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LINKED-CLUSTER EXPANSIONS IN THE EQUATIONS OF MOTION METHOD FOR NONEQUILIBRIUM PROCESSES

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For an arbitrary irreversible process taking place in a closed physical system equations of motion are derived directly from the Liouville equation without introducing any projection operator. These equations are of nonmarkowian nature and are exactly valid for any system arbitrarily far from equilibrium. Using field-theoretical techniques the integral kernels in these equations are expanded into a diagram perturbation series which is proved to be linked. For a system having short memory it is shown that the secular divergent terms cancel each other. Then, using the diagram language the equations of motion are obtained in a much simpler form.

1. Introduction

To predict the macroscopic behaviour of a closed physical system of N particles being in a nonequilibrium state at time $t = 0$, it is not necessary to know all the information contained in the density operator $\varrho(t)$ which is the solution of the Liouville equation (LE)

$$\mathrm{i}\frac{\partial}{\partial t}\varrho(t) = L\varrho, \tag{1.1}$$

with a given initial density $\varrho(0)$. Instead, all we need are the expectation values of a given set of operators O_n, $n = 1, \ldots, M$ defined as

$$\bar{O}_n(t) = \mathrm{Tr}\,[O_n\varrho\,(t)]. \tag{1.2}$$

Thus, the many-body problem need not be solved in its entire complexity. This fact can be exploited to simplify the task of calculating the time dependence of the $\bar{O}_n(t)$. One way of doing so consists in the derivation of closed exact equations of

motion (EM), *i.e.*, equations where the time derivative of $\bar{O}_n(t)$ is expressed as a functional over the $\bar{O}_n(t)$

$$\dot{\bar{O}}_n(t) = \mathscr{F}\{\bar{O}_1(), \ldots, \bar{O}_M(), t\}, \tag{1.3}$$

the functional depending explicitly on the time t.

For the operators O_n corresponding to the macroscopic observables of the system such EM's were first derived by Robertson[1]) and were used in several applications[2]). These equations are nonlocal memory-retaining integro-differential equations and are valid for any system arbitrarily far from equilibrium. In the past several years a great amount of work has been done to derive closed exact kinetic equations, *i.e.*, EM's for the matrix elements of the n-particle density operator $\varrho^{(n)}(t)$, $n = 1, 2, \ldots$ or for the corresponding distribution functions in the classical case[3]).

A common feature of these derivations consists in the introduction of a projection operator P. In general, P is quite complicated and causes serious difficulties if one tries to calculate the coefficients occurring in the EM's from the microscopic point of view. To avoid this difficulty in section 2 we derive exact EM's directly from the LE without introducing any projection operator. These equations are valid independently of the nature of the operators O_n and thus with a suitable choice of the O_n kinetic equations can be obtained as well.

To derive these EM's we introduce an operator $\eta_s(t)$ the time dependence of which is given implicitly by the time dependence of the expectation values $O_n(t)$, *i.e.*,

$$\eta_s(t) = \eta_s\{\bar{O}_1(t), \ldots, \bar{O}_M(t)\}. \tag{1.4}$$

In other words $\eta_s(t)$ is an operator that depends parametrically on the functions $\bar{O}_n(t)$.

In the derivation of the EM's the operator $\eta_s(t)$ serves two purposes. On the one hand $\eta_s(t)$ is a formal quantity which allows us to introduce the $\bar{O}_n(t)$ into the density-operator formalism of the Liouville equation and to convert this markowian equation into the nonmarkowian equations of motion. On the other hand $\eta_s(t)$ has to be chosen such that, at time $t = 0$, it represents the given initial density distribution, *i.e.*,

$$\eta_s(0) = \varrho(0), \tag{1.5}$$

otherwise $\eta_s(t)$ may be chosen arbitrarily.

To chracterize $\eta_s(t)$ more closely we observe that from (1.5) it follows that

$$\bar{O}_n(0) = \mathrm{Tr}\,[O_n \eta_s(0)] \tag{1.6}$$

and since (1.6) must be valid independently of the choice of the values of $\bar{O}_k(0)$, $k = 1, \ldots, M$ we find together with (1.4) that at all times $\eta_s(t)$ yields the correct expectation values

$$\bar{O}_n(t) = \mathrm{Tr}\,\{O_n \eta_s(t)\} = \mathrm{Tr}\,\{O_n \varrho(t)\}. \tag{1.7}$$

However, this is valid for the operators O_n only and shows that $\eta_s(t)$ may be regarded as a density operator in a certain restricted sense. It is obvious that $\eta_s(t)$ does not obey the LE. A special kind of $\eta_s(t)$ is the information-theoretical ensemble $\sigma(t)$ used by Robertson.

Since the EM's (2.7) do not contain a projection operator the calculation of the corresponding integral kernels simplifies considerably. In particular, in this paper we shall derive a linked-cluster perturbation series for the kernels. To obtain this expansion we use for $\eta_s(t)$ an exponential operator called $\sigma(t)$. This has the advantage that we may work in the occupation-number representation and that the field-theoretical techniques developped in the theory of thermodynamic Green functions[4]) can be applied. Using this expansion for any given system and any set of operators O_n the EM's can be written as a series expansion in powers of the interaction and the expectation values $\bar{O}_n(t)$. Renormalization and partial-summation procedures are possible as usual in the known linked-cluster expansions of the many-body theory[5]).

To make the derivation more lucid in section 3 Green functions are defined in the ensemble $\sigma(t)$. For these a linked-cluster expansion is obtained using the well known Matsubara technique[6]). By means of these Green functions in section 4 the linked-cluster expansion of the integral kernels is written down.

In section 5 we shall discuss some properties of this expansion. Specifically, we shall show that for a system having short memory the secular divergent terms cancel each other. Using this fact, a much simpler form of the EM's is derived which is well suited for practical applications.

2. The equations of motion

The derivation of the equations of motion was already given in[14]). Since we want to use the interaction representation here and since the derivation is quite short we shall start again from the Liouville equation (LE).

