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ON THE FUNCTIONAL RELATION BETWEEN THE GENERALIZED VAN HOVE TIME-DEPENDENT CORRELATION FUNCTIONS

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A functional relation between the self and total time-correlation functions, which are a generalization of the Van Hove time-correlation functions, is derived by the application of the projection operator technique. The relation is exact and generalizes the well-known Vineyard's convolution approximation. The low density limit is also discussed. Only classical systems are considered.

In recent years a great deal of interest is observed in studies of the time-correlation functions. A variety of techniques which allow a theoretical analysis and to a certain extent also an explicit calculation of the functions, have been developed. Up to the present time a number of time-correlation functions connected either with the theory of transport coefficients or with the theory of relaxation processes, have been considered. There are, however, two functions of a special interest in the theory. If we denote by $\boldsymbol{x} = (\boldsymbol{r}, \boldsymbol{p})$ a particular point of the phase space and by $\boldsymbol{x}_i = (\boldsymbol{r}_i, \boldsymbol{p}_i)$ the position and momentum vectors of the i-th particle, we can define them as

$$G_{\mathrm{self}}(\boldsymbol{x}|\boldsymbol{x}'; t) = \frac{\Omega}{\overline{N}} \langle \sum_{i=1}^{N} \delta(\boldsymbol{x}-\boldsymbol{x}_i)\delta[\boldsymbol{x}'-\boldsymbol{x}_j(-t)]\rangle \tag{1}$$

and

$$G_{\mathrm{total}}(\boldsymbol{x}|\boldsymbol{x}'; t) = \frac{\Omega}{\overline{N}} \langle \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(\boldsymbol{x}-\boldsymbol{x}_i)\delta[\boldsymbol{x}'-\boldsymbol{x}_j(-t)]\rangle. \tag{2}$$

By Ω we denote here the volume of the system; $\overline{N}$ is the mean number of particles; $\delta(\boldsymbol{x}-\boldsymbol{x}_i) = \delta(\boldsymbol{r}-\boldsymbol{r}_i)\,\delta(\boldsymbol{p}-\boldsymbol{p}_i)$ is the six-dimensional Dirac delta function and by $\langle \quad \rangle$ we mean an averaging over the grand canonical equilibrium distribution defined by

$$\langle A(\boldsymbol{x}^N)\rangle = \Xi^{-1} \sum_{N=1}^{\infty} \frac{\alpha^N}{N!} \int d\boldsymbol{x}^N A(\boldsymbol{x}^N) e^{-\beta u_N} \prod_{i=1}^{N} \varphi(\boldsymbol{p}_i). \tag{3}$$

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The functions defined by the equations (1) and (2) are simple momentum dependent generalizations of the well-known Van Hove correlation functions which, with various modifications, have been studied recently by several authors [1–7]. The Van Hove functions itself can be obtained by integration of (1) and (2) over the momentum variables $\boldsymbol{p}$ and $\boldsymbol{p}'$. The theoretical importance of the functions follows from the fact that an arbitrary, one--particle time correlation function can be expressed as an integral of the appropriate one--particle function and one of the function (1) or (2). For example the velocity correlation function can be expressed as

$$\langle V_i(0)V_i(-t)\rangle = \frac{1}{\Omega}\int dx' dx G_{\text{self}}(x|x'; t)VV'.$$

A number of other time correlation functions can be determined in a similar manner.

It is the aim of the present paper to show that the functions (1) and (2) are not independent and can be connected by a functional relation. Thus the whole theoretical problem is reduced in principle to the study of motion of a single marked particle in the heat bath of the other particles of the system. To obtain the exact functional relation we apply two versions of the projection operator technique. The first, based on the well-known Zwanzig formulas [8] leads to the relation which contains a convolution in time. Such time delocalization is frequently interpreted as a kind of "memory" which appears in the mechanical systems [9, 10]. The second approach, based on our modification of the projection operator formalism proposed recently by Fuliński, Kramarczyk and Voss [11, 12], gives a convolutionless form of the relation. Both the functionals are in their general forms exact and equivalent. However, when a particular approximation procedure (as for example the density expansion) is applied, the successive steps of the approximation, the schemes are different. Up to the present time it is not known which of the formalisms will be more effective in practical calculations.

