Physica **109A** (1981) 221–236 *North-Holland Publishing Co.*

CLOSED TIME PATH GREEN'S FUNCTIONS AND NONLINEAR RESPONSE THEORY

Bai-lin HAO*

Faculté des Sciences, Université Libre de Bruxelles, Campus Plaine, U.L.B., C.P. 231, 1050 Brussels, Belgium

Received 19 March 1981

This paper presents yet another application, perhaps the simplest one, of the Closed Time Path Green's Function (hereafter abbreviated to CTPGF) technique to nonequilibrium problems. General expressions for nonlinear responses are derived using CTPGF. Various arguments leading to relations among high order response functions are outlined.

1. Introduction

Linear response theory, centered on the reciprocal relation for kinetic coefficients and the fluctuation-dissipation theorem[1-3]), no doubt belongs to one of the most successful chapters in nonequilibrium statistical physics. Nevertheless, nonlinear response has not yet become an active field of research, in spite of a few formal developments[4-8]). Indeed there are some reasons for this slow-footed advance in nonlinear response theory.

First, usual criticism on linear response theory, cf., for example[9]), refers to nonlinear response to even larger extent. In addition, nonlinear response theory has its own difficulty of principle. Linear response reflects intrinsic properties of a physical system, independent upon boundary conditions. On taking into account nonlinear terms in external fields there appears the heating effect. In order to keep the system in stationary state, one has to remove the heat thus generated. Therefore, generally speaking, nonlinear response would depend not only on the physical system itself, but also on boundary conditions; still, one can manage to avoid the heating problem in practice. For instance, two-dimensional systems immersed in liquid helium, owing to high heat conductivity of helium, could provide good objects for measuring nonlinear response.

Second, except for nonlinear optics and a few other cases there has not been urgent necessity in nonlinear response theory. Moreover, nonlinear

* On leave from the Institute of Theoretical Physics, Academia Sinica, Beijing, China.

0378-4371/81/0000–0000/$02.75

response deals with functions of many time arguments which require more subtle data acquisition and processing techniques to be used in measurement. Four-point correlation functions have attracted more attention quite recently[10]. Progress in picosecond technique and multichannel analysis of time signal sequences will certainly make the measurement of multi-point response functions practical thing. Provided the nonlinearity of a physical system being notable, the study of nonlinear response should yield more knowledge about the system. Therefore, it seems desirable to have a more detailed analysis of various relations among multi-point response functions.

Third, the formulation of nonlinear response theory has become tedious due to the lack of systematic and concise notations. It was difficult to tell the general form of various relations. Nevertheless, the development of the closed time path Green's function technique has provided a suitable tool for analysing nonlinear response. Many relations obtainable otherwise by more or less complicated means look very simple in the language of CTPGF.

In view of the success of linear response theory, one should not hesitate at the criticism mentioned before. At least, the problem of an overall analysis of the formal relations in nonlinear response theory is ripe for settlement. This is the motivation of our paper.

2. Closed time path Green's functions

First introduced by Schwinger[11] and further elaborated by Keldysh[12] and many others, the CTPGF technique has since furnished powerful means to treat equilibrium and nonequilibrium problems in a unique way, yet its potentiality has not been widely recognized (see[13] and references cited therein). In particular, the transformation relations among three sets of CTPGF's[14,15] lead naturally to a unique definition of multipoint retarded, advanced and correlated functions and automatically fulfil the causality requirement at every step of derivation. Incorporated with generating functional formalism, the perturbative expansion of averages of physical quantities and their fluctuations leads directly to general formulae for nonlinear response. We shall not repeat the detailed discussion of various properties of CTPGF, given in [13–15], but only list here the notations and definitions needed below.

n-point Green's function $G_p(1, 2, \ldots, n)$, defined on the closed time path, are nth variational derivatives of the generating functional $Z[J]$ or $W[J]$. Various relations, written in terms of G_p, retain a maximum parallelism with quantum field theory. By fixing the time branch of each argument G_p becomes 2^n functions $G_{\alpha\beta\ldots\gamma}(1, 2, \ldots, n)$, where the Greek indices take the value $+$ or $-$. They may be viewed as components of a matrix Green's function $\hat{G}$. They are needed for calculating the Feynman diagrams. Genuine physical relations are expressed through linear combinations of these $G_{\alpha\beta\ldots\gamma}$. They are components $G_{ij\ldots k}(1, 2, \ldots, n)$ of another matrix Green's function $\tilde{G}$, the Latin indices being 1 or 2.

External sources J_+ and J_- on the positive and negative time branches will be put equal to the physical external field $J_+ = J_- = J$ only at the last stage of calculation. The difference $J_+ - J_-$ plays the role of the fictitious external source in Schwinger's formalism of generating functionals. Equalities $J_+ = J_- = J$ and $J = 0$ may be taken at two distinct steps. This leads from the normalization condition of the generating functionals

$$Z[J_+, J_-]\,|_{J_+=J_-=J} = 1, \tag{2.1}$$

$$W[J_+, J_-]\,|_{J_+=J_-=J} = 0, \tag{2.2}$$

to the identity

$$\sum_{\alpha\beta\ldots\gamma} \alpha\beta\ldots\gamma G_{\alpha\beta\ldots\gamma} = 0, \tag{2.3}$$

or, in terms of $\tilde{G}$,

$$G_{11\ldots1} = 0. \tag{2.4}$$

Therefore, only $2^n - 1$ components of $\tilde{G}$ are different from zero. We shall see later that algebraic and physical consideration will decrease further the number of independent components.