Given a system with a hamiltonian

$$H = H_0 + W, \tag{2.1}$$

the LE is

$$\frac{\partial}{\partial t}\varrho(t) = -\frac{\mathrm{i}}{\hbar}[W(t), \varrho(t)] = -\mathrm{i}L(t)\varrho(t), \tag{2.2}$$

where $W(t)$, $L(t)$ are the interaction and the Liouville operators in interaction representation, respectively.

$$W(t) = \mathrm{e}^{(\mathrm{i}/\hbar)H_0 t}\, W\, \mathrm{e}^{-(\mathrm{i}/\hbar)H_0 t}, \qquad L(t)\cdots = (1/\hbar)\,[W(t), \ldots]. \tag{2.3}$$

The expectation values of the operators O_n are now given by

$$\bar{O}_n(t) = \mathrm{Tr}\,\{O_n(t)\,\varrho(t)\}, \qquad O_n(t) = \mathrm{e}^{(\mathrm{i}/\hbar)H_0 t}\, O_n\, \mathrm{e}^{-(\mathrm{i}/\hbar)H_0 t}.$$

Given a density operator $\varrho(t')$ at time t' the density operator at time t can be obtained using the formal solution of (2.2)

$$\varrho(t) = U(t, t')\,\varrho(t'), \qquad U(t, t') = T_\vartheta \exp\left(-\mathrm{i}\int_{t'}^{t} L(\vartheta)\,\mathrm{d}\vartheta\right), \tag{2.4}$$

where T_ϑ is the Wick time-ordering operator.

The operator $\eta_s(t)$ introduced in section 1 is in interaction representation

$$\eta(t) = \mathrm{e}^{(\mathrm{i}/\hbar)H_0 t}\, \eta_s(t)\, \mathrm{e}^{-(\mathrm{i}/\hbar)H_0 t}.$$

Using the initial condition (1.5) we get the formal solution of (2.2) as

$$\varrho(t) = U(t, 0)\,\eta(0). \tag{2.5}$$

This solution is valid for $t \geq 0$. For times $t < 0$ we will assume that the liouvillean in (2.2) and the boundary conditions at $t \to -\infty$ are chosen such that at $t = 0$ we have just $\varrho(0) = \eta(0)$. This way, we select the retarded solution of the LE and thus introduce irreversibility[7]).

Starting from (2.5) we use the identity

$$\frac{\mathrm{d}\varrho}{\mathrm{d}t} = -\mathrm{i}L(t)\,U(t, 0)\,\eta(0) = -\mathrm{i}L(t)\,\eta(t) + \mathrm{i}L(t)\int_0^t \mathrm{d}t'\left(\frac{\mathrm{d}}{\mathrm{d}t'}\,U(t, t')\,\eta(t')\right) \tag{2.6}$$

and carry out the time derivations using the properties of $U(t, t')$ and

$$\frac{\mathrm{d}}{\mathrm{d}t}\,\eta(t) = \sum_n \left(\frac{\partial}{\partial \bar{O}_n(t)}\,\eta(t)\right)\dot{\bar{O}}_n(t) + \mathrm{i}L_0\eta(t),$$

where

$$\dot{\bar{O}}_n(t) = \frac{\mathrm{d}}{\mathrm{d}t}\,\bar{O}_n(t), \qquad L_0\cdots = \frac{1}{\hbar}\,[H_0, \ldots].$$

Multiplying both sides of (2.6) by $O_n(t)$ and taking the trace we finally get

$$\dot{\bar{O}}_n(t) = -\mathrm{i}\Omega_n^{(0)}(t) - \int_0^t \mathrm{d}t' \left(\Omega_n^{(1)}(t, t') - \mathrm{i} \sum_m \dot{\bar{O}}_m(t') \frac{\partial}{\partial \bar{O}_m(t')} \Omega_n^{(2)}(t, t') \right), \tag{2.7}$$

$$\Omega_n^{(0)}(t) = \mathrm{Tr}\,\{O_n(t)\,[L(t) + L_0]\,\eta(t)\}, \tag{2.8}$$

$$\Omega_n^{(1)}(t, t') = \mathrm{Tr}\,\{O_n(t)\,[L(t) + L_0]\,U(t, t')\,[L(t') + L_0]\,\eta(t')\}, \tag{2.9}$$

$$\Omega_n^{(2)}(t, t') = \mathrm{Tr}\,\{O_n(t)\,[L(t) + L_0]\,U(t, t')\,\eta(t')\}. \tag{2.10}$$

Since $\eta(t)$ depends on the functions $\bar{O}_n(t)$, eqs. (2.7) are a set of closed exact equations describing the time evolution of the expectation values. They can be considered as the desired equations of motion. They are memory retaining and in coordinate representation of nonlocal nature. Actually, the appearance of the time derivatives $\dot{\bar{O}}_n(t)$ on the r.h.s. of (2.7) is an unusual feature in an equation of motion.

By iteration we can remove these derivatives from the r.h.s. To make the structure of the equations thus obtained more obvious we introduce a formal multiplication by

$$\int_0^t \mathrm{d}t'\, A(t, t')\, B(t') = A * B,$$

where A and B are arbitrary functions. Eqs. (2.7) are written as

$$\dot{\bar{O}}_n = \Gamma_n + \sum_{n_1} \Delta_{nn_1} * \dot{\bar{O}}_{n_1}, \tag{2.11}$$

where

$$\Gamma_n(t) = -\mathrm{i}\Omega_n^{(0)}(t) - \int_0^t \mathrm{d}t'\, \Omega_n^{(1)}(t, t'), \qquad \Delta_{nn_1}(t, t') = \mathrm{i} \frac{\partial}{\partial \bar{O}_{n_1}(t')} \Omega_n^{(2)}(t, t').$$

Iterating (2.11) we obtain

$$\dot{\bar{O}}_n = \Gamma_n + \sum_m \Delta_{nm} * \Gamma_m + \sum_{m,p} \Delta_{nm} * \Delta_{mp} * \Gamma_p + \cdots, \tag{2.12}$$

from which equations of motion can be obtained in their usual form. Introducing a quantity $K_{n,m}(t, t')$ by

$$K_{n,m} = 1 + \Delta_{nm} + \sum_p \Delta_{np} * \Delta_{pm} + \cdots,$$

(2.12) is written more compactly as

$$\dot{\bar{O}}_n(t) = \sum_m \int_0^t \mathrm{d}t' \, K_{n,m}(t, t') \, \Gamma_m(t'), \tag{2.13}$$

where both K and Γ depend on the expectation values $\bar{O}_n(t)$.