Let us define an auxilliary function $F_N^{(j)}(x^N; t)$ by the equation

$$F_N^{(j)}(\boldsymbol{x}^N; t) = e^{-tK_N}\delta(\boldsymbol{x}'-\boldsymbol{x}_j)e^{-\beta u_N}\prod_{i=1}^{N}\varphi(\boldsymbol{p}_i) \tag{4}$$

where K_N is the Liouville operator of the N-particle system [10],

$$K_N = K_N^0+\delta K_N$$

where

$$K_N^0 = \sum_{i=1}^{N} \boldsymbol{v}_i\cdot\partial/\partial\boldsymbol{r}_i$$

and

$$\delta K_N = -\sum_{i<j}\partial u(|\boldsymbol{r}_i-\boldsymbol{r}_j|)/\partial\boldsymbol{r}_i\cdot(\partial/\partial\boldsymbol{p}_i-\partial/\partial\boldsymbol{p}_j).$$

The functions (1) and (2) can now be expressed in the form

$$G_{\text{self}}(\boldsymbol{x}|\boldsymbol{x}'; t) = \frac{\Omega}{N\Xi}\sum_{N=1}^{\infty}\frac{\alpha^N}{(N-1)!}\int d\boldsymbol{x}^N\delta(\boldsymbol{x}-\boldsymbol{x}_1)F_N^{(1)}(\boldsymbol{x}^N; t) \tag{5}$$

and

$$G_{\text{total}}(x|x';t) = \frac{\Omega}{\bar{N}\Xi}\sum_{N=1}^{\infty}\frac{\alpha^N}{N!}\int dx^N \sum_{i=1}^{N}\delta(x-x_i)\sum_{j=1}^{N}F_N^{(j)}(x^N;t). \tag{6}$$

By the application of the projection operators we obtain

$$F_N^{(j)}(t) = P_j F_N^{(j)}(t) + Q_j F_N^{(j)}(t)$$

where

$$P_j = \prod_{i=1}^{N}\varphi(p_i)\frac{e^{-\beta u_N}}{\varphi(p_j)}\frac{\Omega}{\bar{N}\Xi}\sum_{N=1}^{\infty}\frac{\alpha^N}{(N-1)!}\int dx_{\neq j}^{N-1} \tag{7}$$

$$Q_j = 1 - P_j.$$

The projection operator P_j was chosen in such a manner that $Q_j F_N^{(j)}(x^N; 0) = 0$. Following the Zwanzig method [8] we express the function $Q_j F_N^{(j)}(t)$ as a functional of $P_j F_N^{(j)}(t)$ and finally obtain

$$G_{\text{total}}(x|x';t) = \int dx'' G_{\text{total}}(x|x'';0) G_{\text{self}}(x''|x';t)\,[\varphi(p'')]^{-1} -$$

$$-\frac{\Omega}{\bar{N}}\int dx''\left\langle \sum_{i=1}^{N}\delta(x-x_i)\sum_{j=1}^{N}\int_0^t d\tau Q_j e^{-\tau Q_j K_N}\delta(x''-x_j)\,[\varphi(p_j)]^{-1}\right\rangle G_{\text{self}}(x''|x';t-\tau) \tag{8}$$

with

$$G_{\text{total}}(x|x';0) = \delta(x-x')\,\varphi(p') + \bar{N}/\Omega\, g_2(r,r')\,\varphi(p')\varphi(p). \tag{9}$$

By $g_2(r_i, r_j)$ we denote the equilibrium pair correlation function [13].

The exact relation (8) is a generalization of the Vineyard's convolution approximation [14] discussed recently by Nossal [15] and Stecki and Narbutowicz [16]. The original Vineyard approximation can be obtained if one retains only the first term of the right-hand side of the equation (8) and integrates over the momentum variables.

An equivalent but convolutionless form of the functional relation can be obtained by the application of our modified version [17] of the formalism of Fuliński, Kramarczyk and Voss [11, 12]. We obtain

$$G_{\text{total}}(x|x';t) = \int dx'' G^0_{\text{total}}(x|x':t) G_{\text{self}}(p'', r''+v''t|x';t)\,[\varphi(p'')]^{-1} -$$

$$-\frac{\Omega}{\bar{N}}\int dx''\left\langle \sum_{i=1}^{N}\delta(x-x_i)\sum_{j=1}^{N}Q_j(t)E_N(t)\,[1-P_j(t)E_N(t)]^{-1}e^{-tK_N^0}\times\right.$$

$$\left.\times[\varphi(p_j)]^{-1}\delta(r''-r_j-v_j t)\delta(p''-p_j)\right\rangle G_{\text{self}}(x''|x';t) \tag{10}$$

where we have introduced a time-dependent projection operator defined as

$$P_j(t) = \frac{\prod_{i=1}^{N} \varphi(p_i)}{\varphi(p_j)} e^{-t^{K_N{}^0}} e^{-\beta u_N e^{tv_j\partial/\partial r_j}} \frac{\Omega}{\overline{N}\Xi} \sum_{N=1}^{\infty} \frac{\alpha^N}{(N-1)!} \int dx_{\neq j}^{N-1}. \tag{11}$$

By $Q_j(t)$ we denote, as usual, the operator $I-P_j(t)$ and by $E_N(t)$ the operator defined by

$$E_N(t) = 1-e^{-tK_N} e^{t^{K_N{}^0}}.$$

The function $G^0_{\text{total}}(x|x'; t)$ given by the equation

$$G^0_{\text{total}}(x|x'; t) = (\Omega/\overline{N}) \langle \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(x-x_i) e^{-t^{K_N{}^0}} \delta(x'-x_j) \rangle =$$

$$= \delta(r'+v't-r)\delta(p'-p)\varphi(p) + \frac{\overline{N}}{\Omega}\, g_2(r-vt, r')\varphi(p')\varphi(p) \tag{12}$$

is the linear trajectory approximation form of the G_{total}.