Except for (2.4), all other components of $\tilde{G}$ are averages of $n-1$ nested commutators and anticommutators. In particular, $G_{211,\ldots,1}$, being combination of averages of $n-1$ nested commutators, is the fully retarded n-point function, i.e., the r-functions in the LSZ field theory[16]), and $G_{222\ldots2}$, being combination of averaged $n-1$ nested anticommutators, is the n-point correlation function without any retarded or advanced relation among its time arguments.

Take for example, the case $n = 3$. Formulae (2.3) and (2.4) concretize to

$$G_{+++} + G_{+--} + G_{-+-} + G_{--+} = G_{---} + G_{++-} + G_{+-+} + G_{-++}$$

and

$$G_{111} = 0, \tag{2.5}$$

where

$$G_{+++}(123) = (-\mathrm{i})^2\langle T(123)\rangle,$$

$$G_{++-}(123) = (-\mathrm{i})^2\langle 3T(12)\rangle,$$

$$G_{+--}(123) = (-\mathrm{i})^2\langle \tilde{T}(23)1\rangle,$$

$$G_{---}(123) = (-\mathrm{i})^2\langle \tilde{T}(123)\rangle,$$

etc., T and $\tilde{T}$ being the chronological and antichronological operators. The absence of averages of $\langle T(12)3\rangle$ or $\langle 1\tilde{T}(23)\rangle$ types, as will be shown later, does not lead to any difficulty on taking into account time reversal symmetry.

3. General expressions for nonlinear response

In fact, the derivation of general expressions for nonlinear response is the simplest application of the transformation relations among three sets of CTPGF's[14]).

Assume the system was in equilibrium state described by Hamiltonian $\mathcal{H}_0$ and density matrix

$$\rho_0 = \frac{1}{z}\,\mathrm{e}^{-\beta\mathcal{H}_0}, \quad z = \mathrm{Tr}\,\mathrm{e}^{-\beta\mathcal{H}_0} \tag{3.1}$$

in the remote past $t_0 = -\infty$ and then a time-dependent external field $J(t)$ has been included adiabatically which drives the system out of equilibrium. The external field J is coupled to dynamic variable Q of the system and the total Hamiltonian becomes

$$\mathcal{H}(t) = \mathcal{H}_0 - J(t)Q. \tag{3.2}$$

Hereinafter we adopt the simplified notation of[15]) and[17]), i.e., we omit the summation or integration sign and even ignore the arguments and subscripts. For instance, we use

$$JQ \equiv \sum_i \int \mathrm{d}x\, J_i(x, t)Q_i(x). \tag{3.3}$$

In order to indicate the time dependence sometimes we retain the time argument t alone.

We restrict ourselves to the case (3.2) of linear coupling of the system with external field. We do not consider nonlinear couplings, such as $(\boldsymbol{nE})^2$ or $(\boldsymbol{nH})^2$ couplings in liquid crystals or $E_iE_jP_{ij}$ (P_{ij} being the polarization tensor) coupling in second order light scattering. We mention in addition that all these cases may be treated as linear ones by using composite operators in the CTPGF formalism. The problem of thermal disturbance will not be touched in this paper either.

Q in (3.2), being operator in the Schrödinger picture, does not depend explicitly on t. Operators in the Heisenberg and interaction pictures will be denoted by $U^{\mathrm{H}}(t)$ and $Q^{\mathrm{I}}(t)$, respectively. The average of a dynamic variable may be calculated in any picture, e.g.,

$$\langle Q(t)\rangle = \mathrm{Tr}(Q\rho(t)) = \mathrm{Tr}(Q^{\mathrm{H}}(t)\rho_0). \tag{3.4}$$

The merit of Heisenberg picture consists in putting all the time dependence on the operator $Q^{\mathrm{H}}(t)$ and one can use the equilibrium density matrix ρ_0 of the initial state to compute the average. We denote hereafter

$$\mathrm{Tr}(\cdots\ \rho_0) \equiv \langle\cdots\rangle_0. \tag{3.5}$$

In accordance with the very spirit of classical statistical physics the statistical average is carried out for the initial distribution only and the evolution of the system obeys dynamical equation, independent on statistical properties. If for a set of dynamical variables of the system $\{Q_i, i = 1, 2, \dots, n\}$, we know the various average values

$$\begin{aligned} &\langle Q_i(t)\rangle,\\ &\langle Q_i(t_1)Q_j(t_2)\rangle,\\ &\langle Q_i(t_1)Q_j(t_2)Q_k(t_3)\rangle,\\ &\dots \end{aligned} \tag{3.6}$$

we would have a more and more detailed statistical description of the nonequilibrium properties of the physical system.

In the quantum case not every product of operators corresponds to the physical observable. Here appears the problem of operator ordering. According to Dirac[18]) it requires that (1) the product has real eigenvalues, i.e. it is a hermitian operator, (2) it has a complete set of eigenstates, (3) it satisfies certain physical supplementary conditions. Without losing generality we can take all Q_i's to be hermitian, but it is hard to say anything about completeness in general. Nevertheless, the hermiticity of operator products can still serve as a guideline. For example, for A and B both hermitian and complete $A + B$ remains hermitian, but may not be complete, and AB may be neither hermitian, nor complete. Yet both combinations $AB + BA$ and $\mathrm{i}(AB - BA)$ will be hermitian, the former being the correlation function $G_c \equiv G_{22}$ and the latter being $G_{21} - G_{12} = G_r - G_a = G_{+-} - G_{-+}$; i.e. the spectral function for two-point function made of A and B.

