

# Modification of linear response theory for mean-field approximations

**Citation for published version (APA):**

Hütter, M., & Öttinger, H. C. (1996). Modification of linear response theory for mean-field approximations. *Physical Review E: Statistical, Physics, Plasmas, Fluids, and Related Interdisciplinary Topics*, 54(3), 2526-2530. <https://doi.org/10.1103/PhysRevE.54.2526>

**DOI:**

[10.1103/PhysRevE.54.2526](https://doi.org/10.1103/PhysRevE.54.2526)

**Document status and date:**

Published: 01/01/1996

**Document Version:**

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

**Please check the document version of this publication:**

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

**General rights**

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

[www.tue.nl/taverne](http://www.tue.nl/taverne)

**Take down policy**

If you believe that this document breaches copyright please contact us at:

[openaccess@tue.nl](mailto:openaccess@tue.nl)

providing details and we will investigate your claim.

## Modification of linear response theory for mean-field approximations

Markus Hütter and Hans Christian Öttinger

*Eidgenössische Technische Hochschule Zürich, Department of Materials, Institute of Polymers, CH-8092 Zürich, Switzerland*

(Received 25 January 1996)

In the framework of statistical descriptions of many particle systems, the influence of mean-field approximations on the linear response theory is studied. A procedure, analogous to one where no mean-field approximation is involved, is used in order to determine the first order response of the distribution function to the perturbation. Subsequently, the effect of the mean-field approximations is examined when formulating Green-Kubo relations for transport coefficients on the deterministic Liouvillean level and the stochastic Fokker-Planck level. On the deterministic level, the Vlasov equation is employed to prove the Green-Kubo formula for the electric conductivity tensor in its well known form. One finds that the interpretation of the Green-Kubo formula is changed when applying Vlasov's mean-field approximation. On the stochastic level, the Gaussian approximation of the bead-spring model for dilute polymer solutions, including hydrodynamic interaction, is considered in homogeneous shear flow. The commonly known Green-Kubo formula for the viscosity is found to be invalid in the Gaussian approximation, and the appropriate modification to the formula is given. [S1063-651X(96)13209-8]

PACS number(s): 05.70.Ln, 05.20.-y, 05.60.+w

### I. INTRODUCTION

The complexity of many particle systems is frequently the motivation for introducing mean-field approximations so as to simplify and solve the complicated equations of motion or the time evolution equation for the probability distribution function in configuration space. In this paper, we exclusively concentrate on the statistical description and not on the trajectory-wise formulation. One is often interested in the linear response of such a system to a small external influence, starting from the equilibrium situation. The usual procedure is to calculate the first order deviation of the distribution function from its equilibrium form. This can easily be done if the statistical model equation is linear in the distribution function, as is the case, for example, in the Liouville equation. However, if the statistical model equation is not linear in the distribution function, one encounters a remarkable change on which we will focus our attention. Here we only look at the case where such a nonlinearity is introduced by the application of certain mean-field approximations. These approximations are found to affect the commonly known Green-Kubo relations [1,2], which say that the space (time) integral of the flux-flux equilibrium correlation function divided by  $k_B T$  gives the corresponding steady-state transport coefficient. Before studying on an abstract level the influence of mean-field approximations on linear response theory in general and on Green-Kubo relations in particular, both deterministic and stochastic examples shall briefly be presented, with their main points outlined in order to have a concrete idea in mind when proceeding to the more general Sec. III.

### II. PROTOTYPE EXAMPLES

The linear response to an external influence is studied on the level of the distribution function. The subsequent sections are valid both for the Liouville equation with reversible dynamics and the dissipative Fokker-Planck equation. The

partial differential equation that governs the time evolution of the distribution function is of the general form

$$\frac{\partial}{\partial t} p(\mathbf{x}, t) = (L + L^P) p(\mathbf{x}, t), \quad (2.1)$$

where  $L$  and  $L^P$  are differential operators in the phase space variables  $\mathbf{x}$ , respectively representing a time independent equilibrium operator and a small time dependent perturbation of the system.

