Mean Velocity Equation for Turbulent Fluid Flow: An Approach via Classical Statistical Mechanics

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October 16, 2018

Abstract

The possibility to derive an equation for the mean velocity field in turbulent flow by using classical statistical mechanics is investigated. An application of projection operator technique available in the literature is used for this purpose. It is argued that the hydrodynamic velocity defined there, in situations where the fluid is turbulent, is to be interpreted as the mean velocity field; in that case, the momentum component of the generalized transport equation derived there is the mean velocity equation.

In this paper, stationary incompressible flow for constant mass density and temperature is considered. The stress tensor is obtained as a nonlinear functional of the mean velocity field, the linear part of which is the Stokes tensor. The formula contains a time correlation function in local equilibrium. Presently, there exists a microscopic theory for time correlations in total equilibrium only. For this reason and as a preliminary measure, the formula has been expanded into a power series in the mean velocity; though this limits the applicability to low Reynolds number flow. The second order term has been evaluated in a former paper of the author. For the third order term, the form of the kernel function is derived. Its calculation with the aid of the mode-coupling theory is completed; it will be reported in a separate paper. An numerical application with the data of the circular jet is under way.

Key words: statistical thermodynamics, projection operator technique, turbulent flow

1 Introduction

In turbulence experiments, very often the relevant variables - those which can be related to the external conditions of the experiment - are not the actual
quantities but their mean values. The process is then described by a statistical theory. It is well known that it can be very difficult to derive equations for mean values which are closed. It can be argued that the reason is that it is difficult to construct the multi-point probability distribution for the process.

In this paper, the possibility to derive an equation for the mean velocity field in turbulent flow by using classical statistical mechanics is investigated. Then, in principle the probability distribution of the process can always be constructed starting from the total equilibrium distribution. On the other hand, it will be necessary to distinguish between macroscopic and microscopic parts of the motion and to formulate the latter in a way suitable for hydrodynamic purpose.

It is known that the Navier-Stokes equation can be derived from Statistical Mechanics. This has been performed first by Chapman and Enskog in 1916 and 1917, with the Boltzmann equation as a starting point; see, e. g., Huang [1]. More recently, a formalism has been developed which starts from the Liouville equation and applies projection operator technique; see Zwanzig [2], Mori [3]. Here, the presentation of Grabert [4] is used as a reference. In the relevant part of this work, a generalized transport equation is derived; the application for simple fluids and a suitable approximation of the stress tensor lead to the Navier-Stokes equation. In the present paper, arguments are given that for situations where the fluid flow is turbulent, the momentum component of the generalized transport equation for simple fluids actually is the mean velocity equation. The formulation is restricted to stationary flow in incompressible fluid of constant density and temperature.

In section 2, some definitions of Statistical Mechanics and the basic steps which lead to the generalized transport equation are referenced from [4]. The interpretation of the momentum component as the mean velocity equation is explained. It is known that the form of this equation is very similar to the Navier-Stokes equation, with an additional friction force term (Reynolds force). There are numerous approaches to formulate this quantity (see, e. g., [5] and the references therein); it is seen that it is nonlinear in the velocity and, after all evidence, also nonlocal. As a preliminary measure, the friction force has been expanded into a power series in the velocity; though this limits the application to low Reynolds number flow. This is explained in section 3. The main results for the 2nd order term reported earlier [6], [7] are quoted; the calculation of the formula for the 3rd order term is presented in this paper.

## 2 Mean velocity equation

In this section, the definitions and the basic steps of the derivation of the generalized transport equation are referenced from Grabert [4]; the notation is slightly different. The fluid is considered to be a system of $N$ particles of mass $m$ with positions $y_j$ and velocities $v_j$ (simple fluid) which are combined to the phase space vector $z$. Vector components are described by Latin indices, e. g. $y_j = \{y_{jn}\}$. The particles interact with a symmetric, short-ranged, pairwise additive interparticle potential. The system is enclosed in a box of Volume $V$.
A function \( g(z) \) is called a phase space function, or microscopic variable. Especially, we need the space densities of the conserved quantities particle number, energy and momentum \( n, e, p \) which are collected to a 5-element linear matrix \( \mathbf{a} \). They are functions of an additional space variable \( x \):

\[
\mathbf{a} = \sum_{j=1}^{N} \tilde{a}_j \delta(x - y_j) \tag{2.1}
\]

For the particle functions \( \tilde{a}_j \) we have \( \tilde{n}_j = 1 \), \( \tilde{p}_j = mv_j \), while the energy function contains the interparticle potential. The quantities \( \mathbf{a} \) obey the conservation relations:

\[
\dot{\mathbf{a}} = -\nabla \cdot \mathbf{s} \tag{2.2}
\]

The fluxes \( \mathbf{s} \) have the same general structure as the \( \mathbf{a} \) (2.1); the particle functions can be found in [4]; especially, we have \( s_1 = p/m \). The time evolution of any phase space function \( g \) is described by the Liouville equation:

\[
\dot{g} = i\mathcal{L}g \tag{2.3}
\]