From products of three hermitian operators one can form even more hermitian combinations, e.g., $ABC + CBA$, $BCA + ACB$, $CAB + BAC$, $\mathrm{i}(ABC - CBA)$, $\mathrm{i}(BCA - ACB)$, $\mathrm{i}(CAB - BAC)$ and various linear combinations of them. In the classical limit averages of first three combinations will give the same result, but they differ from each other in high orders of quantum corrections. To our understanding this concerns not yet completely solved problem of operator ordering in quantum-classical correspondence.

One needs supplementary physical consideration to make choice. Since in the $\hbar = 0$ limit all products of the same set of operators, including partially or fully symmetrized products, lead to the same average value, we make the following fundamental assumption: in the quantum case the quantity which corresponds to the average of the product of dynamic variables in (3.6) is just that component of $\tilde{G}$ whose subscripts are all equal to 2. For the two-point function G_{22} it is the fully symmetrized correlation function [19]), but G_{222}, G_{2222}, etc., are only partially symmetrized averages.

Thus we shall consider all $G_2 = \langle Q \rangle$, G_{22}, $G_{222}, \ldots$, as functions of the external field J, to be observable physical quantities. To write down general expressions for nonlinear response we first extend the definition of external field J to positive and negative time branches, putting $J_+ = J_-$ at the end. We expand CTPGF's of all orders

$$\begin{aligned} G_p(1) &= \langle Q^{\mathrm{H}}(t) \rangle_0 = \langle T_p(Q^{\mathrm{I}}(t) S_p \rangle_0, \\ G_p(12) &= -\mathrm{i} \langle T_p(Q^{\mathrm{H}}(1) Q^{\mathrm{H}}(2)) \rangle_0 = -\mathrm{i} \langle T_p(Q^{\mathrm{I}}(1) Q^{\mathrm{I}}(1) S_p \rangle_0, \\ G_p(123) &= (-\mathrm{i})^2 \langle T_p(Q^{\mathrm{H}}(1) Q^{\mathrm{H}}(2) Q^{\mathrm{H}}(3)) \rangle_0 = (-\mathrm{i})^2 \langle T_p(Q^{\mathrm{I}}(1) Q^{\mathrm{I}}(2) Q^{\mathrm{I}}(3) S_p \rangle_0, \\ &\ldots . \end{aligned} \tag{3.7}$$

in powers of J. All times in (3.7) are taken on the closed time path p. Chronological operator T_p and S-matrix S_p on p has been defined in[13-15]). Here we have

$$S_p = T_p \exp\left(-\mathrm{i} \int_p J Q^{\mathrm{I}} \,\mathrm{d}x\right).$$

Therefore, in order to expand (3.7) in terms of J one can proceed from the generating functional for a "free field"

$$Z[J] = \langle S_p \rangle_0$$

and the definition of the generating functional

$$W[J] = \mathrm{i} \ln Z[J] \tag{3.8}$$

as an analytic functional

$$W[J] = \sum_{n=1}^{\infty} \frac{1}{n!} \Delta_p(1, \ldots, n) J(1) \ldots J(n), \tag{3.9}$$

where the connected Green's functions of the "free field" have been denoted by

$$\Delta_p(1, 2, \ldots, n) = \left. \frac{\delta^n W[J]}{\delta J(1) \delta J(2) \ldots \delta J(n)} \right|_{J=0}. \tag{3.10}$$

"Free field" operator $Q^{\mathrm{I}}(t)$ in the interaction picture is merely free from the external field J. It contains all inherent interactions of the system.

From (3.10) we see immediately that

$$\left.\begin{aligned}
&G_p(1) = \Delta_p(1) + \Delta_p(12)J(2) + \frac{1}{2!}\Delta_p(123)J(2)J(3) + \dots,\\
&G_p(12) = \frac{\delta G_p(1)}{\delta J(2)} = \Delta_p(12) + \Delta_p(123)J(3) + \frac{1}{2!}\Delta_p(1234)J(3)J(4) + \dots,\\
&G_p(123) = \frac{\delta G_p(12)}{\delta J(3)} = \Delta_p(123) + \Delta_p(1234)J(4) + \dots,\\
&\dots .
\end{aligned}\right\} \quad (3.11)$$

Usually $\Delta_p(1)$ is taken to be zero.