In section 4 the quantities $\Omega_n^{(1)}$ shall be expanded into a diagram series. Since we want to work in the occupation-number representation and use the Matsubara technique[4, 6]) we take as an "ansatz" for $\eta(t)$ the exponential operator

$$\sigma(t) = \exp\left(-\lambda_0(t) - \sum_n \lambda_n(t) \, O_n(t) - X(t)\right), \tag{2.14}$$

where $X(t) = \mathrm{e}^{(1/\hbar) H_0 t} \, X \, \mathrm{e}^{-(1/\hbar) H_0 t}$. Contrary to the "ansatz" (1.4) for $\eta(t)$ in (2.14) the $\bar{O}_n(t)$ do not occur explicitly. But the $\lambda(t)$ will depend on these $\bar{O}_n(t)$. The relation between these quantities is given by (1.7) together with $\mathrm{Tr}\, \sigma(t) = 1$.

In section 3 it will be shown how from the diagram expansion of the corresponding Green functions the explicit calculation of the relations between the $\lambda_k(t)$ and the $\bar{O}_n(t)$ can be carried through. If the operator X in (2.14) were equal to zero (2.14) would be the usual form of an information-theoretical ensemble[8]) as used, *e.g.*, by Robertson[1, 2]). However, in some applications this form of $\sigma(t)$ is not very convenient to reproduce the correct physical initial condition (1.5). To have more freedom in the choice of the initial conditions the operator X was introduced.

For the derivation of the diagram series of $\Omega_n^{(1)}(t, t')$ two kinds of perturbation expansions will be necessary. On the one hand we expand the exponential operator $U(t, t')$. Since we used the interaction representation this expansion is immediately obtained as a series in powers of the interaction strength. On the other hand we shall use the perturbation expansion of the exponential operator $\sigma(t)$. This one is obtained by using a kind of interaction representation with respect to imaginary time. In order to be able to combine both of these perturbation series and to write down the diagram expansion of $\Omega_n^{(1)}(t, t')$ as a first step we shall define Green functions in the exponential ensemble $\sigma(t)$ and expand them into a diagram series.

3. Green functions in an exponential ensemble

As discussed above, two kinds of interaction representation are used in this paper. To avoid confusing time factors we shall define the Green functions (GF) in the Schrödinger representation. Then, only the interaction representation with respect to imaginary time [see (3.9) below] is used in this section. As shall be seen in section 4 we can introduce these GF's without difficulty into the expansion of $U(t, t')$ which is written in interaction representation with respect to real time.

In Schrödinger representation (2.14) becomes

$$\sigma_s(t) = \exp(-\Lambda_0(t) - \sum \Lambda_n(t)\, O_n - X). \tag{3.1}$$

$\sigma_s(t)$ depends on time t only implicitly *via* the $\Lambda(t)$ and therefore in the GF's the time t is treated simply as a parameter. In analogy with the usual definition of thermodynamic GF's we define generalized many-particle GF's in the ensemble (3.1) by

$$G_t(1\tau_1, \ldots, m\tau_m, (m+1)\tau_{m+1}, \ldots, n\tau_n)$$
$$= -\mathrm{Tr}\{T_\tau[\tilde{a}_1(\tau_1) \cdots \tilde{a}_m(\tau_m)\, \tilde{\tilde{a}}_{m+1}(\tau_{m+1}) \cdots \tilde{\tilde{a}}_n(\tau_n)]\, \sigma_s(t)\}. \tag{3.2}$$

T_τ is the Wick time-ordering operator[6]) acting on the imaginary times τ_i. The $\tilde{\tilde{a}}$, $\tilde{a}$ are the Heisenberg operators with respect to times τ_i and are related to the Schrödinger reaction and annihilation operators a^+, a by

$$\tilde{\tilde{a}}(\tau) = \sigma_s^{-\tau T} a^+ \sigma_s^{\tau T}, \qquad \tilde{a}(\tau) = \sigma_s^{-\tau T} a \sigma_s^{\tau T}. \tag{3.3}$$

For convenience, we assume the basis to be chosen so as to diagonalize the unperturbed hamiltonian H_0, *i.e.*, $H_0 = \sum \varepsilon_n a_n^+ a_n$. The fictitious time-dependent "temperature" $T = T(t)$ is introduced for formal reasons to obtain closest formal agreement with the usual formalism of temperature-dependent Green functions[4]). For the same purpose we introduce a generalized hamiltonian $\mathscr{H}(t)$ by

$$\mathscr{H}(t) = T(t)\left(\sum_n \Lambda_n(t)\, O_n + X\right) + \mu(t)\, \hat{N}, \tag{3.4}$$

where $\hat{N}$ is the particle-number operator of the system and in the same way as $T(t)$ the "chemical potential" $\mu = \mu(t)$ is introduced as a formal quantity. Using this definition, $\sigma_s(t)$ may be written as

$$\sigma_s(t) = \exp[(\Omega + \mu\hat{N} - \mathscr{H})/T], \qquad \Omega = \Omega(t) = -\Lambda_0(t)\, T(t). \tag{3.5}$$

Using (3.5), we see from (3.2) and (3.3), that the definition (3.2) agrees formally with the usual definition of temperature-dependent GF's in a grand-canonical ensemble having hamiltonian $\mathscr{H}$. Thus, all the properties of the temperature-dependent Green functions are preserved.

In particular the generalized single-particle GF $G_t(1\tau_1, 2\tau_2)$ depends on the "time" difference $\tau = \tau_1 - \tau_2$ only and fulfils the symmetry relation

$$G_t(1, 2; \tau) = \mp G_t\left(1, 2; \tau + \frac{1}{T}\right) \quad \text{for} \quad \begin{matrix}\text{fermions} \\ \text{bosons,}\end{matrix} \quad \tau < 0, \tag{3.6}$$

which is of great importance for the diagram expansion. To introduce perturbation theory, we split the "hamiltonian" $\mathscr{H}$ into a unperturbed hamiltonian $\mathscr{H}_0(t)$ and a generalized interaction $\mathscr{H}_1(t)$

$$\mathscr{H}(t) = \mathscr{H}_0(t) + \mathscr{H}_1(t) = \mathscr{H}_0(t) + \sum \lambda_n(t)\, Q_n. \tag{3.7}$$

$\mathscr{H}_0(t)$ has to be a single-particle operator but may otherwise be chosen conveniently. After having chosen $\mathscr{H}_0(t)$, (3.7) defines, together with (3.4), the $\lambda_n(t)$ and the operators Q_n.