There are several ways of introducing mean-field approximations into the operators  $L$  and  $L^P$ . They all have in common that the resulting operators, denoted by  $M$  and  $M^P$  (for mean field), contain averages with respect to the distribution function  $p(\mathbf{x}, t)$ . The mean-field analog to Eq. (2.1) is written as follows:

$$\frac{\partial}{\partial t} p(\mathbf{x}, t) = (M + M^P) p(\mathbf{x}, t). \quad (2.2)$$

The Vlasov equation [3], which is frequently used in plasma physics, is clearly the prototype example for a mean-field approximation to the Liouville equation. For the present discussion, it suffices to consider the simplest case with only one species of  $N$  particles with mass  $m$  and charge  $q$  in the electrostatic limit. The generalization to different species of particles is obvious, and is omitted in this paper for reasons of simplicity. Vlasov's approximation, which says that any two particles are uncorrelated, leads to a partial differential equation in the coordinate  $\mathbf{r}_1$  and the momentum  $\mathbf{p}_1$  for the one-particle distribution function  $f^{(1)}(\mathbf{r}_1, \mathbf{p}_1, t)$ . This equation is of the form (2.2), with the following assignments for  $M$  and  $M^P$ , if the interaction of the particles is only electrostatic in origin:

$$M = - \left[ \frac{\mathbf{p}_1}{m} \cdot \frac{\partial}{\partial \mathbf{r}_1} + q \bar{\mathbf{E}}^{\text{int}}(\mathbf{r}_1) \cdot \frac{\partial}{\partial \mathbf{p}_1} \right] \quad (2.3)$$

and

$$M^P = -q \mathbf{E}^{\text{ext}}(\mathbf{r}_1) \cdot \frac{\partial}{\partial \mathbf{p}_1}, \quad (2.4)$$

with the smoothed internal electric field

$$\begin{aligned} \bar{\mathbf{E}}^{\text{int}}(\mathbf{r}_1) \equiv & -\frac{\partial}{\partial \mathbf{r}_1} \bar{\phi}^{\text{int}}(\mathbf{r}_1) := -\frac{\partial}{\partial \mathbf{r}_1} (N-1) \int d\mathbf{r}_2 d\mathbf{p}_2 \\ & \times \phi^{\text{coul}}(|\mathbf{r}_1 - \mathbf{r}_2|) f^{\{1\}}(\mathbf{r}_2, \mathbf{p}_2, t). \end{aligned} \quad (2.5)$$

Here,  $\phi^{\text{coul}}$  denotes the Coulomb potential of a point particle, and  $\mathbf{E}^{\text{ext}}$  is the external electric perturbation field. The phase space integral of  $f^{\{1\}}(\mathbf{r}_1, \mathbf{p}_1, t)$  is normalized to unity. As a consequence of the Vlasov approximation, the sum of the external and an *internal* electric field occurs in the time-evolution equation for  $f^{\{1\}}$  [4]. Thus, Eqs. (2.3) and (2.5) exhibit the physics behind the Vlasov approximation: every particle “sees” all the others as a continuum rather than as separate particles.

The prototype example on the stochastic Fokker-Planck level is taken to be the Gaussian approximation [5–7] to a bead-spring model [8] for dilute polymer solutions. We consider the case where the polymer is modeled by only two beads connected by a spring, so-called dumbbells. On account of the nonlinearity introduced by the hydrodynamic interaction [5,8], the Fokker-Planck equation for the connector vector  $\mathbf{Q}$  of the two beads cannot be solved analytically in nonequilibrium situations. When concentrating on the case of homogeneous, incompressible shear flow of the solvent, i.e.,  $\mathbf{v}(\mathbf{r}) = \boldsymbol{\kappa} \cdot \mathbf{r} = (\dot{\gamma}y, 0, 0)$ , where  $\dot{\gamma}$  denotes the shear rate, and the Fokker-Planck equation for the connector vector is of the form (2.1). The assignments for  $L$  and  $L^P$  are given as follows, if the connector vector force law is of the Hookean form  $\mathbf{F}^c(\mathbf{Q}) = H\mathbf{Q}$ :

$$L = \frac{1}{2\lambda_H} \frac{\partial}{\partial \mathbf{Q}} \cdot \left[ [1 - \zeta \boldsymbol{\Omega}(\mathbf{Q})] \cdot \left( \mathbf{Q} + \frac{k_B T}{H} \frac{\partial}{\partial \mathbf{Q}} \right) \right] \quad (2.6)$$

and

$$L^P = -\frac{\partial}{\partial \mathbf{Q}} \cdot \boldsymbol{\kappa} \cdot \mathbf{Q}. \quad (2.7)$$

$\zeta$  denotes the frictional coefficient of the beads,  $\boldsymbol{\Omega}$  the hydrodynamic interaction tensor [5,8],  $\lambda_H := \zeta/(4H)$  the fundamental time constant,  $k_B$  the Boltzmann constant, and  $T$  the absolute temperature. The convention for the differential operators is such that they operate on every function to the right of them, the distribution function in (2.1) included, if not indicated otherwise by appropriate brackets.

