\omega)$ as normalized by the corresponding maximum values (solid curves) together with $k_2'(\omega)$ and $k_2''(\omega)$ (dotted curves) for a single ac field determined previously by Ogawa and Oka[9] and by Thurston and Bowling[10] who obtained

$$\Phi^{(\infty)}(t) \propto k_2'(\omega)\cos(2\omega t)+k_2''(\omega)\sin(\omega t) ,$$

where

$$k_2'(\omega)=\frac{6-\omega^2}{(\omega^2+4)(4\omega^2+36)}$$

and

$$k_2''(\omega)=\frac{5\omega}{(\omega^2+4)(4\omega^2+36)} .$$

It should be noted that the maximum of $X''(\omega)$ appears higher on the frequency side than that of $k''(\omega)$. In fact, it follows that the maximum frequencies $\omega_{\max}$ for the former and latter are 2.372 and 1.385, respectively.

It is hoped that theoretical predictions in this paper will be checked experimentally, and used as useful techniques.

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