As usual we introduce a $\sigma_0(t)$ by

$$\sigma_0(t) = \exp\{[\Omega_0(t) + \mu(t)\,\hat{N} - \mathscr{H}_0(t)]/T(t)\}, \qquad \operatorname{Tr}\sigma_0(t) = 1 \tag{3.8}$$

and proceed to the interaction representation with respect to imaginary time τ. In this representation the creation and annihilation operators become

$$\tilde{a}(\tau) = \sigma_0^{-\tau T} a^+ \sigma_0^{\tau T}, \qquad a(\tau) = \sigma_0^{-\tau T} a \sigma_0^{\tau T}. \tag{3.9}$$

Using these operators free single-particle GF's are defined as

$$G_t^{(0)}(1\tau_1, 2\tau_2) = G_t^{(0)}(1, 2; \tau_1 - \tau_2) = -\operatorname{Tr}\{T_\tau [a_1(\tau_1)\, \tilde{a}_2(\tau_2)]\, \sigma_0(t)\}. \tag{3.10}$$

To give an explicit expression for $G_t^{(0)}$ we have to introduce a basis b_i^+, b_k that diagonalizes $\mathscr{H}_0$, *i.e.*,

$$\mathscr{H}_0(t) = \sum_p \eta_p(t)\, b_p^+ b_p. \tag{3.11}$$

Expanding the operators a_i^+, a_k into the b_l^+, b_m

$$a_i^+ = \sum_p \alpha_p^{(+)}(i)\, b_p^+, \qquad a_k = \sum_p \alpha_p(k)\, b_p, \tag{3.12}$$

we find in the usual way[4]),

$$G_t^{(0)}(1, 2; \tau) = -\sum_p \alpha_p(1)\, \alpha_p^{(+)}(2) \exp\{-[\eta_p(t) - \mu(t)]\,\tau\}\, R_p(t), \tag{3.13}$$

where

$$R_p(t) = \begin{cases} \varkappa n_p(t), & \tau < 0, \\ 1 + \varkappa n_p(t), & \tau > 0, \end{cases} \qquad \varkappa = \begin{cases} +1 & \text{bosons}, \\ -1 & \text{fermions}, \end{cases} \quad \text{for} \tag{3.14}$$

and

$$n_p(t) = \{\exp[\eta_p(t) - \mu(t)] - \varkappa\}^{-1}. \tag{3.15}$$

The S matrix relating $\sigma_s(t)$ and $\sigma_0(t)$ by $e^{-\tau(\mathscr{H}-\mu N)} = e^{-\tau(\mathscr{H}_0-\mu N)} S_t(\tau)$, is

$$S_t(\tau) = T_{\tau'} \exp\left(-\int_0^{\tau} \mathscr{H}_1(t, \tau')\, d\tau'\right), \tag{3.16}$$

where

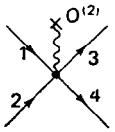
$$\mathscr{H}_1(t, \tau) = \sigma_0^{-\tau T}\, \mathscr{H}_1(t)\, \sigma_0^{\tau T}. \tag{3.17}$$

Using these operators, the Green function (3.2) may be written as

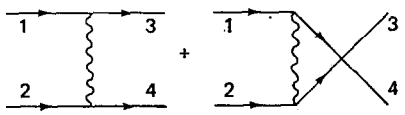
$$G_t(1\tau_1, \ldots, n\tau_n) = -\frac{\mathrm{Tr}\,\{T_\tau [a_1(\tau_1) \cdots \bar{a}_n(\tau_n)\, S_t(1/T)]\, \sigma_0(t)\}}{\mathrm{Tr}\,[S_t(1/T)\, \sigma_0(t)]}, \tag{3.18}$$

which differs from the corresponding expression of a thermodynamic GF only in the parametric time dependence of the quantities $S_t(1/T)$ and $\sigma_0(t)$. Thus (3.18) is given by a linked-cluster diagram expansion. In the following, the diagram rules will be given in Hugenholtz notation[9]). In this notation, the vertex corresponding to an arbitrary operator A is given by a dot with n lines entering and m lines leaving, n and m being the numbers of creation and annihilation operators occurring in the definition of A, respectively. We will call these vertices σ-vertices and mark them by a wavy line.

This way of drawing diagrams is especially suited for our case, since we do not want to restrict ourselves to including into $\mathscr{H}_1(t)$ one- and two-particle operators only. As an example a two-particle operator $O^{(2)}$ is represented by the vertex



corresponding to



(3.19)

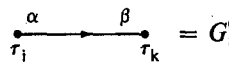
in the usual representation[4]).

3.1. *Diagram rules*

(i) An arbitrary diagram of kth order occurring in the expansion of G_t of (3.18) is obtained by drawing n endpoints and k vertex points. These points are connected by directed lines in an arbitrary manner. It should be observed, however, that the number of lines entering and leaving a given vertex point depends on the nature of the corresponding operator as described above. Only a single line enters or leaves each endpoint depending on whether the corresponding operator is $\bar{a}$ or a, respectively. The endpoints are labelled by the quantum numbers occurring in the argument of G_t in (3.18) and all the line ends entering or leaving a vertex point by quantum numbers α, β, ... Each vertex point is labelled by a time τ_i.

(ii) With each vertex is associated a matrix element of the operator $V = \sum' \lambda_n(t) \times Q_n + X$ where $\sum'$ means, that the sum includes only these operators Q_n which are described by the vertex considered. The detailed prescription for the association of the matrix elements to the vertex depends on the concrete type of the interaction and will not be specified here.

(iii) With each line connecting two points i, k there is associated a free single-particle Green function



$$= G_t^{(0)}(\alpha, \beta; \tau_i - \tau_k), \tag{3.20}$$

where $G_t^{(0)}(\alpha, \beta, \tau)$ is given by (3.13).

(iv) Summations and integrations are carried out over all quantum numbers $\alpha, \beta, \ldots$ and all times τ_i.

(v) The resulting expression is multiplied by the usual sign factor obtained from the topological structure of the diagram.

The definition (3.1) of the GF's allows us to introduce the frequencies ω_i instead of the imaginary "times" τ_i for, as stated above, the symmetry relation (3.6) is valid. It should be noted that all the renormalization and partial summation procedures known from the Matsubara technique are applicable in our case, too. Especially we could replace all the light lines representing $G_t^{(0)}$ by heavy ones representing exact single-particle GF's.

Again, as in the case of thermodynamic GF's, we see from the definition (3.2), that the expectation value of any operator O_n can be obtained from the corresponding N-particle GF by letting $\tau_i \to 0$ in the argument of the GF preserving, however, the correct time order. As follows from the above rule (ii) in the diagrams occurring in the expansions of this GF, the $\lambda_k(t)$ appear simply as multiplying factors. Thus, the relation between the $\lambda_k(t)$ and the $\bar{O}_n(t)$ can be obtained from the diagram series.