One can try to achieve tractable equations by the application of mean field approximations. In order to improve the preaveraging [9] and the consistent averaging method [10], both of which replace the hydrodynamic interaction tensor by averages, the Gaussian approximation has been introduced. The postulated Gaussian property of the probability distribution leads to closed first and second moment equations. Furthermore, an approximate stochastic process can be

defined [5]. It is this process which we will study below. The Gaussian approximation leads to a mean-field-type Fokker-Planck equation with

$$\begin{aligned} M = & \frac{1}{2\lambda_H} \frac{\partial}{\partial \mathbf{Q}} \cdot \langle [1 - \zeta \boldsymbol{\Omega}(\mathbf{Q})]_{\alpha_i, \Theta_i} \cdot \left( \mathbf{Q} + \frac{k_B T}{H} \frac{\partial}{\partial \mathbf{Q}} \right) \\ & - \frac{1}{2\lambda_H} \frac{\partial}{\partial \mathbf{Q}} \cdot \left\langle \left[ \frac{\partial}{\partial \mathbf{Q}} \zeta \boldsymbol{\Omega}(\mathbf{Q}) \right] \cdot \mathbf{Q} \right\rangle_{\alpha_i, \Theta_i}^T \cdot \mathbf{Q} \end{aligned} \quad (2.8)$$

and

$$M^P = -\frac{\partial}{\partial \mathbf{Q}} \cdot \boldsymbol{\kappa} \cdot \mathbf{Q}. \quad (2.9)$$

The vector  $\alpha_i$  is the mean value and  $\Theta_i$  is the covariance matrix of the Gaussian distribution function as obtained from the first and second moment equations. The second of the two averages in (2.8) can be interpreted as accounting for the hydrodynamic fluctuations, because it is absent in the preaveraging and the consistent averaging method. Below, it is called the “fluctuation term,” and will be of major importance.

Equations (2.3)–(2.5) and Eqs. (2.8) and (2.9) constitute the two prototype examples of mean-field theories, for which we will study the linear response theory in Sec. III, and the formulation of Green-Kubo relations in Sec. IV.

### III. GENERALIZED LINEAR RESPONSE THEORY

The linear response of the system to a small perturbation is determined by means of Eq. (2.1) or (2.2), respectively. The first order contributions resulting from the corresponding partial differential equation is used to find the first order deviation  $p_1(\mathbf{x}, t)$  of the distribution function from its equilibrium value  $p_{\text{eq}}(\mathbf{x})$ . However, there is a fundamental difference in this procedure depending on whether or not mean-field approximations are involved. Whereas the operator  $L$  included by definition no effect of the perturbation, this is not the case for the mean-field approximation  $M$ , because there might be additional terms due to the first order of the distribution function in the averages contained in  $M$ . This is the source of the modification of linear response theory discussed in this paper. The transition to the mean-field theory can thus be written as

$$L \rightarrow M := M_0 + M_1 + \dots \quad (3.1)$$

and

$$L^P \rightarrow M^P := M_1^P + \dots, \quad (3.2)$$

where the right side of the definitions in (3.1) and (3.2) are the Taylor expansions of the operators with respect to the external perturbation up to the first order. The first order dependence  $M_1$  of  $M$  results from the dependence on the first order contribution to the distribution function, and is therefore only implicitly time dependent, whereas the first order dependence  $M_1^P$  is directly due to the operator  $L_1^P$ , leading to an explicit time dependence of  $M_1^P$ . The latter contains at most averages with respect to the equilibrium distribution function, because second and higher order ef-

fects are not included. After the mean-field approximation we have a grouping into zeroth and first order operators. The equilibrium operator is now given by  $M_0$ , whereas the first order operator consists of two parts,  $M_1$  and  $M_1^P$ . It is important to note that the first part stems from the original equilibrium operator  $L$ .