To transform into the third set of CTPGF it is sufficient to insert Pauli matrix σ_1[14]):

$$\left.\begin{aligned}
&\tilde{G}(1) = \tilde{\Delta}(12)(\sigma_1 J)(2) + \frac{1}{2!}\tilde{\Delta}(123)(\sigma_1 J)(2)(\sigma_1 J)(3) + \dots,\\
&\tilde{G}(12) = \tilde{\Delta}(12) + \tilde{\Delta}(123)(\sigma_1 J)(3) + \frac{1}{2!}\tilde{\Delta}(1234)(\sigma_1 J)(3)(\sigma_1 J)(4) + \dots,\\
&\tilde{G}(123) = \tilde{\Delta}(123) + \tilde{\Delta}(1234)(\sigma_1 J)(4) + \dots,\\
&\dots .
\end{aligned}\right\} \quad (3.12)$$

According to the discussion at the beginning of this section we have to retain only the last component in these CTPGF's, i.e. the component with subscripts all equal to 2, and put $J_+ = J_- = J$. In this way we get the general expressions for nonlinear response:

$$\left.\begin{aligned}
&G_2(1) = \langle Q^{\mathrm{H}}(t)\rangle = \Delta_{21}(12)J(2) + \frac{1}{2!}\Delta_{211}(123)J(2)J(3) + \dots,\\
&G_{22}(12) = \Delta_{22}(12) + \Delta_{221}(123)J(3) + \frac{1}{2!}\Delta_{2211}(1234)J(3)J(4) + \dots,\\
&G_{222}(123) = \Delta_{222}(123) + \Delta_{2221}(1234)J(4) + \dots,\\
&\dots .
\end{aligned}\right\} \quad (3.13)$$

In these formulae $J(t)$ is taken on the ordinary time axis. The first two lines of (3.13) contain results obtained previously in[4]) by explicit manipulation of integrals. In the language of CTPGF the structure of high order terms is evident.

In accordance with the convention in literature[4–8]) Δ_{21}, Δ_{211}, $\Delta_{2111}, \dots$ should be called response functions of the averaged physical variable to external field, their Fourier transforms–the admittance function of various order. G_{22}, $G_{222}, \dots$ and Δ_{22}, $\Delta_{222}, \dots$ are called nonequilibrium and equilibrium fluctuations of different order, and Δ_{221}, Δ_{2211}, $\Delta_{2221}, \dots$ are response functions of these fluctuations to external field.

Other components of (3.12), e.g., nonequilibrium retarded function

$$G_{21}(12) = \Delta_{21}(12) + \Delta_{211}(123)J(3) + \frac{1}{2!}\Delta_{2111}(1234)J(3)J(4) + \dots, \tag{3.14}$$

being straightforward extension of the usual definition of linear response

$$\Delta_{21}(12) = \left.\frac{\delta\langle Q^{\mathrm{H}}(1)\rangle}{\delta J(2)}\right|_{J=0} \tag{3.15}$$

to

$$G_{21}(12) = \frac{\delta\langle Q^{\mathrm{H}}(1)\rangle}{\delta J} \tag{3.16}$$

by dropping the requirement $J = 0$, may just be named nonlinear response function. The variational derivative in (3.16) means

$$\delta\langle Q^{\mathrm{H}}(t)\rangle = \int G_{21}(12)\delta J(2)\,\mathrm{d}2. \tag{3.17}$$

In fact, by integrating (3.14) with respect to J one gets the first formula in (3.13). Consequently, there is no additional information contained in G_{21} as well as in those terms, which have disappeared in going from (3.12) to (3.13) due to putting $J_+ = J_-$.

Independent functions which may be measured in principle are those listed in the following table and their high order extensions.

	Average	2-point correlation	3-point correlation	4-point correlation
Without external field	$(\Delta_2 = 0)$	Δ_{22}	Δ_{222}	Δ_{2222}
Linear response to external field	Δ_{21}	Δ_{221}	Δ_{2221}	Δ_{22221}
2nd order response	Δ_{211}	Δ_{2211}	Δ_{22211}	Δ_{222211}
3rd order response	Δ_{2111}	Δ_{22111}	Δ_{222111}	$\Delta_{2222111}$

In this table on each oblique line, from lower left to upper right, there are components of one and the same $\tilde{G}$ function, so the relations indicated in[4,6,7]) look very natural.

To sum up, observables in nonlinear response theory are partially symmetrized nonequilibrium correlation (fluctuation) functions G_2, G_{22}, $G_{222}, \dots,$ etc., as functions of the external field J, in particular, their initial derivatives

$$\Delta_{\underbrace{2\dots2}_{k}\underbrace{1\dots1}_{k}} = \left.\frac{\delta^l}{\delta J^l} G_{\underbrace{2\dots2}_{k}}\right|_{J=0}. \tag{3.18}$$

The possibility to measure them in practice depends on the nonlinearity of the system itself, i.e., the notability of functions (3.18), and the strength of the external field J.

4. General considerations on the relations among multi-point response functions

The n-point function $\tilde{G}$ has $2^n - 1$ nonzero components. By imposing different physical requirements, such as the initial state being in thermal equilibrium, the time reversal symmetry and so on, one can derive many relations among these components, including the various extensions of fluctuation–dissipation theorems to nonlinear case. Generally speaking, there are four groups of relations to be used. We list them below.