\( i\mathcal{L} \) is the Liouville operator, a linear differential operator the form of which can be found in any textbook of statistical mechanics. From (2.3), the formal solution for \( g(t) \) given the initial value \( g \) is:

\[
g(t) = e^{i\mathcal{L}t} g \tag{2.4}
\]

In the statistical model, \( z \) and \( N \) are considered random variables; that is, the probability density \( f(z, N) \) is of grand canonical type. The ensemble mean value (expectation) of a phase space function \( g \) is defined in the ‘Heisenberg’ picture:

\[
\langle g \rangle(t) = \sum_{N=1}^{\infty} \int d\Omega \sum_{N=1}^{\infty} \int d\Omega \langle z, N, t \rangle f(z, N) \tag{2.5}
\]

In this formula, \( f(z, N) \) is the initial probability distribution, and \( g(z, N, t) \) is the value of \( g \) at time \( t \) if the initial positions and velocities of the particles are described by \( z \). The operation (integration + Summation) is sometimes indicated by the symbol ‘tr’:

\[
\text{tr}\{\Omega\} = \sum_{N=1}^{\infty} \int d\Omega(z, N) \tag{2.6}
\]

Certain probability densities (also called distributions here) are frequently used in the analysis. One of them is the (total) equilibrium distribution which corresponds to macroscopic rest:

\[
f_0 = \psi(N) \exp(\Phi_0 + \beta(\mu N - H(z))) \tag{2.7a}
\]

\[
\psi(N) = N! \left( \frac{m}{\hbar} \right)^{3N} \tag{2.7b}
\]
Here, \( h \) is Planck’s constant, \( \beta = 1/(k_B T) \), \( k_B \) being Boltzmann’s constant and \( T \) the temperature, \( \mu \) is the chemical potential which is a function of mass density and temperature, and \( H(z) \) is Hamilton’s function which describes the total energy of the fluid. For the normalization constant, we have \( \Phi_0 = -\beta PV \), \( P \) being the equilibrium pressure. Expectations with respect to the equilibrium distribution are denoted by \( \langle \rangle_0 \). In case of a simple fluid, the ‘relevant probability distribution’ of Grabert’s formalism (see [4], sec. 2.2) is the local equilibrium distribution:

\[
f_L(t) = \psi(N) \exp(\Phi(t) - \mathbf{a}(z) \star \mathbf{b}(t)),
\]

(2.8a)

\[
\mathbf{b} = \{\beta(\frac{m}{2}u^2 - \mu), \beta, -\beta \mathbf{u}\},
\]

(2.8b)

\[
\Phi(t) = -\log(\text{tr}\{\psi \exp(-\mathbf{a} \star \mathbf{b}(t))\}).
\]

(2.8c)

Here the symbol \( \star \) is introduced for the operation: Multiplication, plus Summation over the 5 elements of the linear matrices \( \mathbf{a}, \mathbf{b} \), plus Integration over geometrical space. The elements of \( \mathbf{b} \) are called the conjugate parameters; they are functions of the quantities \( \beta, \mu \) and \( u \) which we will sometimes call the thermodynamic parameters. \( \beta = 1/(kT) \), with \( k \) being Boltzmann’s constant and \( T \) the absolute temperature; \( \mu \) is the chemical potential which is a function of temperature and pressure, and \( u \) is the hydrodynamic velocity. These quantities will be considered slowly varying functions of space and time. The \( \mathbf{b} \) are defined such that the expectations of the \( \mathbf{a} \) are identical to their expectations in local equilibrium:

\[
\langle \mathbf{a} \rangle = \langle \mathbf{a} \rangle_L
\]

(2.9)

The projection operator technique (POT) is a means for separating macroscopic and microscopic parts of the random variables. It starts by defining the set of phase space functions which are relevant for the description of the process. For simple fluids, this set is identified with the densities of conserved variables, \( \mathbf{a} \). A projection operator is defined which projects out of any microscopic variable \( g \) the part which is proportional to the relevant variables. It reads:

\[
P g = \langle g \rangle_L + \langle g \delta \mathbf{a} \rangle_L \star \langle \delta \mathbf{a} \delta \mathbf{a} \rangle_L^{-1} \star \delta \mathbf{a}
\]

(2.10)

Here, \( \delta \mathbf{a} = \mathbf{a} - \langle \mathbf{a} \rangle_L \); \( \langle \rangle_L^{-1} \) denotes the inverse of the expectation matrix in the formula. For stationary flow, \( P \) is time independent. The analysis in [4] starts by splitting the exponential operator (2.4):

\[
e^{i\mathcal{L}t} = e^{i\mathcal{L}t} P + \int_0^t dt' e^{i\mathcal{L}t'} P i\mathcal{L}(1-P) e^{(1-P)i\mathcal{L}(t-t')} + (1-P) e^{(1-P)i\mathcal{L}t} \]

(2.11)

This corresponds to [4], formula (2.4.1), specialized to stationary flow, where especially \( P \) = const\((t)\). With (2.11), the Liouville equation (2.3) is reformulated:

\[
\mathbf{a} = e^{i\mathcal{L}t} P i\mathcal{L} \mathbf{a} +
\int_0^t dt' e^{i\mathcal{L}t'} P i\mathcal{L}(1-P) e^{(1-P)i\mathcal{L}(t-t')} i\mathcal{L} \mathbf{a} + (1-P) e^{(1-P)i\mathcal{L}t} i\mathcal{L} \mathbf{a}
\]