The equation for the first order contributions resulting from (2.2) can be transformed into an integral equation. Without loss of generality one may assume the time dependence of the perturbation operator  $L^P$  to be of the Heaviside form (step function). This leads to a Heaviside time dependence of  $M_1^P$ , and therefore for the deviation from the equilibrium distribution function one finds

$$p_1(\mathbf{x}, t) = \int_0^t ds \exp([t-s]M_0) \{ [M_1(s) + M_1^P] p_{\text{eq}}(\mathbf{x}) \} \quad \text{for } t \geq 0, \quad (3.3)$$

which can be verified by differentiation. Even though  $M_1(s)$  depends on  $p_1(\mathbf{x}, s)$ , and (3.3) is thus not a solution for  $p_1(\mathbf{x}, t)$ , this form is sufficient for our purpose. It is now used to determine the deviation of an arbitrary, not explicitly time dependent function  $B(\mathbf{x})$ , defined on the phase space, from its equilibrium value:

$$\Delta \langle B \rangle(t) \equiv \langle B \rangle_{p(t)} - \langle B \rangle_{p_{\text{eq}}} \approx \int d\mathbf{x} p_1(\mathbf{x}, t) B(\mathbf{x}). \quad (3.4)$$

Using Eq. (3.3), the phase space integral in (3.4) can be replaced by a covariance or correlation function, denoted by  $\langle\langle f(\mathbf{x}_t), g(\mathbf{x}_s) \rangle\rangle = \langle f(\mathbf{x}_t) g(\mathbf{x}_s) \rangle - \langle f(\mathbf{x}_t) \rangle \langle g(\mathbf{x}_s) \rangle$ , in both the Liouvillean and Fokker-Planck cases [11]. The result for the linear response can then be written in the following form:

$$\Delta \langle B \rangle(t) = \int_0^t ds \left\langle \left\langle B(\mathbf{x}_t), \left( \frac{[M_1(s) + M_1^P] p_{\text{eq}}(\mathbf{x})}{p_{\text{eq}}(\mathbf{x})} \right) \Big|_{\mathbf{x}=\mathbf{x}_s} \right\rangle \right\rangle_{\text{eq}}. \quad (3.5)$$

The long time limit of the linear response has to be studied separately on the Liouvillean and Fokker-Planck levels. In both cases the long time behavior of the equilibrium correlation function is of primary interest. On the Liouvillean level we assume that the ergodicity holds whether the system considered contains mean-field approximations or not. Under this assumption, the correlation function in (3.5) is only non-vanishing when  $s$  approaches  $t$  [12]. On the Fokker-Planck level it can be shown that the equilibrium correlation function has an exponential decay for large time differences  $|t-s|$  if the diffusion tensor is positive definite [13], where again the system considered may or may not contain mean-field approximations. In the long time limit a stationary solution is therefore approached in both cases. If in  $M_1(s)$ , as contained in Eq. (3.5), the function  $p_1(\mathbf{x}, s)$  is replaced by the stationary deviation  $p_1^{\text{stat}}(\mathbf{x})$ , then an appropriate variable transformation and the time translation invariance of the equilibrium correlation function lead to

$$\Delta \langle B \rangle^{\text{stat}} = \int_0^\infty dt \left\langle \left\langle B(\mathbf{x}_t), \left( \frac{[M_1^{\text{stat}} + M_1^P] p_{\text{eq}}(\mathbf{x})}{p_{\text{eq}}(\mathbf{x})} \right) \Big|_{\mathbf{x}=\mathbf{x}_0} \right\rangle \right\rangle_{\text{eq}}. \quad (3.6)$$

Let us comment on expressions (3.5) and (3.6). If no mean-field approximation is included in the model equation considered, the operator  $M_1(s)$  or  $M_1^{\text{stat}}$ , respectively, is absent. Furthermore, the application of mean-field approximations may alter the equilibrium distribution function  $p_{\text{eq}}(\mathbf{x})$  as well as the equilibrium operator, which propagates the configurations between the distinct times in the correlation function, from  $L$  to  $M_0$ . In Sec. IV we proceed to the application of this linear response theory to the two prototype examples, where we will try to establish Green-Kubo relations.