4.1 *Exact algebraic relations*

The explicit definition of $G_{ij\ldots k}(1, 2, \ldots, n)$ contains θ-functions, nested commutators and anticommutators, which satisfy a few exact algebraic relations. For example, for θ-functions, there are normalization and summation formulae[14]), and commutators satisfy Jacobi identity and its generalization. Moreover, the fundamental property (2.4) of CTPGF's has many equivalent forms. For instance, it is very easy to rewrite it for the three-point function either in "retarded" combination

$$\tfrac{1}{2}(G_{211} + G_{121} + G_{221}) = G_{+++} - G_{++-}, \tag{4.1}$$

or in "correlated" combination

$$\tfrac{1}{2}(G_{112} + G_{122} + G_{212} + G_{222}) = G_{+++} + G_{++-}. \tag{4.2}$$

Similarly for the 4-point functions we have

$$\tfrac{1}{2}(G_{2111} + G_{1211} + G_{2211}) = G_{++++} + G_{++--} - G_{+++-} - G_{++-+}, \tag{4.3}$$

$$\tfrac{1}{4}(G_{2111} + G_{1211} + G_{1121} + G_{2211} + G_{2121} + G_{1221} + G_{2221}) = G_{++++} - G_{+++-}, \tag{4.4}$$

and

$$\tfrac{1}{2}(G_{2222} + G_{1222} + G_{2122} + G_{1122}) = G_{++++} + G_{+++-} + G_{++-+} + G_{+++-}, \tag{4.5}$$

$$\tfrac{1}{4}(G_{2222} + G_{1112} + G_{2112} + G_{1212} + G_{1122} + G_{2212} + G_{2122} + G_{1222}) = G_{++++} + G_{+++-}. \tag{4.6}$$

By inspection one easily discovers the rule to write analogous formulae for multi-point functions. We emphasize that all of them are equivalent to (2.4) and do not contain new information. Nevertheless, (4.1) and (4.3) were derived in[6])*, using very inconvenient notation and not recognizing them as identities. They were used by the same author[20]) to draw further conclusions on the relation among multi-point functions.

4.2. *KMS condition*[3,21])

A basic assumption in response theory consists in the system being in equilibrium described by density matrix (3.1) for $t_0 = -\infty$. Introducing time-dependent external field, the average of operators $Q^{\mathrm{I}}(t)$ in the interaction picture satisfies the following relation ($\hbar = 1$, $\beta = (kT)^{-1}$)

$$\langle Q_j^{\mathrm{I}}(t) Q_i^{\mathrm{I}}(t_1)\rangle_0 = \langle Q_i^{\mathrm{I}}(t_1) Q_j^{\mathrm{I}}(t + \mathrm{i}\beta)\rangle_0 = \mathrm{e}^{\mathrm{i}\beta\partial/\partial t}\langle Q_i^{\mathrm{I}}(t_1) Q_j^{\mathrm{I}}(t)\rangle_0. \tag{4.8}$$

Owing to time-translational invariance of the equilibrium state, (4.8) can be written as

$$\langle Q_j^{\mathrm{I}}(t) Q_i^{\mathrm{I}}(0)\rangle_0 = \mathrm{e}^{\mathrm{i}\beta\partial/\partial t}\langle Q_i^{\mathrm{I}}(0) Q_j^{\mathrm{I}}(t)\rangle_0. \tag{4.9}$$

Fourier transform

$$Q_j^{\mathrm{I}}(t) = \int \frac{\mathrm{d}\omega}{2\pi}\,\mathrm{e}^{-\mathrm{i}\omega t} Q_j^{\mathrm{I}}(\omega)$$

corresponds to replacement $\partial/\partial t \Rightarrow -i\omega$ in (4.9)

$$\langle Q_j^{\mathrm{I}}(\omega) Q_i^{\mathrm{I}}(0)\rangle_0 = \mathrm{e}^{\beta\omega}\langle Q_i^{\mathrm{I}}(0) Q_j^{\mathrm{I}}(\omega)\rangle_0. \tag{4.10}$$

This is the so-called KMS[3,21]) condition. For systems with infinite number of degrees of freedom the range of validity for the KMS condition is wider than that for the density matrix. From (4.10) follows a relation between commutator and anticommutator:

$$\langle\{Q_j^{\mathrm{I}}(\omega), Q_i^{\mathrm{I}}\}\rangle_0 = \coth\left(\frac{\beta\omega}{2}\right)\langle[Q_j^{\mathrm{I}}(\omega), Q_i^{\mathrm{I}}]\rangle_0. \tag{4.11}$$

This is the fluctuation–dissipation theorem for a 2-point function.

We are concerned with the KMS condition and fluctuation–dissipation theorems, satisfied by multi-point functions. First of all, for any function, invariant under time translation

$$F(t_1, t_2, \ldots, t_n) = F(t_1 - t_n, t_2 - t_n, \ldots, 0), \tag{4.12}$$

we have

$$\sum_{i=1}^{n} \frac{\partial}{\partial t_i} F = 0,$$

* Labelled as (2.23) and (2.24) in[6]).

or, symbolically after Fourier transform,

$$\sum_{i=1}^{n} \omega_i = 0. \tag{4.13}$$

Next, let us consider the averaged product of n operators. Transposing the leftmost operator to the rightmost, one at each time, as we did in deriving (4.8), we get

$$\begin{aligned}\langle Q_1(t_1)Q_2(t_2)\dots Q_n(t_n)\rangle_0 &= e^{i\beta\partial/\partial t_1}\langle Q_2(t_2)Q_3(t_3)\dots Q_n(t_n)Q_1(t_1)\rangle_0\\ &= e^{i\beta(\partial/\partial t_1+\partial/\partial t_2)}\langle Q_3(t_3)Q_4(t_4)\dots Q_1(t_1)Q_2(t_2)\rangle_0\\ &= \dots\\ &= e^{-i\beta\partial/\partial t_n}\langle Q_n(t_n)Q_1(t_1)\cdots Q_{n-2}(t_{n-2})Q_{n-1}(t_{n-1})\rangle_0.\end{aligned}$$

