Theory of nonlinear response

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(Received 24 February 1986)

The problem of nonlinear response is considered by employing a general time-evolution equation, and a Green's function which is the transition or conditional probability density for an unperturbed system. Expansion of the Green's function in terms of orthonormal functions enables us to express the distribution function describing the nonlinear behavior by means of matrix products whose elements are composed of correlation functions in the absence of the perturbation. In other words, it is shown how the distribution function induced by a strong perturbation may be calculated by knowing the Green's function without the perturbation. As the special case of the linear response, we have obtained Kubo's relation. The Laplace-transform technique with respect to time is found quite useful in developing the present theory in which the transient effect is also taken into account. As an application of the theory, a new relation valid in the region of the second-order perturbation connecting the transient rise and decay with the stationary alternating perturbations has been obtained.

INTRODUCTION

Although the general theory of linear response is available and widely used to interpret various phenomena,[1] that of nonlinear response has been in an infant stage.[2] This paper is devoted to shedding light on the latter.

Instead of starting from the Liouville equation for the distribution function, which Kubo took in developing his theory of linear response,[1] we use a general evolution equation for a classical system, and consider how a system may respond to a strong external perturbation. By introducing a Green's function which is the transition- or conditional-probability density for the evolution equation without the perturbation, and expanding it in terms of orthonormal functions, we find terms characterizing the nonlinear responses with matrix products consisting of correlation functions obtained without taking into account the perturbation. In other words, we show how the nonlinear terms in the distribution function induced by the strong perturbation may be calculated once the transition-probability density (the Green function) is obtained without considering the perturbation.

The transient processes are included in the present theory. As an application, we have shown for a physical variable observed in the second-order perturbation region how the transient rise and decay experiments are related to the observable arising from a stationary alternating perturbation.

Previously we have considered the transient behavior of the electric polarization and birefringence by using the Smoluchowski equation for a rigid symmetric body which undergoes the rotational Brownian motion.[3] The Smoluchowski equation was expanded by means of Legendre polynomial, and the Laplace transform technique with respect to time was employed. It was shown that in some cases, the Laplace transforms of the electric polarization and birefringence have been expressed exactly in terms of an infinite continued fraction. We suggested[3,4] that the technique of the Laplace transform and the continued fraction might play a significant role in considering the nonlinear relaxation phenomena. This point is also appreciated in a later work.[5] In the present study, we take a similar approach in developing the general theory except when introducing the Green function. New general interpretations of various nonlinear relaxation phenomena using results of the present work will be made in future publications. At the same time, new phenomena predicted theoretically from the work will be considered.

THEORETICAL FORMALISM

We shall calculate the distribution function $f(x,t)$ satisfying the following evolution equation:

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

and to obtain the average value $\langle\langle B(t)\rangle\rangle$ of a physical variable $B(x)$ by using

$$\langle\langle B(t)\rangle\rangle=\int B(x)f(x,t)dx , \tag{2}$$

where x is a set of variables other than the time t specifying $f(x,t)$, $\hat{D}_0(x)$ and $\hat{D}_1(x)$ are unperturbed and perturbed operators, respectively, $p(t)$ is a function of t, ε is the small parameter, and $\langle\langle \cdots \rangle\rangle$ and $\langle \cdots \rangle$ represent the ensemble averages with and without considering the perturbation, respectively. The Fokker-Planck and Liouville equations can be written as given in Eq. (1). The complete statistical-mechanical information on the unperturbed system is contained in the conditional-probability-density function or the transition-probability density $g(x,x',t,t')$ which satisfies

$$\frac{\partial g(x,x',t,t')}{\partial t}=\hat{D}_0(x)g(x,x',t,t') \tag{3}$$

with the initial condition

$$g(x,x',t,t')=\delta(x-x') \text{ at } t=t' , \tag{4}$$

where $\delta(x)$ is Dirac's δ function.