This property is especially important in the case of a system being in the vicinity of equilibrium. Then we could think of an expansion of our GF's about equilibrium. This is achieved by observing that in most cases the hamiltonian H of the system can be written as a linear combination of the operators O_n [1]), *i.e.*, $H = \sum_n \beta_n O_n$ and we can write

$$\sigma_s(t) = \exp\{[(\Omega + \mu N - H)/T] - \sum \Delta\Lambda_n(t)\, O_n + X\}. \tag{3.21}$$

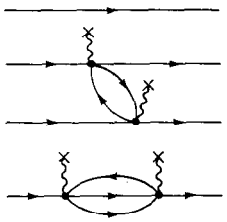
Using (2.1) we see immediately that the "interaction" $\mathscr{H}_1(t, \tau)$ (3.17) is now given by

$$\mathscr{H}_1(t, \tau) = W(\tau) - T \sum \Delta\Lambda_n(t)\, O_n(\tau) + X, \tag{3.22}$$

the $\Delta\Lambda_n(t)$ being small near equilibrium. By grouping together all the diagrams containing the same number n ($n > 0$) of factors $\Delta\Lambda_n(t)$ we obtain an expansion

of the GF's in powers of the small parameters $\Delta\Lambda_n(t)$ characterizing the deviation from equilibrium. It should be noted, that in this case T has the usual meaning of the temperature of the system in equilibrium and μ is its chemical potential.

Let us introduce the notion of a σ-part for later use. Any completely linked diagram occurring in the expansion of the n-particle GF will be called an n-particle σ-part. As an example the diagram



(3.23)

occurring in the expansion of the four-particle GF consists of a one-particle and a two-particle σ-part and a single line representing a free GF.

4. Diagram expansion of the integral kernels

We are now able to derive the diagram expansion of the integral kernels $\Omega_n^{(0)}$, $\Omega_n^{(1)}$, $\Omega_n^{(2)}$ occurring in the equations of motion (2.7). To unify treatment we introduce a new quantity

$$\Omega_n(t, t') = \mathrm{Tr}\,[O_n(t)\, U(t, t')\, \sigma(t')]. \tag{4.1}$$

Using the properties of $U(t, t')$ we easily find the formal relations

$$\begin{aligned}
\Omega_n^{(0)}(t) &= \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}\,\Omega_n(t, t')|_{t=t'}, \\
\Omega_n^{(1)}(t, t') &= \frac{\mathrm{d}}{\mathrm{d}t}\,\frac{\partial}{\partial t'}\,\Omega_n(t, t') = -\frac{\mathrm{d}^2}{\mathrm{d}t^2}\,\Omega_n(t, t'), \\
\Omega_n^{(2)}(t, t') &= \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}\,\Omega_n(t, t') = -\mathrm{i}\frac{\partial}{\partial t'}\,\Omega_n(t, t'),
\end{aligned} \tag{4.2}$$

where the partial derivative $\partial/\partial t'$ means that we must not differentiate the $\bar{O}_n(t')$. The second equality signs in (4.2) are easily proved using for $U(t, t')$ the representation[‡]

$$U(t, t') = \mathrm{e}^{\mathrm{i}L_0 t}\,\mathrm{e}^{-\mathrm{i}L(t-t')}\,\mathrm{e}^{-\mathrm{i}L_0 t'}$$

[‡] This form of $U(t, t')$ is proved by inserting it into the differential equation obtained from the expression (2.4) of U.

and the cyclic invariance of the trace. Because of (4.2) only the diagram expansion of $\Omega_n(t, t')$ has to be known. Instead of (2.4) we will use the explicit series for $U(t, t')$

$$U(t, t') = 1 + \sum_{n=1}^{\infty} (-\mathrm{i})^n \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \mathrm{d}t_1 \cdots \mathrm{d}t_n$$

$$\times \theta(t - t_1) L(t_1) \theta(t_1 - t_2) L(t_2) \cdots L(t_n) \theta(t_n - t'), \tag{4.3}$$

$\theta(t_i - t_k)$ being the Heaviside step function. Inserting the nth-order term into (4.1) we have to evaluate a trace of the kind

$$\mathrm{Tr}\,[O_n(t_0) L(t_1) \cdots L(t_n) \sigma(t')]. \tag{4.4}$$

Because of the commutators contained in the definition of L (4.4) actually consists of a sum of terms with different arrangements of the corresponding operators $W(t_i)$ with respect to $\sigma(t')$. In this sum, there is exactly one term which is obtained from (4.4) by replacing all the $L(t_i)$ by $W(t_i)$, *i.e.*,

$$\mathrm{Tr}\,[O_n(t_0) W(t_1) \cdots W(t_n) \sigma(t')],$$

which is by virtue of the cyclic invariance of the trace equal to

$$\mathrm{Tr}\,[O_n(t_0 - t') W(t_1 - t') \cdots W(t_n - t') \sigma_s(t')], \tag{4.5}$$

σ_s being the Schrödinger representation of σ.

This term shall be considered first. The operators W and O_n are written explicitly as

$$W(t_i - t') = \sum_{i_1 \cdots i_n} \langle i_1 \cdots | W(t_i - t') | i_n \cdots \rangle a_{i_1}^{+} \cdots a_{i_n}, \tag{4.6}$$

$$O_n(t - t') = \sum_{j_1 \cdots j_m} \langle j_1 \cdots | O_n(t - t') | j_m \cdots \rangle a_{j_1}^{+} \cdots a_{j_m}, \tag{4.7}$$

where the time dependence has been included into the matrix elements. This is easy to do since in the basis chosen H_0 is diagonal, *i.e.*,

$$\mathrm{e}^{(1/\hbar) H_0 t} | j_k \cdots \rangle = \mathrm{e}^{(1/\hbar)(\varepsilon_{j_k} + \cdots) t} | j_k \cdots \rangle. \tag{4.8}$$

Taking the matrix elements out of the trace, we have to evaluate traces of the kind

$$\mathrm{Tr}\,[a_{p_1}^{+} \cdots a_{\alpha_n} \sigma(t')]. \tag{4.9}$$

Using the operators introduced in (3.3) this trace may, apart from a sign, be written as

$$\mathrm{Tr}\,\{T_\tau [\tilde{a}_{\alpha_n}(\tau_{\alpha_n}) \cdots \tilde{\tilde{a}}_{p_1}(\tau_{p_1})] \sigma(t')\}, \tag{4.10}$$

provided the imaginary times τ_i are chosen such that always $|\tau_i| < \varepsilon$ with ε sufficiently small and that T_τ restores the same time ordering as in (4.9). Then, (4.10) is nothing but a many-particle GF of the kind introduced in section 2, and is given by a linked-cluster diagram series. We introduce this series into (4.5) and consider one term from the expansion thus obtained. This term consists of a GF diagram multiplied by a number of matrix elements.