We can stop at any step, introduce two functions

$$\begin{aligned}F^{(-)}(t_1,\dots,t_i;t_{i+1},\dots,t_n) &= \langle Q_1(t_1)\dots Q_i(t_i)Q_{i+1}(t_{i+1})\dots Q_n(t_n)\rangle_0,\\ F^{(+)}(t_1,\dots,t_i;t_{i+1},\dots,t_n) &= \langle Q_{i+1}(t_{i+1})\dots Q_n(t_n)Q_1(t_1)\dots Q_i(t_i)\rangle_0,\end{aligned} \tag{4.14}$$

and write

$$F^{(-)}(t_1,\dots,t_n) = e^{i\beta(\partial/\partial t_1+\dots+\partial/\partial t_i)}F^{(+)}(t_1,\dots,t_n). \tag{4.15}$$

After Fourier transform one has the generalized KMS condition

$$F^{(-)}(\omega_1,\dots,\omega_n) = e^{\beta(\omega_1+\dots+\omega_i)}F^{(+)}(\omega_1,\dots,\omega_n). \tag{4.16}$$

Defining two more functions

$$\begin{aligned}F^{(c)} &= F^{(-)}+F^{(+)} = \langle\{Q_1(t_1)\dots Q_i(t_i),\, Q_{i+1}(t_{i+1})\dots Q_n(t_n)\}\rangle_0,\\ F^{(a)} &= F^{(-)}-F^{(+)} = \langle[Q_1(t_1)\dots Q_i(t_i),\, Q_{i+1}(t_{i+1})\dots Q_n(t_n)]\rangle_0,\end{aligned}$$

then we have

$$\begin{aligned}&F^{(c)}(\omega_1,\dots,\omega_i;\omega_{i+1},\dots,\omega_n)\\ &\quad= \coth\frac{\beta(\omega_1+\dots+\omega_i)}{2}\,F^{(a)}(\omega_1,\dots,\omega_i;\omega_{i+1},\dots,\omega_n).\end{aligned} \tag{4.17}$$

In fact, relations similar to (4.16) and (4.17) can be written for functions of more general type, i.e.

$$F^{(-)} = \langle P(Q_1(t_1)\dots Q_i(t_i))P'(Q_{i+1}(t_{i+1})\dots Q_n(t_n))\rangle_0, \tag{4.18}$$

where P or P' may denote chronological product T, antichronological product $\tilde{T}$, symmetrized product Sym, normal product N or ordinary product ($P = 1$). It is clear from the derivation that it is even not necessary to factorize $P'(\dots)$ in (4.18) into $n-i$ factors.

For 2-point functions the KMS condition relates different components of the CTPGF, leading to the usual fluctuation–dissipation theorem. In the case of multi-point functions it can only relate the symmetric and antisymmetric parts of one and the same component. For example, writing the 4-point function G_{++--} in the form

$$G_{++--}(1234) = \frac{(-i)^3}{2}(\langle \tilde{T}(34)T(12)\rangle_0 + \langle T(12)\tilde{T}(34)\rangle_0) + \frac{(-i)^3}{2}(\langle \tilde{T}(34)T(12)\rangle_0 - \langle T(12)\tilde{T}(34)\rangle_0), \tag{4.19}$$

and considering the two parenthesized terms as $F^{(c)}$ and $F^{(a)}$, respectively, we would have a relation similar to (4.17). Therefore, KMS condition alone can not give the fluctuation–dissipation theorem, relating different components of a multi-point GTPGF. One should impose supplementary constraints on the system, e.g. require it to be invariant under time reversal.

4.3 *Time reversal symmetry*

For macroscopic systems time reversal invariance is a very strong constraint. It leads to the detailed balance and the existence of "potential functions" (see, e.g.,[22]) and references cited therein).

Initial state of macrosystem may depend on some external parameters λ_i and its dynamics, i.e., the Hamiltonian of the system, may depend on external fields J_j. Under time reversal classical quantities λ_i and J_j transform to

$$\lambda_i \to \epsilon_i \lambda_i, \quad J_j \to \epsilon_j J_j, \tag{4.20}$$

with the signature ϵ_i or ϵ_j being ± 1.

In quantum mechanics time reversal is described by antiunitary operator R. In the Schrödinger picture operators do not depend on time explicitly, so there appears only a signature under time reversal:

$$Q_i \to RQ_iR^+ = \epsilon_i Q_i, \quad \epsilon_i = \pm 1. \tag{4.21}$$

We shall not describe the details of time reversal. In agreement with[22]) we consider a system to be time reversal invariant if its dynamics satisfies

$$\mathscr{H}[J] \to R\mathscr{H}[J]R^+ = \mathscr{H}[\epsilon J] \tag{4.22}$$

and its initial state wave function transforms as

$$\Psi_{t_0}(\lambda) \to R\Psi_{t_0}(\lambda) = \Psi_{t_0}(\epsilon\lambda). \tag{4.23}$$

The last requirement may be imposed on the initial density matrix

$$\rho_0(\lambda) \to R\rho_0(\lambda)R^+ = \rho_0(\epsilon\lambda). \tag{4.24}$$

Merely a special class of macrosystems satisfy conditions (4.22–4.24), but for the time being knowledge about systems beyond this class is very poor. We confine ourselves to this class only.