At this stage, it is appropriate to obtain some of important properties of $g(x,x',t,t')$. To this end, by putting $t'=0$, taking the Laplace transform of both sides of Eq. (3) with respect to t, and using Eq. (4), we find that

$$[s-\hat{D}_0(x)]\tilde{G}(x,x',s)=\delta(x-x') , \tag{5}$$

where

$$\tilde{G}(x,x',s)=\mathscr{L}[g(x,x',t,0)] = \int_0^\infty g(x,x',t,0)e^{-st}dt . \tag{6}$$

The tilda above the symbol indicates the Laplace transform with respect to t. It should be pointed out here that $\tilde{G}(x,x',s)$ can be regarded as Green's function for the operator $[s-\hat{D}_0(x)]$. Hence after taking the Laplace transform of both sides of Eq. (1), we can write it in the integral equation

$$\tilde{F}(x,s)=\int \tilde{G}(x,x',s)f_0(x')dx' + \varepsilon \int \tilde{G}(x,x',s)\hat{D}_1(x')\mathscr{L}[p(t)f(x',t)]dx' \tag{7}$$

whose inverse transform gives

$$f(x,t)=\int g(x,x',t,0)f_0(x')dx' + \varepsilon \int \int_0^t g(x,x',t-t',0) \times \hat{D}_1(x')p(t')f(x',t')dx'dt' , \tag{8}$$

where $f_0(x)=f(x,0)$, and $\tilde{F}(x,s)=\mathscr{L}[f(x,t)]$.

To go further, by calculating

$$f(x,t)=f_0(x)+\varepsilon f_1(x,t)+\varepsilon^2 f_2(x,t)+\cdots , \tag{9}$$

we have the hierarchy of equations

$$f_1(x,t)=\int \int_0^t g(x,x',t-t')\hat{D}_1(x')p(t')f_0(x')dt'dx' , \tag{10}$$

$$f_j(x,t)=\int \int_0^t g(x,x',t-t')\hat{D}_1(x')p(t')f_{j-1}(x',t')dt'dx' \quad (j=2,3,4,\ldots) \tag{11}$$

which lead to

$$f_j(x,t)=\int\int_{t\geq t_1\geq t_2\geq \cdots \geq t_j\geq 0}\cdots\int dt_1 dt_2\cdots dt_j \int\int\cdots\int dx_1 dx_2\cdots dx_j\, g(x,x_1,t-t_1)\hat{D}_1(x_1) \times g(x_1,x_2,t_1-t_2)\hat{D}_1(x_2)\cdots g(x_{j-1},x_j,t_{j-1}-t_j) \times \hat{D}_1(x_j)f_0(x_j)p(t_1)p(t_2)\cdots p(t_j) . \tag{12}$$

By using the relation

$$\hat{D}_0(x)f_0(x)=0$$

and Eq. (5), it follows that

$$f_0(x)=\int g(x,x',t,0)f_0(x')dx' ,$$

which should be in view of the facts that $g(x,x',t)$ is the transition probability and $f_0(x)$ is the equilibrium distribution function in the absence of the perturbation. We introduce a set of orthonormal eigenfunctions $g_n(x)$ which satisfies the eigenequation

$$\hat{D}_0(x)g_n(x)=-\lambda_n g_n(x) \tag{13}$$

with the eigenvalue $-\lambda_n$. Then by writing

$$\delta(x-x')=\sum_n g_n(x)g_n^*(x')$$

and using Eq. (13), we find from Eq. (5) after translating the origin of t from 0 to t' that

$$g(x,x',t,t')=g(x,x',t-t')=\sum_n e^{-\lambda_n(t-t')}g_n(x)g_n^*(x') . \tag{14}$$

Therefore, it follows by substituting Eq. (14) in Eq. (12) and carrying out integrations that

$$f_j(x,t)=\int\int_{t\geq t_1\geq \cdots \geq t_j\geq 0}\cdots\int \underline{g}\underline{D}(t-t_1)\underline{D}(t_1-t_2)\cdots \underline{D}(t_{j-2}-t_{j-1})\underline{f}(t_{j-1}-t_j)p(t_1)p(t_2)\cdots p(t_j)dt_1dt_2\cdots dt_j \tag{15}$$

where

$$\underline{g}=[g_1,g_2,g_3,\ldots] , \tag{16}$$

$$\underline{f}(t)=\begin{bmatrix} e^{-\lambda_1 t}(g_1^*,\hat{D}_1 f_0) \\ e^{-\lambda_2 t}(g_2^*,\hat{D}_1 f_0) \\ e^{-\lambda_3 t}(g_3^*,\hat{D}_1 f_0) \\ \vdots \end{bmatrix} = \begin{bmatrix} (g_1^*(t)\,|\,\hat{D}_1 f_0) \\ (g_2^*(t)\,|\,\hat{D}_1 f_0) \\ (g_3^*(t)\,|\,\hat{D}_1 f_0) \\ \vdots \end{bmatrix} = \begin{bmatrix} \langle g_1^*(t)Q(x)\rangle \\ \langle g_2^*(t)Q(x)\rangle \\ \langle g_3^*(t)Q(x)\rangle \\ \vdots \end{bmatrix}, \tag{17}$$