(2.12)
By averaging over the initial probability density, and after some manipulations, Grabert’s generalized transport equation [4], (2.5.17) is obtained. Below, this equation is presented for stationary flow in simple fluids. It is postulated in POT that the initial probability density is of the form of the relevant probability density. Grabert states that this should not be considered a general restriction of the method but a means to form the general particle system into the type specially considered; see [4], sec. 2.2. In [4], sec. 8.3, it is shown that for simple fluids the relevant probability density is that of local equilibrium. For the present approach this means that turbulent flow is considered which initially developed from laminar flow with suitable velocity gradient. - It is a consequence of this postulate that the last term in (2.12) vanishes after averaging. Moreover, it is shown that:

$$\langle e^{i\mathcal{L}_t}\mathcal{P}_i\mathcal{L}_a \rangle = \langle \hat{a} \rangle_L = -\nabla \cdot \langle s \rangle_L$$  \hspace{1cm} (2.13)

In the last step, the conservation relations (2.2) are introduced. Stationary flow is considered to be the process described by the generalized transport equation under stationary conditions and for very large times. One obtains:

$$0 = -\nabla \cdot \langle s \rangle_L + D$$  \hspace{1cm} (2.14)

$$D_\alpha(x) = -\nabla_c \int dx' \int_0^\infty dt \left\langle [e^{(1-P)\mathcal{L}_t} \tilde{s}_{ac}(x)]\tilde{s}_{\beta d}(x') \right\rangle \nabla'_d b_\beta(x')$$  \hspace{1cm} (2.15)

$$\tilde{s}_{ac}(x) = (1-P)s_{ac}(x)$$  \hspace{1cm} (2.16)

Latin and greek indices run over 3 and 5 values, respectively; this is sometimes expressed by saying that, e.g., the index $\alpha$ runs over 1, 2 and the latin index $a$. Eqs. (2.14), (2.15) correspond to [4], (8.1.13), (8.5.1) for stationary flow. From these, now the momentum equation is taken, for which one obtains ([4], (8.4.15)):

$$\langle s_{ac} \rangle_L = \rho u_au_c + P\delta_{ac}$$  \hspace{1cm} (2.17)

Here, $\delta_{ac}$ is the Kronecker symbol, $\rho$ the mass density and $u$ the fluid velocity defined by:

$$\langle p \rangle = \rho u$$  \hspace{1cm} (2.18)

([4], (8.3.12)). At this point, the continuity equation is introduced. This actually is the mass density component of (2.14), and for incompressible constant density flow it reduces to:

$$\nabla \cdot u = 0$$  \hspace{1cm} (2.19)

With these formulas and (2.8b), (2.14), (2.15) obtain their final form:

$$\rho u \cdot \nabla u = -\nabla P + \nabla \cdot R$$  \hspace{1cm} (2.20)

$$R_{ac}(x) = \int dx' S_{abcd}(x,x')\nabla'_d u_b(x')$$  \hspace{1cm} (2.21)

$$S_{abcd}(x,x') = \beta \int_0^\infty dt \left\langle [e^{(1-P)\mathcal{L}_t} \tilde{s}_{ac}(x)]\tilde{s}_{bd}(x') \right\rangle_L$$  \hspace{1cm} (2.22)
It is seen immediately that (2.20) is the hydrodynamic velocity equation for stationary incompressible flow. The stress Tensor $R$ is, in general, a nonlinear functional of $u$. Grabert, in [4], sec. 8.5, performs an approximation to the first order of $\nabla u$ and obtains exactly the Stokes form of the tensor. Therefore, in this approximation, (2.20) is the stationary Navier-Stokes equation.

By (2.18), $u$ is essentially equal to the expectation of the momentum density. By definition from probability theory, the expectation is an average built from a set of realisations of the process, which can be interpreted as repetitions of the experiment under identical external conditions. If the flow exhibits macroscopic, i.e. turbulent, fluctuations, the averaging process includes these. There is barely another possibility than, in this case, to interpret $u$ as the mean velocity of the flow. On the other hand, if one wants to define the 'point' velocity of turbulent flow, it would be necessary to introduce a conditional expectation, which excludes the macroscopic fluctuations, with respect of which the mean quantity would still be a random variable. - The preceding statement is quite general; it is still valid if one performs a projection operator analyses. Thus, in case of stationary turbulent flow (2.20) is the mean velocity equation. It is of course necessary to check this theoretical statement by bringing the equation into a form that can be evaluated, and comparing the results with a turbulent flow experiment.