Denote the averaged product of Heisenberg operators by

$$F_{i_1\ldots i_n}(t_1,\ldots t_n;J,\lambda) = \langle Q^{\mathrm{H}}_{i_1}(t_{i_n})\ldots Q^{\mathrm{H}}_{t_1}(t_n)\rangle_0, \tag{4.25}$$

where the J-dependence comes from $\mathcal{H}[J]$ and the λ-dependence from $\rho_0(\lambda)$. Using (4.22)–(4.24) it is easy to prove

$$\begin{aligned} F_{i_1\ldots i_n}(t_1,\ldots t_n;J,\lambda) &= \epsilon_{i_1}\ldots\epsilon_{i_n}F_{i_n\ldots i_1}(-t_n,\ldots -t_1;\epsilon J,\epsilon\lambda) \\ &= \epsilon_{i_1}\ldots\epsilon_{i_n}F^*_{i_1\ldots i_n}(-t_1,\ldots -t_n;\epsilon J,\epsilon\lambda). \end{aligned} \tag{4.26}$$

The second line in (4.26) is based on an equality

$$\mathrm{Tr}(AB\ldots D) = \mathrm{Tr}(D\ldots BA)^*,$$

satisfied by hermitian operators. Since ρ_0 and Q^{H}_i are all hermitian, we have

$$F_{i_1\ldots i_n}(t_1,\ldots t_n;\,J,\lambda) = F^*_{i_n\ldots i_1}(t_n,\ldots .\, t_1;\,J,\lambda). \tag{4.27}$$

Components of CTPGF are linear combinations of averaged operator products, so for systems with time reversal symmetry one can write down the time reversal properties, using (4.26). For example, owing to

$$\begin{aligned} \langle 3T(12)\rangle^J &= \epsilon_1\epsilon_2\epsilon_3\langle T(-1\ -2)-3\rangle^{\epsilon J}, \\ \langle T(12)3\rangle^J &= \epsilon_1\epsilon_2\epsilon_3\langle -3T(-1\ -2)\rangle^{\epsilon J}, \end{aligned} \tag{4.28}$$

where only one superscript J has been used to represent both J and λ, we can split 3-point function G_{++-} into two parts

$$G_{++-}(123;J) = G^{\mathrm{S}}_{++-}(123;J) + G^{\mathrm{A}}_{++-}(123;J), \tag{4.29}$$

where

$$\begin{aligned} G^{\mathrm{S}}_{++-}(123;J) &= G^{\mathrm{S}}_{++-}(-1\ -2\ -3;\epsilon J) = \frac{(-\mathrm{i})^2}{2}(\langle 3T(12)\rangle^J + \epsilon_1\epsilon_2\epsilon_3\langle T(12)3\rangle^J), \\ G^{\mathrm{A}}_{++-}(123;J) &= -G^{\mathrm{A}}_{++-}(-1\ -2\ -3;\epsilon J) = \frac{(-\mathrm{i})^2}{2}(\langle 3T(12)\rangle^J - \epsilon_1\epsilon_2\epsilon_3\langle T(12)3\rangle^J). \end{aligned} \tag{4.30}$$

This is another way, different from (4.19), to divide a multi-point function into symmetric and anti-symmetric parts. Further use of the KMS condition leads to, e.g.

$$G^{S}_{++-}(\omega_1\omega_2\omega_3; J) = \frac{1-\epsilon_1\epsilon_2\epsilon_3\, e^{\beta\omega_3}}{1+\epsilon_1\epsilon_2\epsilon_3\, e^{\beta\omega_3}}\, G^{A}_{++-}(\omega_1\omega_2\omega_3; J). \tag{4.31}$$

4.4. *Fourier transform and spectral representation*

Fourier transform alone does not bring about new information, but it is more convenient to incorporate KMS condition and time reversal invariance after performing the Fourier transform. Therefore, we discuss in general the Fourier transform of n-point functions.

The Fourier transform of a function, invariant under time translation (4.12) may be written

$$F(\omega_1, \dots, \omega_n) = 2\pi\delta(\omega_1 + \dots + \omega_n) F_1(\omega_1, \dots, t_k = 0, \dots, \omega_n), \tag{4.32}$$

where in F_1 the Fourier transform has been carried out only for $n-1$ arguments and the untransformed argument is written explicitly as $t_k = 0$ with k taking any value from 1 to n. In other words, the Fourier integral of a n-point function looks like

$$F(t_1, \dots, t_n) = \int \frac{d\omega_1 \dots d\hat{\omega}_k \dots d\omega_n}{(2\pi)^{n-1}}\, e^{-i[\omega_1(t_1-t_k)+\dots+\hat{\omega}_k+\dots\,\omega_n(t_n-t_k)]} \times F_1(\omega_1, \dots, t_k = 0, \dots, \omega_n), \tag{4.33}$$

where a caret denotes the absent factor.