The function $G_{\text{self}}(x|x'; t)$ is the solution of the self-diffusion type kinetic equation. A number of such equations have been proposed and discussed recently [1, 3, 5, 7] within the framework of the convolution formalism. For completeness we present here the convolutionless form of the formalism equation. We have [17]

$$\partial_t G_{\text{self}}(x|x'; t) + v \cdot \partial/\partial r G_{\text{self}}(x|x'; t) + (\Omega/N) \int dx'' \times$$

$$\times \langle \sum_{i=1}^{N} \delta(x-x_i)\delta K_N e^{-t^{K_N{}^0}} \delta(x''-e^{v_i t\cdot\partial/\partial r_i} x_i)\, [\varphi(p_i)]^{-1} \rangle G_{\text{self}}(x''|x'; t) =$$

$$= \frac{\Omega}{\overline{N}} \int dx'' \left\langle \sum_{i=1}^{N} \delta(x-x_i)\delta K_N Q_i(t) E_N(t)\, [1-P_i(t)E_N(t)]^{-1} \times \right.$$

$$\left. \times\, e^{-t^{K_N{}^0}} [\varphi(p_i)]^{-1} \delta(x''-e^{v_i t\cdot\partial/\partial r_i} x_i) \right\rangle G_{\text{self}}(x''|x'; t). \tag{13}$$

It can be easily shown that in the low density approximation this equation reduces to the familiar Boltzmann-Enskog kinetic equation and in the weak coupling limit the Fokker-Planck equation can be obtained. Finding the solution of the equations is a problem in itself which we do not intend to discuss here. Yet even if the exact form of the self-function is known, the relations (8) and (10) have to be approximated. In fact, it is hardly possible to solve the N-body problem as it is necessary for the application of the exact form of the functional relation. If we however restrict ourselves to the case of dilute gas we can expand the second term of the right-hand side of the relations in powers of the absolute activity

α ($\lim\limits_{\bar{N}/\Omega\to 0} \alpha = \bar{N}/\Omega$) and obtain

$$G_{\text{total}}(x|x'; t) = \int dx'' G_{\text{total}}(x|x''; 0) G_{\text{self}}(x''|x'; t) [\varphi(p'')]^{-1} -$$
$$-\alpha \int dx'' \int dx_1 dx_2 \delta(x-x_1) \int_0^t d\tau K_2 e^{-\tau K_2} \delta(x''-x_2) \times$$
$$\times \varphi(p_1) e^{-\beta u(|r_1-r_2|)} G_{\text{self}}(x''|x'; t-\tau) \tag{14}$$

and

$$G_{\text{total}}(x|x'; t) = \int dx'' G^0_{\text{total}}(x|x''; t) G_{\text{self}}(p'', r''+V''t|x'; t) [\varphi(p'')]^{-1} -$$
$$-\alpha \int dx'' \int dx_1 dx_2 \delta(x-x_1) [e^{-tK_2^0} - e^{-tK_2}] \varphi(p_1) \times$$
$$\times \delta(r''-r_2+v_2 t) \delta(p''-p_2) e^{-\beta u(|r_1-r_2|)} G_{\text{self}}(x''|x'; t) \tag{15}$$

in the convolution and convolutionless approaches, respectively.

The calculations can proceed if an explicit form of the interparticle potential is assumed. For example for particles interacting *via* the hard-core potential, equation (15) can be expressed in the form of the familiar collision integral [13]

$$G_{\text{total}}(x|x'; t) = \int dx'' G^0_{\text{total}}(x|x''; t) G_{\text{self}}(p'', r''+v''t|x'; t) [\varphi(p'')]^{-1} +$$
$$+\alpha \int dp_2 \int d\hat{\sigma}\sigma^2 \int_0^t d\tau |(v-v_2)\cdot\hat{\sigma}| \{G_{\text{self}}(r+\sigma+\tau(v_2^*-v), p_2^*|x'; t)\varphi(p^*) -$$
$$- G_{\text{self}}(r-\sigma+\tau(v_2-v), p_2|x'; t)\varphi(p)\}. \tag{16}$$

The functional relations (8) and (10) could be also applied for the determination of the closed kinetic equation for the function G_{total} itself. We hope to discuss the problem in the subsequent paper.

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