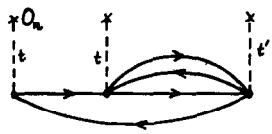


Fig. 1a. Diagram of lowest order contributing to $\Omega_n^{(1)}(t, t')$ for the case that O_n is a one-particle and W a two-particle operator. It contains no σ-part. Its time dependence is δ-function like and thus the diagram contributes to the integral kernel in (5.4).

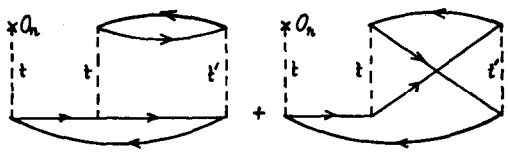


Fig. 1b. The diagrams corresponding to the Hugenholtz diagram in fig. 1a. In these diagrams the two-particle interaction is drawn in the usual way. The association with the matrix elements is now as described in ref. 4.

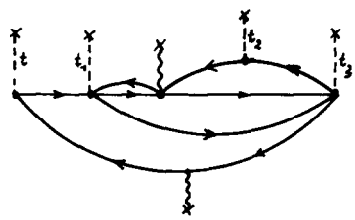


Fig. 2a. A typical diagram occurring in the expansion of $\Omega_n(t, t')$. The diagram contains both LO-vertices and σ-parts.

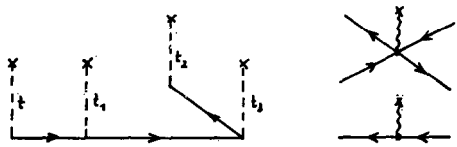
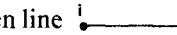


Fig. 2b. The diagram of fig. 2a with the σ-parts drawn separately. From (4.17) it follows that the contribution of this diagram is equal to zero.

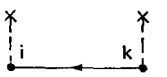
Now we associate with each of these matrix elements a vertex point which is labelled by a dashed line •– – –× and carries a time t_i, $i = 0, 1, \ldots, n$. These vertices will be called *LO*-vertices because they represent both the operator L and the operator O_n. We introduce a time ordering in the drawing plane by agreeing that all the *LO*-vertices are arranged from left to right in such a way, that the vertex i occurs to the left (right) of the vertex k, if $t_i < t_k$ ($t_i > t_k$). The arrangement of the $G_{t'}^{(0)}$ lines and σ-parts with respect to the *LO*-vertices is arbitrary.

As the next step we connect the free ends of the GF diagram with the corresponding vertex points. Thus we obtain a new diagram containing both *LO*-vertices and σ-parts and having no free ends. The explicit description for the construction of these diagrams is given in rule (i) below. Some examples may be found in figs. 1 and 2.

From the time ordering introduced above it follows immediately that for any given line 

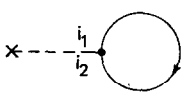
connecting two *LO*-vertices we have always $\tau_i > \tau_k (\tau_i < \tau_k)$ if this line is directed to the right (left). Since the τ_i were introduced only to reproduce the correct time ordering we may now let $\varepsilon \to 0$. Thus, with every directed line connecting two *LO*-vertices a factor is associated in the following way:

$$= G_{t'}^{(0)}(i, k; 0^+) = g^{>}(i, k, t'), \tag{4.11}$$



$$= G_{t'}^{(0)}(k, i; 0^-) = g^{<}(k, i, t'), \tag{4.12}$$

where $G_{t'}^{(0)}$ was defined in (3.13). For a line connected with only one vertex point we find by the usual reasoning[4])



$$= g^{<}(i_1, i_2, t'). \tag{4.13}$$

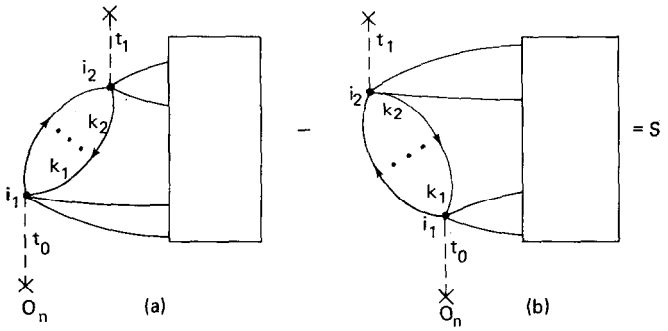
Having established the diagram expansion of (4.5) we now proceed to carry out the commutators contained in (4.4). Replacing $W(t_1)$ with $L(t_1)$ in (4.5) we have to consider, instead of (4.5), the expression

$$\mathrm{Tr}\,[O_n(t_0)\, W(t_1) \cdots W(t_n)\, \sigma(t')] - \mathrm{Tr}\,[W(t_1)\, O_n(t_0) \cdots W(t_n)\, \sigma(t')]$$

$$= T_1 - T_2,$$

where the cyclic invariance of the trace was used. All the diagrams representing T_2 are obtained from those of T_1 by simply "pulling" the $W(t_1)$ vertex across the

$O_n(t_0)$ vertex. As an example consider the two diagrams



(4.14)

where we suppose diagram (a) to be one of the diagrams occurring in the expansion of T_1. Then the second diagram is the corresponding diagram occurring in T_2. Applying (4.11) and (4.12) we write the contribution of diagram (a) in (4.14) as

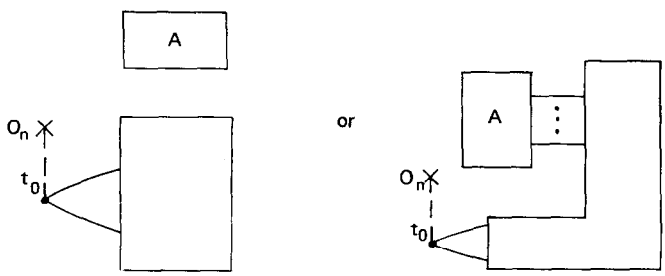
$$[g^{>}(i_1, i_2, t') \cdots g^{<}(k_2, k_1, t')]\, R, \tag{4.15}$$

where R contains all the remaining factors. Using (4.11), (4.12) again we find for the sum (4.14) the expression

$$S = [g^{>}(i_1, i_2, t') \cdots g^{<}(k_2, k_1, t') - g^{<}(i_1, i_2, t') \cdots g^{>}(k_2, k_1, t')]\, R. \tag{4.16}$$

This sum is immediately obtained from diagram (a) if we agree to associate the bundle of lines running from the t_1 vertex to the left (*i.e.* to the t_0 vertex) with the first factor of the r.h.s, of (4.16). By repeating this way of arguing with all the *LO*-vertices we find that we obtain the trace (4.4) by summing all diagrams belonging to (4.5) provided in these diagrams we do not associate lines with factors $g^{<}$, $g^{>}$ but instead consider the line bundles and associate these with the factors introduced in (4.16). By a line bundle belonging to an *LO*-vertex j we understand the set of all lines connecting the *LO*-vertex j with *LO*-vertices to its left. The lines belonging to σ-parts are not included into the bundles.