$$\underline{D}(t)=\begin{bmatrix} d_{11} & d_{12} & d_{13} & \cdots \\ d_{21} & d_{22} & d_{23} & \cdots \\ d_{31} & d_{32} & d_{33} & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{bmatrix}, \tag{18}$$

in which $n=1,2,3,\ldots$ have been taken and

$$\begin{aligned} &\hat{D}_1(x)f_0(x)=Q(x)f_0(x)\,, \\ &d_{ij}(t)=e^{-\lambda_i t}(g_i^*,\hat{D}_1 g_j)=(g_i^*(t)\,|\,\hat{D}_1 g_j)=\langle g_i^*(t)\eta_j\rangle\,. \end{aligned} \tag{19}$$

In the foregoing equations,

$$\begin{aligned} &(A^*,B)=\int A^*(x)B(x)dx\,, \\ &(A^*(t)\,|\,B)=\int\int A^*(x)g(x,x',t)B(x')dx'\,dx\,, \\ &\langle A^*(t)B\rangle=(A^*(t)\,|\,Bf_0)\,, \\ &\hat{D}_1(x)g_j(x)=\eta_j(x)f_0(x)\,. \end{aligned}$$

The difference between $(A^*(t)\,|\,B)$ and the correlation function $\langle A^*(t)B\rangle$ should be noted. In the special case where $f_0(x)$ is independent of x, $(A^*(t)\,|\,B)$ is equivalent to $\langle A^*(t)B\rangle$. Hence, it has been shown that once $g(x,x',t,t')$ is obtained or a stochastic equation without the perturbation is solved with the initial condition, we can determine $(A^*(t)\,|\,B)$ and $\langle A^*(t)B\rangle$ and finally $f_j(x,t)$ from Eqs. (15)—(19).

Equation (15) leads to

$$\begin{aligned} \underline{a}(t)=\varepsilon\int_0^t \underline{f}(t-t_1)p(t_1)dt_1+\varepsilon^2\int_0^t\int_0^{t_1}\underline{D}(t-t_1)\underline{f}(t_1-t_2)p(t_1)p(t_2)dt_2\,dt_1 \\ +\varepsilon^3\int_0^t\int_0^{t_1}\int_0^{t_2}\underline{D}(t-t_1)\underline{D}(t_1-t_2)\underline{f}(t_2-t_3)p(t_1)p(t_2)p(t_3)dt_3\,dt_2\,dt_1+\cdots\,, \end{aligned} \tag{20}$$

where

$$\underline{a}(t)=\begin{bmatrix} \langle\langle g_1^*(t)\rangle\rangle-\langle g_1^*\rangle_0 \\ \langle\langle g_2^*(t)\rangle\rangle-\langle g_2^*\rangle_0 \\ \langle\langle g_3^*(t)\rangle\rangle-\langle g_3^*\rangle_0 \\ \vdots \end{bmatrix} \tag{21}$$

in which

$$\langle g_m^*\rangle_0=(g_m^*,f_0)\,. \tag{22}$$

In the Appendix, it has been shown that $\underline{a}(t)$ obtained without using the Green function agrees fully with that in Eq. (20), which gives a check of the validity of Eq. (15) from a different approach, although this approach does not allow the physical interpretation of $d_{ij}(t)$ in Eq. (19).