The difference is that for turbulent flow the nonlinear part of the stress tensor $R$ is essential. The definition formula for the stress tensor kernel function $S$ (2.22) contains a time correlation function in local equilibrium. This is a quantity which, for processes with constant mass density and temperature, is a functional of the velocity field. It has to be evaluated in advance, by a separate statistical-mechanical formalism. At present there is no theoretical means to perform this; instead, it is possible to calculate correlation functions for total equilibrium. It should be emphasized that, since total equilibrium corresponds to macroscopic rest, the latter quantities do not depend on the flow properties; they are material ‘constants’ of the fluid. - In order to pursue the analysis, $S$ has been expanded into a functional power series in $u$; as will be seen, the coefficients of the series contain total equilibrium correlations. It will be necessary then to evaluate the lowest order terms of the expansion and to work with formulas (2.20), (2.21) with an approximated quantity $S$. When the formalism is applied to a given flow configuration, it is possible to render all variable quantities in the expansion dimension-free, which causes certain constant factors to appear in the terms of it. The author elaborates on an application to circular jet flow; where these factors show up actually as increasing powers of the Reynolds number $Re$. Thus, it is seen that in this case the application should be restricted to low Reynolds number flow, just beyond the laminar-turbulent transition.

3 Expansion of the kernel function
$S$ depends on $u$ via the quantities $b$ (2.8b) in the formula for the local equilibrium distribution. The series expansion of $S$ is performed by expanding it with respect to the $b$ at the point $b = b_0$ which corresponds to $u = 0$:

$$b_0 = \{-\beta \mu, \beta, 0\}$$ (3.1)

$$b - b_0 = \{\frac{\beta m}{2} u^2, 0, -\beta u\}$$ (3.2)

Replacing $b$ by $b_0$ changes the local equilibrium distribution (2.8a) into the total equilibrium distribution (2.7a) with the prescribed mass density and temperature. The power expansion of $S$ reads:

$$S = S|_{b_0} + \frac{\delta S}{\delta b}|_{b_0} \ast (b - b_0) + \frac{1}{2!} \frac{\delta^2 S}{\delta b \delta b}|_{b_0} \ast \ast \{(b - b_0), (b - b_0)\} + \cdots$$

$$= S^{(0)} + S^{(1)} + S^{(2)} + \cdots$$ (3.3)

In the second row, symbols are applied to the different orders of the expansion. The expansion in $u$ is obtained from (3.3) by restricting the summation inherent in the $\ast$-operation to the last element of $b - b_0$ in (3.2). It is seen there that the first element also depends on $u$. But for the present investigation, where no sound or heat conduction processes are considered, the expansion coefficients come out to be non-zero only for 'Latin' values of the indices; thus the first element of $b$ does not contribute.

The linear part of $R$ which results from the constant term $S^{(0)}$ of the expansion (3.3) leads to the Stokes form of the stress tensor, which coincides with the result of Grabert. At present, the 2nd and 3rd order terms of $R$ have been analyzed. From (2.21) it can be seen that these stem from the parts $S^{(1)}$ and $S^{(2)}$ of the $S$-series, respectively. To obtain these formulas, it is necessary to calculate the first and second order functional derivatives of $S$. The first of these has been done in Piest [6]. For completeness, the derivation is repeated in the appendix. The result is formula (a.17); by setting $b = b_0$ one obtains:

$$\frac{\delta S_{abcd}(x, x')}{\delta b_e(x'')} \bigg|_{b=b_0} = -\beta \int_0^\infty dt \langle x^{(1-P_0)} \rangle \langle 1 - P_0 \rangle s_{ac}(x) \langle (1 - P_0) s_{bd}(x') \rangle p_e(x'') \rangle_0$$ (3.4)

$P_0$ is the total equilibrium projection operator:

$$P_0 g = \langle g \rangle_0 + \langle g \delta_0 a \rangle_0 * \langle \delta_0 a \delta_0 a \rangle_0^{-1} * \delta_0 a$$ (3.5)

Here, $\delta_0 g = g - \langle g \rangle_0$, and we have $\langle p \rangle_0 = 0$. The total equilibrium triple correlation function contained in (3.4) can be calculated using the mode coupling technique in the form of Martin et al. [8], which is a systematic version of the method of Kawasaki [9], and has been complemented by Dekker and Haake.
The formulas have been evaluated by the author, and applied using the experimental data of the circular jet (Piest [7]). One obtains the solution again in form of a power series. The expansion parameter $\chi$ reads:

$$\chi = \frac{1}{\beta \nu^2 \rho x}$$  \hspace{1cm} (3.6)

$\nu$ is the kinematic viscosity, $x$ the distance of the observation point from the orifice. With a typical value $x = 0.3$ [m], for a laboratory experiment in air, one obtains $\chi = 5.8 \cdot 10^{-11}$, which is so small that practically only the zero order term of the expansion counts.- It was rather surprising that for the linear term of the $u$-series of $S$ (3.3), a zeroth order $\chi$-Term is found which leads to a second order term of the friction force $D = \nabla \cdot R$:

$$D^{(2,0)} = \rho (u \cdot \nabla u) - \frac{\lambda}{2} \nabla (u \cdot u)$$  \hspace{1cm} (3.7)

$\lambda = \alpha / (\gamma c_V)$ is a physical parameter of the fluid, $\alpha$ being the thermal expansion coefficient, $\gamma$ the isothermal compressibility, and $c_V$ the specific heat for constant volume. The apparent existence of this term poses a problem to the interpretation of equation (2.20). It should be noticed that, since for sufficient low Reynolds number the flow is laminar, there are no macroscopic fluctuations then, and $u$ equals the classical hydrodynamic ‘point’ velocity. Therefore, for decreasing $Re$, equation (2.20) should reduce to the stationary Navier-Stokes equation. On the other hand, $D^{(2,0)}$ is of equal power in $Re$ as the quadratic term on the left of (2.20) so that, even for small $Re$, (2.20) remains different. Since this is not possible, something must be wrong with the prerequisites of the derivation of (3.7). As a preliminary measure, it is assumed that the term actually does not exist. It is of course one of the most urging requirements for this approach to sufficiently explain this defect.