## IV. APPLICATIONS

### A. Liouvillean level

When studying the influence of an external electric field on a group of charged particles, it is natural to look first for the linear response of the current density. Because the calculation of the ensemble average of the current density  $\hat{\mathbf{j}}(\mathbf{r}; \mathbf{r}_1, \mathbf{p}_1, \dots, \mathbf{r}_N, \mathbf{p}_N)$  is found to require only the one-particle distribution function [3,14], a linear response theory of only the latter suffices. The current density for the  $N$ -particle system to be used with the one-particle distribution function then has the form  $\hat{\mathbf{j}}(\mathbf{r}; \mathbf{r}_1, \mathbf{p}_1) = qN(\mathbf{p}_1/m) \delta(\mathbf{r} - \mathbf{r}_1)$ . The factor  $N$ , which represents the sum over all particles, originates from the formulation based on the *one*-particle distribution function, and will also appear in the following formulas. We now concentrate on the thermodynamic limit, meaning that the particle number and the volume tend to infinity in such a way that the particle density remains constant. In this case, the symmetry of the system demands that in the zeroth order of the perturbation the internal smoothed electric field,  $\bar{\mathbf{E}}_0^{\text{int}}(\mathbf{r}_1)$ , vanishes, and thus the proper equilibrium distribution function is found from (2.3) to be [3]

$$f_{\text{eq}}^{\{1\}}(\mathbf{r}_1, \mathbf{p}_1) = \mathcal{N} \exp\left(-\frac{1}{k_B T} \frac{p_1^2}{2m}\right), \quad (4.1)$$

where  $\mathcal{N}$  is a normalization constant,  $k_B$  is the Boltzmann constant, and  $T$  is the absolute temperature. Notice that the equilibrium distribution function (4.1) does not contain the interaction between the particles that would have occurred in the equilibrium distribution function of the unapproximated Liouville equation in the full phase space.

If a space dependent external electric field  $\mathbf{E}^{\text{ext}}(\mathbf{r})$  is switched on at time  $t=0$ , and the notation  $\mathbf{x} = (\mathbf{r}_1, \mathbf{p}_1)$  is used, the linear response of the electric current density can be written according to Eq. (3.5) as follows:

$$\Delta \langle \hat{\mathbf{j}} \rangle(\mathbf{r}, t) = \frac{1}{N k_B T} \int_0^t ds \times \int d\tilde{\mathbf{r}} \langle \langle \hat{\mathbf{j}}(\tau; \mathbf{x}_t), \hat{\mathbf{j}}(\tilde{\mathbf{r}}; \mathbf{x}_s) \rangle \rangle_{\text{eq}} \cdot [\mathbf{E}^{\text{ext}}(\tilde{\mathbf{r}}) + \bar{\mathbf{E}}_1^{\text{int}}(\tilde{\mathbf{r}}, s)], \quad (4.2)$$

where an additional  $\delta$  function and the integration over  $\tilde{\mathbf{r}}$  have been introduced in order to remove the electric fields from the correlation function. Attention should be paid to the second of the two electric fields that appear in (4.2), the first order  $\bar{\mathbf{E}}_1^{\text{int}}(\tilde{\mathbf{r}}, s)$  of the smoothed internal field. Its presence is the main effect of Vlasov's mean-field approximation. Because the internal smoothed electric field vanishes at equilibrium, the sum of the two electric fields in (4.2) can be considered as the total field in the plasma, although only up to first order. Since Ohm's law, which defines the electric conductivity tensor, gives a relation between the electric current density and the *total* electric field [15], a comparison with (4.2) leads to the following identification for the nonlocal and noninstantaneous conductivity tensor:

$$\underline{\sigma}(\mathbf{r}-\tilde{\mathbf{r}}, t-s) = \frac{1}{Nk_B T} \langle \hat{\mathbf{j}}(\mathbf{r}-\tilde{\mathbf{r}}; \mathbf{x}_{t-s}), \hat{\mathbf{j}}(\mathbf{0}; \mathbf{x}_0) \rangle_{\text{eq}}, \quad (4.3)$$

where the translation invariance of the equilibrium correlation function has been employed. Although no space-time integration is contained in (4.3), we shall refer to the latter as the Green-Kubo relation.

In this example, the mean-field approximation does not change the formal appearance of the Green-Kubo formula. However, it changes the meaning of the conductivity tensor as follows. If the linear response theory had been applied to the unapproximated  $N$ -particle Liouville equation, the Green-Kubo formula would have been identical to (4.3) except for the factor of  $1/N$ , the equilibrium operator, and the equilibrium distribution function. But the relation defining this nonlocal and noninstantaneous conductivity tensor would have been a relation between the current density and the *external* electric field only, which does not correspond to the meaning of Ohm's law. The above Green-Kubo relation seems therefore to be more meaningful in connection with the Vlasov equation rather than with the unapproximated Liouville equation.