CTPGF usually contains products of the n-point function and the θ-function, e.g.,

$$F_R(t_1, t_2, t_3, t_4) = (-i)^3 \theta(4132) F(t_1, t_2, t_3, t_4).$$

Factorizing the θ-function

$$\theta(4132) = \theta(t_4 - t_1)\theta(t_1 - t_3)\theta(t_3 - t_2), \tag{4.34}$$

using the representation

$$\theta(t) = \frac{i}{2\pi} \int_{-\infty}^{+\infty} \frac{d\Omega}{\Omega + i\epsilon}\, e^{-i\Omega t}$$

and noticing the last time in (4.34) being t_2, we use the Fourier transform with $t_2 = 0$ and get

$$F_{1R}(\omega_1, t_2 = 0, \omega_3, \omega_4) = \frac{1}{(2\pi)^3} \int \frac{d\Omega_1\, d\Omega_2\, d\Omega_3}{(\Omega_1 + i\epsilon)(\Omega_2 + i\epsilon)(\Omega_3 + i\epsilon)} \times F_1(\omega_1 + \Omega_1 - \Omega_2, t_2 = 0, \omega_3 + \Omega_2 - \Omega_3, \omega_4 - \Omega_1). \tag{4.35}$$

Subsequent change of variables passes all the ω_i-dependence onto the denominators

$$F_{1R}(\omega_1, t_2 = 0, \omega_3, \omega_4) = \frac{1}{(2\pi)^3} \int \frac{d\Omega_1\, d\Omega_2\, d\Omega_3\, F_1(\Omega_2 - \Omega_1,\ t_2 = 0, \Omega_3 - \Omega_2, \Omega_1)}{(\omega_4 - \Omega_1 + i\epsilon)(\omega_4 + \omega_1 - \Omega_2 + i\epsilon)(\omega_4 + \omega_1 + \omega_3 - \Omega_3 + i\epsilon)}, \tag{4.36}$$

the relation between F_{1R} and F_R being given by (4.32). This is the spectral representation for one of the terms in a component of CTPGF. It is not difficult to read out the rule how to write the spectral representation in a general case*), using the arguments of θ-function to indicate the order. Integration comes from θ-function. KMS condition and time reversal usually decrease the number of independent spectral functions.

It is clear at this point that combined use of the above-mentioned consideration may lead to many relations among high order response functions. This will be done elsewhere in a separate publication with colleagues.

5. Conclusions

We would like to make two remarks in conclusion. Firstly, this paper deals only with the formal aspects of nonlinear response theory. It bypasses such fundamental problems as the origin of irreversibility or the condition for a response function to be different from zero which have been deeply analyzed by the Brussels school. Actually it is limited to situations, not very far from equilibrium and does not touch either the question of practical calculation of response functions for a concrete model. Still it seems useful to have such formal relations in view of possible future experiments, with which our second remark is concerned. In a sense most physical experiments measure responses to one or another disturbance. Development of subtle data acquisition and processing techniques will bring new impact to the measurement of nonlinear responses as well as to a deeper understanding of theoretical relations.

Acknowledgments

It is a great pleasure to express my gratitude to Professor I. Prigogine and to the Université Libre de Bruxelles for the kind hospitality which makes the

* Zhao-bin Su first obtained such spectral representations in a slightly different way.

completion of this work an extremely pleasant experience. I would like to thank Dr. Zhao-bin Su for many clarifying discussions. The financial support from the Instituts Internationaux de Physique et de Chimie, fondés par E. Solvay, is also gratefully acknowledged.

References

1) L. Onsager, Phys. Rev. **37** (1931) 405, **38** (1931) 2265.
2) H.B. Callen and T.A. Welton, Phys. Rev. **83** (1951) 34.
3) R. Kubo, J. Phys. Soc. Japan **12** (1957) 570.
4) W. Bernard and H.B. Callen, Rev. Mod. Phys. **31** (1959) 1017.
5) R.L. Peterson, Rev. Mod. Phys. **39** (1967) 69.
6) G.F. Efremov, Sov. Phys.-JETP **28** (1969) 1232.
7) R.L. Stratonovich, Sov. Phys.-JETP **31** (1970) 864.
8) G.N. Bochkov and Yu.E. Kuzovlev, Sov. Phys.-JETP **72** (1977) 238.
9) N.G. van Kampen, Phys. Norvegica **5** (1971) 279.
10) J.W. Halley, ed., Correlation Functions and Quasiparticle Interactions in Condensed Matter (Plenum, New York, 1978).
11) J. Schwinger, J. Math. Phys. **2** (1961) 407.
12) L.V. Keldysh, Sov. Phys.-JETP **20** (1965) 1018.
13) Guang-zhao Zhou and Zhao-bin Su, Progress in Statistical Physics, Kexue, Beijing (to be published in chinese) chap. 5.
14) Guang-zhao Zhou, Lu Yu and Bai-lin Hao, Acta Phys. Sinica **29** (1980) 878.
15) Guang-zhao Zhou, Zhao-bin Su, Bai-lin Hao and LuYu, Phys. Rev. **B21** (1980) 3855.
16) H. Lehmann, K. Symansik, W. Zimmermann, Nuovo Cimento **6** (1957) 319.
17) Bai-lin Hao, Progress in Statistical Physics, Kexue, Beijing (to be published in chinese) chap. 1.
18) P.A.M. Dirac, The Principles of Quantum Mechanics, 4th ed., sections 10 and 77 (Clarendon, Oxford, 1958).
19) R. Kubo Rep. Progr. Phys. **29** (1966) 255.
20) G.F. Efremov, Izvestie VUZov-Radiofisika **15** (1972) 1207.
21) P.C. Martin, J. Schwinger, Phys. Rev. **115** (1959) 1342.
22) Zhao-bin Su and Guang-zhao Zhou, Institute of Theoretical Physics, Academia Sinica, preprint ASITP-80-009 (1980).