By the same arguments it is seen, that any diagram of the following form is equal to zero



(4.17)

where the box labelled by A contains at least one *LO*-vertex which is connected by $G_{t'}^{(0)}$ lines with *LO*-vertices only to its right. This fact considerably reduces the number of diagrams and especially proves the cancellation of unlinked diagrams.

Having established the kind of diagrams representing the expressions (4.4) we see that $\Omega_n(t, t')$ is given by the sum over all these diagrams having n ($n \geq 1$) *LO*-vertices and an arbitrary number m ($m \geq 0$) of σ-parts. The time integration contained in (4.3) can be correctly carried through by associating with two subsequent *LO*-vertices i, k ($i = 0, 1, \ldots$; $k = 1, 2, \ldots$) a θ function $\theta(t_i - t_k)$ and with the rightmost *LO*-vertex j a θ-function $\theta(t_j - t')$. Then the integration has to be carried out over all times t_i ($i = 1, \ldots, n$) from $-\infty$ to ∞.

In the representation of the diagrams derived till now, diagrams differing only in the relative time ordering of the *LO*-vertices have to be considered as topologically different. This leads to a tremendous increase in the number of different diagrams with increasing number of *LO*-vertices. As usual, this difficulty can be avoided by using the generalized time-ordering procedure[10, 11]). Then the θ functions occurring in (4.3) have to be associated with the lines connecting the *LO*-vertices rather than with the intervals between the *LO*-vertices. Additionally, a θ function $\theta(t_i - t')$ has to be associated with each *LO*-vertex i which is not connected with *LO*-vertices to its right. In this formulation all those diagrams are topologically equivalent which may be obtained from each other by deformations without changing the direction of a line connecting two *LO*-vertices. To conclude this section the diagram rules will be stated in a concise manner.

4.1. *Diagram rules*

(i) The most general diagram occurring in the expansion of $\Omega_n(t, t')$ is obtained by the following procedure. Draw $n \geq 2$ *LO*-vertex points and $m \geq 0$ σ-parts. Connect the *LO*-vertices with each other by directed lines or by σ-parts. No disconnected diagrams or diagrams having free ends must appear. Label the *LO*-vertices from left to right with times t_i ($i = 0, 1, \ldots$) where $t_0 = t$ and associate each end of a line entering or leaving an *LO*-vertex point with an index $\alpha, \beta, \ldots$

(ii) Associate matrix elements of $O_n(t_0 - t')$ with the *LO*-vertex with time t_0, and matrix elements of $W(t_i - t')$ with the *LO*-vertices with time t_i, $i = 1, 2, \ldots$ The indices of the matrix elements depend on the indices of the lines entering or leaving the vertex. The detailed prescription depends on the type of the interaction and will not be given here.

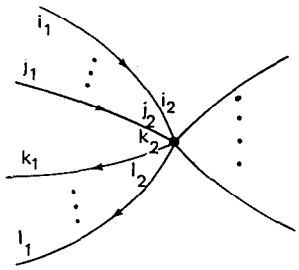
(iii) Now erase the σ-parts from the diagram and associate each σ-part with a factor as described in rules (ii), (iii), (iv) in section 3 (*i.e.*, without the sign factor).

In the following the diagrams are considered without the σ-parts.

(iv) Associate a factor with each line independently of the direction of the line: $\bullet\!\!-\!\!-\!\!\bullet = \theta(t_i - t_k)$.

(v) With each *LO*-vertex j connected with *LO*-vertices only to its left a θ function $\theta(t_j - t')$ has to be associated.

(vi) With each bundle of $n \geq 1$ lines connecting a given *LO*-vertex with *LO* vertices to its left



associate a factor

$$[g^{>}(i_1, i_2, t') \cdots g^{>}(j_1, j_2, t')\, g^{<}(k_2, k_1, t') \cdots g^{<}(l_2, l_1, t')$$

$$- g^{<}(i_1, i_2, t') \cdots g^{<}(j_1, j_2, t')\, g^{>}(k_2, k_1, t') \cdots g^{>}(l_2, l_1, t')].$$

(vii) Integrate over all times t_i, $i = 1, 2, \ldots$ from $-\infty$ to $+\infty$ and sum over all indices $\alpha, \beta, \ldots$

(viii) The resulting expression is multiplied by a factor $(-\mathrm{i}/\hbar)^{N-1}(-1)^{L}$ where N is the number of *LO*-vertices and L is the number of closed fermion loops in the diagram. These loops have to be counted before removing the σ-parts.

5. Discussion

In the preceding section, it was shown how for any given system and any set of operators O_n the diagram expansion of the functions $\Omega_n(t, t')$ of (4.1) can be written down.

Because of the properties of the GF's introduced in section 2 the $\Omega_n(t, t')$ are obtained as a power-series expansion in the parameters $\lambda_i(t')$. By the same procedure as described in section 2 the Ω_n can also be written down as a power-series expansion in terms of the $\Delta\Lambda_i(t')$ characterizing the deviation from equilibrium. Since at least near equilibrium the $\Delta\Lambda_i(t')$ have the physical meaning of the thermodynamic conjugates of the $\bar{O}_n(t)$ [1, 2]) this form of the EM's may be interpreted as generalized Onsager relations. If desired the $\Delta\Lambda_i(t')$ or the $\lambda_i(t')$ can be eliminated by using the GF technique of section 2 to establish the relation between these quantities and the $\bar{O}_n(t)$. In several important applications the elimination of the λ_i is achieved much more easily by summing certain σ-parts in the diagrams up to infinite order.