The third order term of the expansion of $R$ contains, after (2.21) and (3.3), the second-order derivative, which is presented in (a.35). When this formula is applied to $b = b_0$ as in (3.4), the summation in the corresponding term in (3.3) is restricted to the last term of (3.2) and the result is inserted into (2.21), one obtains for the friction force $D = \nabla \cdot R$:

$$D^{(3)}_a (x) = \int dx' dx'' dx''' K_{abcd}(x, x', x'', x''') u_b(x') u_c(x'') u_d(x''')$$  \hspace{1cm} (3.8)

$$K_{abcd}(x, x', x'', x''') = -\frac{1}{2} \beta^3 \int_0^\infty dt (|c(1-\rho_0)\varepsilon t \nabla c(1-\rho_0)| \delta_0[\nabla(1-\rho_0) s_{ae}(x)] \times \nabla_x (1-\rho_0) s_{bf}(x') |\delta_0[p_c(x'') p_d(x''')]) \delta_0$$  \hspace{1cm} (3.9)

For formal reasons, all $\nabla$-operations have been transferred to the correlation function, partly by partial integration. Formulas (3.8), (3.9) are the main result of the present paper. The definition formula for the kernel function $K$ contains
a time integral over a correlation function which is double in time but quadruple in space. To calculate it, the author has again applied the technique described in Martin et al. [8], Deker and Haake [10]; it had to be enlarged slightly so that quadruple correlations could be determined. This investigation will be presented in a separate paper. The resulting formula is rather lengthy and will not be given here. It should be emphasized that with \( K \) obtained as an explicit formula of the four space variables, (2.20), (3.8) form a closed system for calculating the velocity field for a given flow configuration. Moreover, since this formula is the lowest order term of the expansion (see the comment to (3.7)), (2.20), (3.8) is the simplest form of the system for checking, by comparing with experimental results, whether the approach works. As has been mentioned, a numerical test using the data for the circular jet is in progress.

4 Summary

An approach to arrive at the mean velocity equation for turbulent fluid flow has been attempted with the aid of the projection operator technique in classical Statistical Mechanics. The hydrodynamic velocity is defined in this technique via the conjugate thermodynamic fields in the formula for the relevant probability density; multiplied by the mass density, it is identical to the expectation of the microscopic momentum density. It is argued that in situations where the fluid flow is turbulent, this is precisely the mean velocity field of the flow. If this argument is correct, the momentum component of the generalized transport equation derived by this technique is the mean velocity equation.

Stationary incompressible flow for constant mass density and temperature is considered. The formula for the stress tensor is a nonlinear functional of the velocity, the linear part of which has the form of the Stokes tensor. The formula contains a local equilibrium time correlation function. At present, there exists a theory for calculating correlation functions for total equilibrium only. As a preliminary measure, the stress tensor has been developed into a power series in the velocity, though this limits the applicability of the equation to low Reynolds number flow. The coefficients of the expansion contain total equilibrium correlations which can be calculated. The second order term has been evaluated in a former paper of the author. For completeness, the main results have been reported here. The calculation leads to a second order friction term which is comparable in form to the convolution term of the equation. This constitutes a problem to the present approach since from general knowledge about the Reynolds equation such a term cannot appear.

For the third order term, the form of the kernel function has been calculated. The formula has been evaluated with the aid of the mode coupling theory of Statistical Mechanics; the results will be reported in a separate paper. A numerical calculation in order to test the equation with the experimental data for the circular jet is under way.
Appendix:
Calculation of functional derivatives

In this appendix, the first two derivatives, with respect to \( b \), of the kernel function \( S \) (2.22) are calculated. The right hand side of (2.22) depends on \( b \) at four different places; thus we may write:

\[
\frac{\delta S_{abcd}(x, x')}{\delta b_c(x'')} = \sum_{i=1}^{4} \frac{\delta S}{\delta b}
\]  

(a.1)

The definition of the four terms is given in the formulas to follow. In addition, certain auxiliary formulas are written which can be verified directly. For the first term, we use the rule:

\[
\frac{\delta f}{\delta b} = -f \frac{\delta a}{\delta b}
\]

(a.2)

The first term reads:

\[
\frac{\delta S^{(1)}}{\delta b} = \beta \int_{0}^{\infty} dt \text{tr}\{\delta f L \overline{\delta b}(x'') e^{(1-P)iLt} \hat{s}_{ac}(x) \hat{s}_{bd}(x')\} = -\beta \int_{0}^{\infty} dt \langle [e^{(1-P)iLt} \hat{s}_{ac}(x) \hat{s}_{bd}(x') \delta p_{e}(x'')] \rangle_L
\]