DISCUSSION

The present formulation takes into account not only the aged system where the perturbation was switched on at $t=-\infty$, but also the transient response. First let us consider the latter processes of (a) transient rise and (b) decay where $p(t)=p_0$ is time independent. The transient rise experiment is carried out by suddenly applying p_0 at $t=0$ whereas the transient decay is obtained by applying p_0 for sufficiently long time then suddenly at $t=0$ it is switched off. On taking the Laplace transform of both sides of Eq. (15), we find that

$$\tilde{F}_j^{(r)}(x,s)=\mathscr{L}[f_j^{(r)}(x,t)]=\frac{p_0^j}{s}\underline{g}\tilde{\underline{D}}^{\,j-1}(s)\tilde{\underline{f}}(s)\,, \tag{23}$$

where

$$\tilde{\underline{D}}(s)=\mathscr{L}[\underline{D}(t)]\,,$$

$$\tilde{\underline{f}}(s)=\mathscr{L}[\underline{f}(t)]\,.$$

Hence it follows that

$$\tilde{F}^{(r)}(x,s)=\frac{1}{s}f_0(x)+\frac{1}{s}\varepsilon p_0\underline{g}\tilde{\underline{\Phi}}(s)\tilde{\underline{f}}(s)\,, \tag{24}$$

where

$$\tilde{\underline{\Phi}}(s)=\sum_{j=0}^{\infty}\varepsilon^j p_0^j \tilde{\underline{D}}(s)=[\underline{1}-\varepsilon p_0\tilde{\underline{D}}(s)]^{-1}\ , \tag{25}$$

in which $\underline{1}$ is the identity matrix. It is immediately seen that once the diagonalization of $\tilde{\underline{D}}(s)$ is made, we can write $\tilde{F}^{(r)}(x,s)$ in the closed matrix form whose inverse Laplace transform gives $f^{(r)}(x,t)$. Also it should be noted from Eq. (A4) in the Appendix that $\tilde{\underline{A}}(s)=\mathscr{L}[a(t)]$ satisfies the relation

$$[\underline{1}-\varepsilon p_0\tilde{\underline{D}}(s)]\tilde{\underline{A}}(s)=\frac{\varepsilon p_0}{s}\tilde{\underline{f}}(s)$$

which is also obtained directly from Eq. (25). It is sometimes useful to calculate $\tilde{\underline{A}}(s)$ from this relation.[3]

The equilibrium distribution function $f_{\rm eq}(x)$ with the time-independent perturbation p_0 can be obtained at once from Eq. (24),

$$\begin{aligned} f_{\rm eq}(x)&=\lim_{t\to\infty} f^{(r)}(x,t)=\lim_{s\to 0}[s\tilde{F}^{(r)}(x,s)]\\ &=f_0(x)+\varepsilon p_0\underline{g}\tilde{\underline{\Phi}}(0)\tilde{\underline{f}}(0)\ . \end{aligned} \tag{26}$$

The distribution function for the transient decay $f^{(d)}(x,t)$ is obtained from the relation

$$[s-\hat{D}_0(x)]\tilde{F}^{(d)}(x,s)=f_{\rm eq}(x) \tag{27}$$

which leads to

$$\begin{aligned} \tilde{F}^{(d)}(x,s)&=\mathscr{L}[f^{(d)}(x,t)]\\ &=\int \tilde{G}(x,x',s)f_{\rm eq}(x')dx'\ . \end{aligned} \tag{28}$$

In view of Eq. (26), we find that

$$f^{(d)}(x,t)=f_0(x)+\varepsilon p_0\underline{g}^{(d)}(t)\tilde{\underline{\Phi}}(0)\tilde{\underline{f}}(0) \tag{29}$$

where

$$\underline{g}^{(d)}=(e^{-\lambda_1 t}g_1,e^{-\lambda_2 t}g_2,e^{-\lambda_3 t}g_3,\ldots)\ .$$

It should be noted that when the linear response is considered so that higher-order perturbation terms than ε^2 are neglected, we have

$$\tilde{\underline{\Phi}}(s)=\tilde{\underline{\Phi}}(0)=\underline{1}$$

which leads to

$$f^{(r)}(x,t)=f_0(x)+\varepsilon p_0\underline{g}\int_0^t \underline{f}(t')dt'+O(\varepsilon^2) \tag{30}$$

and

$$\begin{aligned} f^{(d)}(x,t)&=f_0(x)+\varepsilon p_0\underline{g}\left[\tilde{\underline{f}}(0)-\int_0^t \underline{f}(t')dt'\right]+O(\varepsilon^2)\\ &=f_{\rm eq}(x)-\varepsilon p_0\underline{g}\int_0^t \underline{f}(t')dt'+O(\varepsilon^2)\ . \end{aligned} \tag{31}$$

It is evident that for $\varepsilon \ll 1$,

$$f^{(r)}(x,t)+f^{(d)}(x,t)=f_0(x)+f_{\rm eq}(x) \tag{32}$$

which is the well-known symmetrical relation between the transient rise and decay in the linear regime and the correlation function matrix $\underline{f}(t)$ determines the dynamical process.