### B. Fokker-Planck level

The general linear response theory is now applied to the Gaussian approximation of the dilute polymer solution model. The equilibrium distribution function for the connector vector  $\mathbf{Q}$  is found to have a mean value zero and covariance matrix  $(k_B T/H)\mathbf{1}$ , i.e.,

$$p_{\text{eq}}(\mathbf{Q}) = \mathcal{N} \exp\left(-\frac{1}{2} \frac{H}{k_B T} Q^2\right), \quad (4.4)$$

where  $\mathcal{N}$  is a normalization constant. Equation (4.4) is valid for the unapproximated model as well as for the Gaussian approximated model. This can be verified by means of Eqs. (2.6) or (2.8), respectively, where one should notice that the fluctuation term in (2.8) vanishes at equilibrium. The first property one is interested in when imposing the shear flow  $\mathbf{v}(\mathbf{r}) = (\dot{\gamma}y, 0, 0)$  on a polymer solution is the response of the polymer contribution to the stress tensor and especially to the shear stress, which for the Hookean dumbbell model and a polymer concentration  $n_p$  is of the form  $\langle \hat{\tau}_{xy}^p(\mathbf{Q}) \rangle = -n_p H \langle Q_x Q_y \rangle$  [8], vanishing at equilibrium. With the definition  $\eta^p(\dot{\gamma}) := -\langle \hat{\tau}_{xy}^p(\mathbf{Q}) \rangle / \dot{\gamma}$  [8] for the polymer contribution to the viscosity and with the identification  $B(\mathbf{x}_t) = \hat{\tau}_{xy}^p(\mathbf{Q}_t)$  one finds, from (3.6),

$$\begin{aligned} \eta^p &= \frac{1}{n_p k_B T} \int_0^\infty dt \langle \langle \hat{\tau}_{xy}^p(\mathbf{Q}_t), \hat{\tau}_{xy}^p(\mathbf{Q}_0) \rangle \rangle_{\text{eq}} \\ &\quad - \frac{2H^2}{\dot{\gamma} k_B T} \int_0^\infty dt \langle \langle \hat{\tau}_{xy}^p(\mathbf{Q}_t), \mathbf{Q}_0 \mathbf{Q}_0 \rangle \rangle_{\text{eq}} : \left\{ \int d\mathbf{Q} p_1^{\text{stat}}(\mathbf{Q}) \right. \\ &\quad \left. \times \left( \left[ \frac{\partial}{\partial \mathbf{Q}} \mathbf{\Omega}(\mathbf{Q}) \right] \cdot \mathbf{Q} \right)^T \right\}. \end{aligned} \quad (4.5)$$

The second of the two terms on the right hand side stems from the fluctuation term, and is therefore an immediate consequence of the Gaussian approximation. It is not present in the preaveraging and the consistent averaging procedure, both of which give the same viscosity when calculated by means of (4.5). The additional first order fluctuation term in Eq. (4.5) changes the viscosity for the Gaussian approximation [16]. This discrepancy can also be observed when using an equivalent procedure; that is, when solving the closed second moment equations in all three cases in the presence of flow and using  $\eta^p(\dot{\gamma}) = n_p H \langle Q_x Q_y \rangle / \dot{\gamma}$  to calculate the viscosity.

One may consider (4.5) as a generalization of the Green-Kubo formula for the viscosity to the Gaussian approximation. One has to remember, however, that this Green-Kubo formula does not give a representation of a transport coefficient in purely equilibrium dynamical terms. If one is interested in the determination of the zero-shear-rate viscosity, one is forced to calculate at least one first order quantity and can only choose which one is preferable, the shear stress or the fluctuation term.

Because the formulation of the Gaussian approximation for stochastic processes is not unique, one can try to find a process that fulfills the Green-Kubo relation in the usual form, i.e., Eq. (4.5), without the fluctuation term. We were able to establish such a solution for dumbbells but not for longer chains.