(a.3)

Next, we need the formula for the differentiation of the projection operator \( P \):

\[
\frac{\delta P}{\delta b} = -P \frac{\delta a}{\delta b} (1 - P)
\]

(a.4)

The second term reads:

\[
\frac{\delta S^{(2)}}{\delta b} = -\beta \int_{0}^{\infty} dt \langle [e^{(1-P)iLt} P \hat{s}_{ac}(x) \delta p_{e}(x'')] \hat{s}_{bd}(x') \rangle_L
\]

\[
= \beta \int_{0}^{\infty} dt \langle \hat{\delta p}_{e}(x'') \hat{s}_{bd}(x') \rangle_L
\]

(a.5)

When (a.4) is applied to the third term, one finds, after some manipulations:

\[
\frac{\delta S^{(3)}}{\delta b} = -\beta \int_{0}^{\infty} dt \langle [e^{(1-P)iLt} \hat{s}_{ac}(x) \delta p_{e}(x'')] \hat{s}_{bd}(x') \rangle_L
\]

\[
= \beta \int_{0}^{\infty} dt \langle (1 - P) e^{(1-P)iLt} \hat{s}_{ac}(x) \hat{s}_{bd}(x') \delta p_{e}(x'') \rangle_L = 0
\]

(a.6)

In the second step, it is used that we have:

\[
e^{(1-P)iLt} (1 - P) = (1 - P) e^{(1-P)iLt} (1 - P)
\]

(a.7)
\[
\langle [(1 - \mathcal{P})g_1]\mathcal{P}g_2 \rangle_L = 0 \tag{a.8}
\]

(a.8) is valid for any microscopic functions \(g_1, g_2\). The part containing the differentiation of the exponential operator is a somewhat more involved. The differentiation formula is:

\[
\frac{\delta e^{(1 - \mathcal{P})i\mathcal{L}t}}{\delta b} = \int_0^t dt' e^{(1 - \mathcal{P})i\mathcal{L}t'} \mathcal{P} \delta a \frac{d}{dt} e^{(1 - \mathcal{P})i\mathcal{L}(t - t')} \tag{a.9}
\]

For the corresponding time integral, it follows after interchanging the succession of integrations:

\[
\int_0^\infty dt \frac{\delta e^{(1 - \mathcal{P})i\mathcal{L}t}}{\delta b(f(x''))} = \int_0^\infty dt' \int_0^\infty dt e^{(1 - \mathcal{P})i\mathcal{L}t'} \mathcal{P} \delta p_c(x'') \frac{d}{dt} e^{(1 - \mathcal{P})i\mathcal{L}t}
\]

\[= \int_0^\infty dt' \lim_{t \to \infty} \left\{ e^{(1 - \mathcal{P})i\mathcal{L}t'} \mathcal{P} \delta p_c(x'') e^{(1 - \mathcal{P})i\mathcal{L}t} - e^{(1 - \mathcal{P})i\mathcal{L}t'} \mathcal{P} \delta p_c(x'') \right\} \tag{a.10}
\]

One obtains for the fourth term:

\[
\frac{\delta S^{(4)}}{\delta b} = \beta \int_0^\infty dt \{ [\delta e^{(1 - \mathcal{P})i\mathcal{L}t} / \delta b_c(x')] \hat{s}_{ac}(x)] \hat{s}_{bd}(x') \}
\]

\[= \beta \int_0^\infty dt' \lim_{t \to \infty} \left\{ \{ e^{(1 - \mathcal{P})i\mathcal{L}t'} \mathcal{P} \delta p_c(x'') e^{(1 - \mathcal{P})i\mathcal{L}t} \hat{s}_{ac}(x)] \hat{s}_{bd}(x') \}
\]

\[- \{ e^{(1 - \mathcal{P})i\mathcal{L}t'} \mathcal{P} \delta p_c(x'') \hat{s}_{ac}(x)] \hat{s}_{bd}(x') \} \tag{a.11}
\]

We have to evaluate the limit expression. We will assume here that in the limit of large times, the factors of a time correlation will become statistically independent so that for stationary processes we have:

\[
\lim_{t \to \infty} \langle [e^{(1 - \mathcal{P})i\mathcal{L}t} A] B \rangle_L = \langle A \rangle_L \langle B \rangle_L \tag{a.12}
\]

For any phase space function \(g\), let us define a quantity \(F(t')\):

\[
F(t') = \lim_{t \to \infty} \langle [e^{(1 - \mathcal{P})i\mathcal{L}t'} \mathcal{P} \delta p_c(x'') e^{(1 - \mathcal{P})i\mathcal{L}t} \hat{s}_{ac}(x)] g \rangle_L \tag{a.13}
\]