Now, let us consider the second-order response from the perturbation. Equation (23) gives rise to

$$\tilde{F}_2^{(r)}(x,s)=\frac{p_0^2}{s}\underline{g}\tilde{\underline{D}}(s)\tilde{\underline{f}}(s)\ , \tag{33}$$

whereas Eq. (29) leads to the following expression:

$$\begin{aligned} \tilde{F}_2^{(d)}(x,s)&=\frac{p_0^2}{s}\underline{g}[\tilde{\underline{D}}(0)-\tilde{\underline{D}}(s)]\tilde{\underline{f}}(0)\\ &=\frac{1}{s}\lim_{t\to\infty} f_2^{(r)}(x,t)-\frac{p_0^2}{s}\underline{g}\tilde{\underline{D}}(s)\tilde{\underline{f}}(0)\ . \end{aligned} \tag{34}$$

Hence it is seen that $\tilde{F}_2^{(d)}(x,s)$ is determined from $\tilde{\underline{D}}(s)$, whereas $\tilde{F}_2^{(r)}(x,s)$ from both $\tilde{\underline{D}}(s)$ and $\tilde{\underline{f}}(s)$ and the symmetrical relation like Eq. (32) no longer holds in the first nonlinear term.

Next, we consider the case where an alternating perturbation

$$p(t)=p_0\cos(\omega t)\ , \tag{35}$$

is applied at $t=0$. It follows from Eq. (15) that

$$f_1^{(a)}(x,t)=p_0\underline{g}\int_0^t \underline{f}(t-t')\cos(\omega t')dt'\ , \tag{36}$$

$$\begin{aligned} f_2^{(a)}(x,t)=p_0^2\underline{g}\int_0^t\int_0^{t_1}&\underline{D}(t-t_1)\underline{f}(t_1-t_2)\\ &\times\cos(\omega t_1)\cos(\omega t_2)dt_2\,dt_1\ . \end{aligned} \tag{37}$$

In the limit of $t\to\infty$, it can be shown that

$$\begin{aligned} \lim_{t\to\infty} f_1^{(a)}(x,t)&=f_1^{(\infty)}(x,t)\\ &=\chi'(\omega)\cos(\omega t)+\chi''(\omega)\sin(\omega t)\ , \end{aligned} \tag{38}$$

$$\begin{aligned} \lim_{t\to\infty} f_2^{(a)}(x,t)&=f_2^{(\infty)}(x,t)\\ &=\alpha_0(\omega)+\alpha_2(\omega)\cos(2\omega t)\\ &\quad+\beta_2(\omega)\sin(2\omega t)\ , \end{aligned} \tag{39}$$

where

$$\chi'(\omega)=p_0\underline{g}\int_0^\infty \underline{f}(t)\cos(\omega t)dt\ , \tag{40a}$$

$$\chi''(\omega)=p_0\underline{g}\int_0^\infty \underline{f}(t)\sin(\omega t)dt\ , \tag{40b}$$

$$\alpha_0(\omega)=\tfrac{1}{2}p_0^2\underline{g}\int_0^\infty \underline{D}(t)dt\int_0^\infty \underline{f}(t)\cos(\omega t)dt\ , \tag{41a}$$

$$\alpha_2(\omega)=\tfrac{1}{2}p_0^2\underline{g}\int_0^\infty\int_0^\infty \underline{D}(t_1)\underline{f}(t_2)\cos[\omega(2t_1+t_2)]dt_1dt_2\ , \tag{41b}$$

$$\beta_2(\omega)=\tfrac{1}{2}p_0^2\underline{g}\int_0^\infty\int_0^\infty \underline{D}(t_1)\underline{f}(t_2)\sin[\omega(2t_1+t_2)]dt_1dt_2\ . \tag{41c}$$

It is seen immediately from Eqs. (30) and (36) that since $f_1^{(r)}(x,t)$ and $f_1^{(\infty)}(x,t)$ for the transient rise and alternating perturbation, respectively, are derived from the same matrix $\underline{f}(t)$,

$$\omega \int_0^\infty f_1^{(r)}(x,t)\cos(\omega t)dt = -\chi''(\omega) , \quad (42a)$$

$$\omega \int_0^\infty f_1^{(r)}(x,t)\sin(\omega t)dt = \chi'(\omega) . \quad (42b)$$