## V. CONCLUSIONS

The previous two examples have shown that the application of mean-field approximations can have two distinct effects on Green-Kubo relations. Either the relation experiences only minor formal changes, with mostly the interpretation of the transport coefficient being modified, as shown in the Vlasov example, or the relation has to be generalized in order not to change the meaning of the transport coefficient. This has been observed in the polymer solution model. We therefore conclude that the commonly known Green-Kubo relations, which say that the space (-)time integral of the flux-flux equilibrium correlation function divided by  $k_B T$  gives the corresponding steady-state transport coefficient, cannot be blindly applied when mean-field approximations are involved. Since the above examples have shown that no easy recipe for the derivation of Green-Kubo relations can be given, it seems to be necessary to derive the modified Green-Kubo relation separately for each problem considered, starting from Eq. (3.5) or (3.6).

## ACKNOWLEDGMENT

We are grateful to Martin Melchior for many discussions.

- [1] R. Kubo, M. Toda, and N. Hashitsume, *Statistical Physics II: Nonequilibrium Statistical Mechanics*, 2nd ed. (Springer, New York, 1985).
- [2] J. A. McLennan, *Introduction to Non-Equilibrium Statistical Mechanics* (Prentice-Hall, Englewood Cliffs, NJ, 1989).
- [3] T. J. M. Boyd and J. J. Sanderson, *Plasma Dynamics* (Nelson, London, 1969).
- [4] For more details on the description of plasmas and on approximation methods of the corresponding Liouville equation in particular, see R. Balescu, *Transport Processes in Plasmas* (North-Holland, Amsterdam, 1988).
- [5] H. C. Öttinger, *Stochastic Processes in Polymeric Fluids: Tools and Examples for Developing Simulation Algorithms* (Springer, Berlin, 1996).
- [6] H. C. Öttinger, *J. Chem. Phys.* **90**, 463 (1989).
- [7] L. E. Wedgwood, *J. Non-Newtonian Fluid Mech.* **31**, 127 (1989).
- [8] R. B. Bird, C. F. Curtiss, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids, Vol. 2, Kinetic Theory*, 2nd ed. (Wiley Interscience, New York, 1987).
- [9] B. H. Zimm, *J. Chem. Phys.* **24**, 269 (1956) [a corrected version of that paper can be found in J. J. Hermans, *Polymer Solutions Properties, Part II: Hydrodynamics and Light Scattering* (Dowden, Hutchinson & Ross, Stroudsburg, 1978)].
- [10] H. C. Öttinger, *J. Chem. Phys.* **86**, 3731 (1987); **87**, 1460(E) (1987).
- [11] The equilibrium correlation  $\langle\langle \cdot, \cdot \rangle\rangle_{\text{eq}}$  instead of only  $\langle \cdot \rangle_{\text{eq}}$  can be used when employing the fact that the phase space integral of  $p_1(\mathbf{x}, t)$  vanishes. Notice that in order to achieve (3.5), on the Liouvillean level the incompressibility of the phase space flow is used. On the Fokker-Planck level, where transition probabilities  $p(\mathbf{x}, t | \mathbf{x}_0, t_0)$  are involved, the form  $p(\mathbf{x}, t | \mathbf{x}_0, t_0) = \exp([t-t_0]M_0)\delta(\mathbf{x}-\mathbf{x}_0)$  was employed, implying a knowledge of the equilibrium distribution function  $p_{\text{eq}}(\mathbf{x})$ .
- [12] S. K. Ma, *Statistical Mechanics* (World Scientific, Philadelphia, 1985).
- [13] The exponential decay of the equilibrium correlation function on the Fokker-Planck level can be verified by analyzing the eigenvalue problem of the equilibrium operator  $M_0$  and using the eigenfunction expansion. For more details on the eigenfunction expansion, see H. Risken, *The Fokker-Planck Equation: Methods of Solution and Applications*, 2nd ed. (Springer, Berlin, 1989).
- [14] H. J. Kreuzer, *Nonequilibrium Thermodynamics and Its Statistical Foundations* (Oxford University Press, Oxford, 1981).
- [15] J. D. Jackson, *Classical Electrodynamics*, 2nd ed. (Wiley, New York, 1975).
- [16] The zero-shear-rate viscosity in the preaveraging and the consistent averaging procedure is determined to be  $\eta^C = \eta^Z = n_p k_B T \lambda_H / (1 - \sqrt{2}h^*)$  for the Oseen-Burgers tensor [7], whereas in the Gaussian approximation it is found to be  $\eta^{\text{GA}} = n_p k_B T \lambda_H / (1 - \frac{7}{10}\sqrt{2}h^*)$  [5], if  $h^*$  denotes the hydrodynamic interaction parameter [7].