The evaluation results in:

\[
F(t') = \lim_{t \to \infty} \{ (\delta p_c(x'')) e^{(1 - \mathcal{P})i\mathcal{L}t} \hat{s}_{ac}(x)] \langle g \rangle_L
\]

\[+ \langle \delta p_c(x'') [e^{(1 - \mathcal{P})i\mathcal{L}t} \hat{s}_{ac}(x)] \delta a \rangle_L * \langle \delta a \delta a \rangle_L^{-1} * \langle [e^{(1 - \mathcal{P})i\mathcal{L}t'} \delta a] g \rangle_L \}
\]

\[= \langle \hat{s}_{ac}(x)] \langle \delta p_c(x'') \rangle_L \langle g \rangle_L + \langle \delta p_c(x'') \delta a \rangle_L *
\]

\[* \langle \delta a \delta a \rangle_L^{-1} * \langle [e^{(1 - \mathcal{P})i\mathcal{L}t'} \delta a] g \rangle_L \} = 0 \tag{a.14}
\]

The first step is the evaluation of \(\mathcal{P}\) using (2.10); next, we use (a.12); finally, the factor outside the curled brackets vanishes, since we have, for any phase space function \(g\):

\[
\langle (1 - \mathcal{P})g \rangle_L = 0 \tag{a.15}
\]
Therefore, in (a.11), the limit term vanishes, and we have:

\[
\frac{\delta S^{(4)}}{\delta b} = \beta \int_{0}^{\infty} dt \langle [e^{(1-P)L^{T}} P \hat{s}_{ac}(x) \delta p_c(x')] \hat{s}_{bd}(x') \delta p_c(x'') \rangle \bigg|_{L} = -\frac{\delta S^{(2)}}{\delta b}
\]

(a.16)

Thus, we obtain:

\[
\frac{\delta S_{abcd}(x, x')}{\delta b_c(x'')} = \frac{\delta S^{(1)}}{\delta b} = -\beta \int_{0}^{\infty} dt \langle [e^{(1-P)L^{T}} \hat{s}_{ac}(x)] \hat{s}_{bd}(x') \delta p_c(x'') \rangle \bigg|_{L} \tag{a.17}
\]

The calculation of the coefficients of the second order derivative of $S$ parallels to a certain extent that of the first order. The right hand side of (a.17) depends on $b$ at five different places; thus we write:

\[
\frac{\delta^2 S_{abcd}(x, x')}{\delta b_c(x'') \delta b_f(x''')} = \sum_{i=1}^{5} \frac{\delta^2 S^{(i)}}{\delta b \delta b}
\]

(a.18)

For the first part, we use (a.2):

\[
\frac{\delta^2 S^{(1)}}{\delta b \delta b} = -\beta \int_{0}^{\infty} dt \text{tr} \left\{ \frac{\delta f_L}{\delta b_f(x'')} [e^{(1-P)L^{T}} \hat{s}_{ac}(x)] \hat{s}_{bd}(x') \delta p_c(x'') \right\}
\]

\[
= \beta \int_{0}^{\infty} dt \langle [e^{(1-P)L^{T}} \hat{s}_{ac}(x)] \hat{s}_{bd}(x') \delta p_c(x'') \delta p_f(x''') \rangle \bigg|_{L} \tag{a.19}
\]

The second term, with (a.4), turns out to be:

\[
\frac{\delta^2 S^{(2)}}{\delta b \delta b} = \beta \int_{0}^{\infty} dt \langle [e^{(1-P)L^{T}} \hat{s}_{ac}(x)] \hat{s}_{bd}(x') \delta p_c(x'') \rangle \bigg|_{L} = -\beta \int_{0}^{\infty} dt \langle [e^{(1-P)L^{T}} P \hat{s}_{ac}(x)] \delta p_f(x''') \rangle \hat{s}_{bd}(x') \delta p_c(x'') \bigg|_{L} \tag{a.20}
\]

In the same way, we have for the third term:

\[
\frac{\delta^2 S^{(3)}}{\delta b \delta b} = \beta \int_{0}^{\infty} dt \langle [e^{(1-P)L^{T}} \hat{s}_{ac}(x)] \delta P \hat{s}_{bd}(x') \delta p_c(x'') \rangle \bigg|_{L} = -\beta \int_{0}^{\infty} dt \langle [e^{(1-P)L^{T}} \hat{s}_{ac}(x)] \delta P \hat{s}_{bd}(x') \delta p_f(x''') \rangle \delta p_c(x'') \bigg|_{L} \tag{a.21}
\]

For the fourth part containing the differentiation of the exponential operator
we have, with (a.10):

\[
\frac{\delta^2 S}{\delta b \delta b} \overset{(4)}{=} -\beta \int_0^\infty dt \left( \frac{\delta}{\delta b_f(x''')} \hat{s}_{ac}(x) \hat{s}_{bd}(x') \delta p_e(x'') \right)_L \\
= -\beta \int_0^\infty dt' \left( \lim_{t' \to \infty} \left[ e^{(1-P)LT} \mathcal{P} \delta p_f(x''') e^{(1-P)LT} \hat{s}_{ac}(x) \hat{s}_{bd}(x') \delta p_e(x'') \right]_L \\
- \left[ e^{(1-P)LT} \mathcal{P} \delta p_f(x''') \hat{s}_{ac}(x) \hat{s}_{bd}(x') \delta p_e(x'') \right]_L \right) \quad (a.22)
\]