A serious problem encountered in all the expansions using time-dependent perturbation theory in nonequilibrium statistical mechanics consists in the occurrence of secular divergencies[11, 12]). These show up in the diagram expansion of the functions $\Omega_n(t, t')$, too. However, provided the memory of the system is short as compared with the relaxation time t_R of the $\bar{O}_n(t)$ we are able to show, that the divergent terms cancel each other approximately and with vanishing memory even exactly.

The assumption of a short memory means that there exists a time t_m such that the integrand in (2.13) contributes nothing for times $t' < t - t_m$. Then, we may replace in (2.13) the lower limit of integration by t_1 where

$$t_1 = \begin{cases} 0, & t - t_m, \\ t < t_m, & t > t_m. \end{cases}$$

The same replacement may be made in (2.7).

To study the time dependence of $\Omega_n^{(2)}$ we derive an integral equation

$$-\mathrm{i}\Omega^{(2)}(t, t') = -\mathrm{i}\Omega_n^{(0)}(t) - \int_{t'}^{t} \mathrm{d}t'' \left(\Omega_n^{(1)}(t, t'') - \mathrm{i} \sum_m \dot{\bar{O}}_m(t'') \frac{\partial}{\partial \bar{O}_m(t'')} \Omega_n^{(2)}(t, t'') \right), \quad (5.1)$$

using the same method as in section 2. Apart from the lower limit of the time integration t' the r.h.s. of (5.1) has the same form as the r.h.s. of (2.7). Thus, for $t > t_m$ we may replace the t' in (5.1) by t_1 obtaining

$$-\mathrm{i}\Omega_n^{(2)}(t, t') = -\mathrm{i}\Omega_n^{(2)}(t, t - t_m) = \dot{\bar{O}}_n(t), \qquad t - t' > t_m. \quad (5.2)$$

For $t = t'$ we find from (5.1) or directly from (2.10)

$$\Omega_n^{(2)}(t, t') = \Omega_n^{(0)}(t), \qquad t = t'. \quad (5.3)$$

From (5.2) and (5.3) we see that in the time interval from $t' = t - t_m$ to $t' = t$ $\Omega_n^{(2)}(t, t')$ changes from $\Omega_n^{(0)}(t)$ to $\dot{\bar{O}}_n(t)$ and for $t_m \to 0$ $\Omega_n^{(2)}$ becomes discontinuous at $t' = t$. The time dependence of $\Omega_n^{(1)}$ is obtained from (4.2) as

$$\Omega_n^{(1)}(t, t') = \mathrm{i} \frac{\mathrm{d}}{\mathrm{d}t} \Omega_n^{(2)}(t, t').$$

This means that for $t_m \ll t_R$, $\Omega_n^{(1)}(t, t')$ has a δ-function like behaviour for $t - t' < t_m$ and a long-time tail given by $\ddot{\bar{O}}_n(t)$ for $t - t' > t_m$. Doing a similar analysis as Prigogine[13]) in his investigation of the diagram expansion of the

Fourier coefficients of $\varrho(t)$ we find that the δ-function like behaviour of $\Omega^{(1)}(t, t')$ is due to the diagrams having no secular divergencies, whereas the long-time tail is caused by the secular-divergent diagrams. Since the nondivergent diagrams are zero for $t - t' > t_m$ we may write, using (4.1), and the finiteness of $\dot{\bar{O}}_n(t)$ and $\Omega_n^{(2)}(t, t')$,

$$\dot{\bar{O}}_n(t) = -i\Omega_n^{(0)}(t) - \int_0^t dt' \, \mathrm{Tr} \{O_n(t) [L(t) + L_0] U(t, t') [L(t') + L_0] \sigma(t')\}_{\mathrm{NSD}}, \qquad (5.4)$$

where NSD means that only diagrams having no secular divergencies have to be taken into account. (5.4) is exactly valid if $t_m \to 0$ and holds to good approximation as long as $t_m \ll t_R$ which is the case for most systems of interest. The EM's (5.4) are much easier than the original equations (2.7) and are valid for any system arbitrarily far from equilibrium provided the memory is not too long.

As a first application of the formalism described we have derived EM's for a harmonic oscillator in a bath, a generalized Boltzmann equation and rate equations of chemical reactions. To obtain these equations only the renormalized diagram of lowest order occurring in (5.4) was taken into account. The renormalization was achieved as usual by summing the two-particle ladders. These lowest-order results yield EM's in a nonlocal and memory-retaining form which reduce to the familiar equations if these effects are neglected. Proceeding to higher orders, the above sketched cancellation of secular divergencies occurring in (2.12) is explicitly observed. The applications of this formalism shall be the subject of forthcoming papers.

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References

1) B. Robertson, Phys. Rev. **144** (1966) 151.
2) B. Robertson, Phys. Rev. **160** (1967) 175, **153** (1967) 391, **166** (1968) 206; J. math. Phys. **11** (1970) 2482.
3) *E.g.*, A. R. Altenberger, Physica **62** (1972) 379 and references therein.
4) A. A. Abrikosov, Quantum Field Theoretical Methods in Statistical Physics (Pergamon Press, New York, 1965).
5) R. D. Mattuck, A Guide to Feynman Diagrams in the Many-Body Problem (McGraw-Hill, New York, 1967).
D. Pines and P. Nozieres, The Theory of Quantum Liquids (Benjamin, New York, 1966).

6) T. Matsubara, Progr. theor. Phys. **14** (1955) 351.
7) I. Prigogine, Nature **246** (1973) 67.
8) A. Katz, Principles of Statistical Mechanics (Freeman, San Francisco, 1967).
9) N. M. Hugenholtz, Physica **23** (1957) 481.
B. H. Brandow, Rev. mod. Phys. **39** (1967) 771, app. B.
10) H. A. Bethe, B. H. Brandow and A. G. Petschek, Phys. Rev. **129** (1963) 225.
11) L. E. Reichl, Physica **58** (1972) 1.
12) J. V. Sengers, Phys. Rev. Letters **15** (1965) 515.
J. V. Sengers, Phys. Fluids **9** (1966) 1333, 1685.
S. Fujita, Phys. Letters **A24** (1967) 235.
J. R. Dorfmann and E. G. D. Cohen, J. math. Phys. **8** (1967) 282.
P. Goldberg and G. Sandri, Phys. Rev. **154** (1967) 188, 199.
13) I. Prigogine, Non-Equilibrium Statistical Mechanics (John Wiley, New York, 1962).
14) R. Der and R. Haberlandt, Phys. Letters **49A** (1974) 157.