These are the well-known results stating that $\chi'(\omega)$ and $\chi''(\omega)$ may be obtained either from the transient rise or decay experiment after carrying out the integration in Eq. (36). To extend this approach to the nonlinear response, we note that

$$\alpha_2(\omega) - i\beta(\omega) = \tfrac{1}{2}p_0^2 \underline{g} \int_0^\infty \int_0^\infty \underline{D}(t_1)\underline{f}(t_2) \times e^{-i\omega(2t_1+t_2)} dt_1\, dt_2 \quad (43)$$

and confine ourselves to the physical variable $g_n^*(x)$ whose contribution to the average value from $f_2(x,t)$ is denoted by

$$\psi_n(t) = \int g_n^* f_2(x,t)dx .$$

It follows from Eqs. (33) and (34) that for the transient rise and decay responses

$$\tilde{\Psi}_n^{(d)}(s) = \mathscr{L}[\psi_n^{(d)}(t)] = \frac{1}{s}\psi_n^{(r)}(\infty) - \frac{p_0^2}{s(s+\lambda_n)} \sum_j \frac{d_{nj}^0 f_j^0}{\lambda_j} , \quad (44a)$$

$$\tilde{\Psi}_n^{(r)}(s) = \mathscr{L}[\psi_n^{(r)}(t)] = \frac{p_0^2}{s(s+\lambda_n)} \sum_j \frac{d_{nj}^0 f_j^0}{s+\lambda_j} , \quad (44b)$$

where

$$\psi_n^{(r)}(\infty) = \lim_{t\to\infty} \psi_n^{(r)}(t), \quad d_{nj}^0 = (g_n^*, \hat{D}_1 g_j) ,$$

and

$$f_j^0 = (g_j^*, \hat{D}_1 f_0) .$$

By putting $s = i\omega$, and $2i\omega$ in Eq. (44a) and $s = i\omega$ in Eq. (44b), we find from Eqs. (41a) and (43),

$$\alpha_0^{(n)}(\omega) = \tfrac{1}{2}p_0^2 \,\mathrm{Re}\left[\frac{1}{\lambda_n}\sum_j \frac{d_{nj}^0 f_j^0}{i\omega+\lambda_j}\right] = \tfrac{1}{2}\mathrm{Re}\left[i\omega \frac{\tilde{\Psi}_n^{(r)}(i\omega)\psi_n^{(r)}(\infty)}{\psi_n^{(r)}(\infty) - i\omega\tilde{\Psi}_n^{(d)}(i\omega)}\right] , \quad (45a)$$

$$\alpha_2^{(n)}(\omega) - i\beta_2^{(n)}(\omega) = \tfrac{1}{2}p_0^2 \frac{1}{2i\omega+\lambda_n} \sum_j \frac{d_{nj}^0 f_j^0}{i\omega+\lambda_j} = \tfrac{1}{2}i\omega\tilde{\Psi}_n^{(r)}(i\omega) \times \frac{\psi_n^{(r)}(\infty) - 2i\omega\tilde{\Psi}_n^{(d)}(2i\omega)}{\psi_n^{(r)}(\infty) - i\omega\tilde{\Psi}_n^{(d)}(i\omega)} , \quad (45b)$$

where

$$\alpha_l^{(n)}(\omega) = (g_n^*, \alpha_l(\omega)) \quad (l = 0 \text{ or } 2) ,$$

$$\beta_2^{(n)}(\omega) = (g_n^*, \beta_2(\omega)) .$$

These are new results relating the stationary alternating and transient nonlinear responses of the physical variable $g_n^*(x)$ caused by the perturbation. It is important to note that Eqs. (45) are valid quite generally and independent of stochastic models as far as the same $\psi_n(t)$ is measured with different kinds of experimental perturbations. Equations (45) enable us to set up an instrument measuring the transient rise and decay processes (the time-domain measurement) and giving rise to data in frequency domain, although the relation becomes more complicated than the linear case.