The evaluation parallels that of the corresponding term of the first derivative. We finally find:

\[
\frac{\delta^2 S}{\delta b \delta b} \overset{(4)}{=} \beta \int_0^\infty dt \left[ e^{(1-P)LT} \mathcal{P} \delta p_f(x''') \hat{s}_{ac}(x) \hat{s}_{bd}(x') \delta p_e(x'') \right]_L = -\frac{\delta^2 S}{\delta b \delta b} \overset{(2)}{=} (a.23)
\]

For the fifth term, we need the differentiation rule for \( \langle a_0 \rangle _L \):

\[
\frac{\delta \langle a_0 \rangle _L}{\delta b} = -\langle \delta a \delta a \rangle _L \quad (a.24)
\]

We obtain:

\[
\frac{\delta^2 S}{\delta b \delta b} \overset{(5)}{=} \beta \int_0^\infty dt \left[ e^{(1-P)LT} \hat{s}_{ac}(x) \hat{s}_{bd}(x') \delta p_e(x'') \right]_L \frac{\delta p_e(x'')}{\delta b_f(x''')} \\
= -\beta \int_0^\infty dt \left[ e^{(1-P)LT} \hat{s}_{ac}(x) \hat{s}_{bd}(x') \delta p_e(x'') \right]_L (\delta p_e(x'') \delta p_f(x'''))_L \quad (a.25)
\]

Finally, we want to show that the term (a.21) vanishes. The first step is to evaluate \( \mathcal{P} \) with the aid of (2.10):

\[
\frac{\delta^2 S}{\delta b \delta b} \overset{(3)}{=} -\beta \int_0^\infty dt \left[ \langle \hat{s}_{bd}(x') \delta p_f(x''') \rangle _L \left[ e^{(1-P)LT} \hat{s}_{ac}(x) \delta p_e(x'') \right]_L \\
+ \langle \hat{s}_{bd}(x') \delta p_f(x''') \delta a \rangle _L \langle \delta a \delta a \rangle _L^{-1} \left[ e^{(1-P)LT} \hat{s}_{ac}(x) \delta a \delta p_e(x'') \right]_L \right) \quad (a.26)
\]

The first term on the right vanishes. Both factors are zero; e. g.:

\[
\langle \hat{s}_{bd}(x') \delta p_f(x''') \rangle _L = \langle s_{bd}(x')(1 - \mathcal{P}) \delta p_f(x''') \rangle _L = 0 \quad (a.27)
\]

To investigate the second term of (a.26), we introduce some auxiliary functions:

\[
Z = \int_0^\infty dt e^{(1-P)LT} \hat{s}_{ac} \\
\]

We have, with a suitable chosen \( Y \):

\[
Z = (1 - \mathcal{P}) Y \quad (a.29)
\]
Therefore:
\[ \langle Z \rangle_L = 0 \quad (a.30) \]
and:
\[ \langle Z \delta a \rangle_L = 0 \quad (a.31) \]
Moreover, we write:
\[ \Xi = \langle Z \delta a \delta p_e \rangle_L \quad (a.32) \]
We want to show \( \Xi = 0 \). We consider the identity:
\[
\frac{\delta \langle Z \delta a \rangle_L}{\delta b_e} = \frac{\delta Z}{\delta b_e} \delta a_L - \langle Z \rangle_L \frac{\delta (\delta a)}{\delta b_e} + \Xi \quad (a.33)
\]
The left hand side is zero because of (a.31); so is the second term on the right because of (a.30). Moreover:
\[
\frac{\delta Z}{\delta b_e} = \int_0^\infty dt \left\{ \frac{\delta}{\delta b_e} e^{(1-P)iLt} \delta_{ac} - e^{(1-P)iLt} \frac{\delta P}{\delta b_e} \delta_{ac} \right\}
\]
\[
= \int_0^\infty dt' \lim_{t \to \infty} e^{(1-P)iLt'} P \delta_{pe} e^{(1-P)iLt} \delta_{ac}(x) \quad (a.34)
\]
The first step is by direct calculation. To the terms, we apply (a.9), (a.4) respectively, to obtain the second step. Comparing this with (a.13), we find that the first term on the right of (a.33) is \( F(t') \) applied to \( g = \delta a \), and is therefore zero. Thus, we have shown that actually (a.26) vanishes. In total, we obtain from (a.18), together with (a.19), (a.23), (a.24):
\[
\frac{\delta^2 S_{abcd}(x,x')}{\delta b_e(x'') \delta b_f(x''')} = \frac{\delta^2 S}{\delta b \delta b} \quad (1) + \frac{\delta^2 S}{\delta b \delta b} \quad (5)
\]
\[
= \beta \int_0^\infty dt \langle [e^{(1-P)iLt} \delta_{ac}(x)] \delta_{bd}(x') \rangle \times \frac{\delta p_e(x'') \delta p_f(x''') - \langle \delta p_e(x'') \delta p_f(x''') \rangle_L}{\delta b_e(x'')} \quad (a.35)
\]

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