By comparing Eqs. (45a) with (41a), one may be tempted to say that since the frequency-dependent parts of both $\chi'(\omega)$ and $\alpha_0(\omega)$ are essentially determined from $\underline{f}(t)$ through Eq. (45a) and

$$\chi'^{(m)}(\omega) = (g_m^*, \chi'(\omega)) = p_0 \,\mathrm{Re}\frac{f_m^0}{i\omega+\lambda_m} , \quad (46)$$

the frequency dependencies are equivalent. But this is not always possible unless

$$d_{nj}^0 f_j^0 = c\delta_{mj} ,$$

where c is a constant, and δ_{ij} is the Kronecker δ.

Kubo treated the linear response starting from the following Liouville equation:[1]

$$\frac{\partial f(x,t)}{\partial t} = [H, f(x,t)] , \quad (47)$$

where H is the Hamiltonian of a system and $[A,B]$ is the Poisson bracket, and $f_1(x,t)$ obtained for the aged system. Equation (12) of our treatment leads in the limit of linear response to

$$f(x,t) - f_0(x) = f_1(x,t) = \int \int_0^t g(x,x',t-t') \times \hat{D}_1(x')f_0(x')p(t')dt'\,dx'$$

which immediately enables us to write for a physical variable $B(x)$:

$$\langle\langle B(t)\rangle\rangle - \langle B\rangle_0 = \int_0^t \phi(t-t')p(t')dt'$$

where

$$\phi(t) = (B(t) \mid \hat{D}_1 f_0) . \quad (48)$$

It should be noted that $\phi(t)$ is independent of the eigenfunction, $g_n(x)$. In other words, $\phi(t)$ can be written if $\langle B(t)\rangle_c$ is obtained and it is integrated with $\hat{D}_1(x')f_0(x')$, where $\langle B(t)\rangle_c$ is the conditional average defined by the equation

$$\langle B(t)\rangle_c = \int B(x)g(x,x',t-t')dx . \quad (49)$$

Kubo obtained the following expression for the function corresponding to $\phi(t)$ [see Eq. (2.11) of the second paper of Ref. 1]:

$$\phi_K(t) = -\int [A, f_0]B(t)dx' \quad (50)$$

where he treated for

$$H = H_0 - \varepsilon p(t)A .$$

If we write Eq. (47) by using our notation, we see that

$$\hat{D}_0(x)\xi(x)=[H_0,\xi] ,$$

$$\hat{D}_1(x)\xi(x)=-[A,\xi] ,$$

from which it follows that

$$\phi(t)=-(B(t)\,|\,[A,f_0]) . \qquad (51)$$

By comparing Eq. (50) with (51), it is seen that $B(t)$ in Kubo's case is corresponding to the conditional average $\langle B(t)\rangle_c$ in the present work, which is the same in the special case of the deterministic process described by the Liouville equation where the transition probability $g(x,x',t,t')$ becomes a δ function. Our case includes stochastic processes as well, and the Liouville operator formalism or the Poisson bracket formalism requires special consideration in obtaining further expressions for $\phi_K(t)$ as demonstrated by Kubo such as the conservation of the element of the phase space.

It is particularly comforting to find that the results of the present treatment lead to those of the previous special example of the nonlinear process arising from the rotational Brownian motion of a rigid symmetric body.

APPENDIX: ANOTHER DERIVATION OF EQ. (20)

On substituting Eq. (9) directly in Eq. (1), we find that

$$\frac{\partial f_j(x,t)}{\partial t}=\hat{D}_0(x)f_j(x,t)+\varepsilon p(t)\hat{D}_1(x)f_{j-1}(x,t) \qquad (\text{A}1)$$

which leads to

$$\left[\frac{\partial}{\partial t}-\hat{D}_0(x)-\varepsilon p(t)\hat{D}_1(x)\right][f(x,t)-f_0(x)] =\varepsilon p(t)\hat{D}_1(x)f_0(x) . \qquad (\text{A}2)$$

And by expanding

$$f(x,t)-f_0(x)=\sum_n a_n(t)g_n(x) \qquad (\text{A}3)$$

where

$$a_n(t)=\langle\langle g_n^*(t)\rangle\rangle-\langle g_n^*\rangle_0 ,$$

and integrating the resulting simultaneous differential equations for $a_n(t)$, we have

$$\underline{a}(t)=\varepsilon\int_0^t \underline{f}(t-t')p(t')dt' +\varepsilon\int_0^t \underline{D}(t-t')\underline{a}(t')p(t')dt' , \qquad (\text{A}4)$$

from which Eq. (20) is derived after carrying out Piccard's successive integrations.

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