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The First Principle Calculation of Green–Kubo Formula with the Two-Time Ensemble Technique*

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Abstract *For weak-coupling electronic plasmas in the presence of small fluctuations, we calculate Green-Kubo formula for transport coefficients employing the ab initio theory, i.e., the two-time ensemble technique. The microscopic interpretations of Onsager's hypothesis on fluctuations are presented in the framework.*

1 Introduction

It is well known that Green–Kubo formula is essential in understanding linear transport processes. However, its generality also arises great difficulties in practice. Since 1950's there have been a few methods of calculating it, but they are all not the *ab initio* theory. Among these is the one imposed by Chandrasekhar then further developed by Mclennan,[1] which is based on Brownian motion, or equivalently, linearized Fokker–Planck equation (FPE). Another important method is the field theory formalism.[2] A great advantage is that collective modes are incorporated, thus it is capable of treating anomalous transport.[3] Nevertheless, the problem still remains that the stochastic dynamical model is in prior, so the method is phenomenological and cannot yield the first principle calculation via Green–Kubo formula.

In many realistic cases like plasmas, it is interesting to understand transport processes through time correlation and of great value to explore calculating transport coefficients through Green–Kubo formula based on the first principle. It is indicated through the exact Green–Kubo formula derived from Liouville equation[4] that generally transport is in the close connection with both the time correlation of the same particle and the correlation of different particles. So we naturally investigate the time correlation by the statistics of Γ space.

In this paper we generalize the method adopted in Ref. [5] to dissipative cases. For simplicity, we discuss the correlation function of the weak-coupling plasma, taking into account neutral ion background and small static electric fluctuations caused by electronic motions. Then we calculate the transport coefficients employing the two-time ensemble technique.[5] The better and deeper understanding of the previous theories are presented.

2 The Two-Time Ensemble Technique

The similar idea was illustrated by Balescu.[6] However, no further research has been pursued to our knowledge. In Ref. [5], we introduced the so-called two-time ensemble technique for analyzing the time correlation.

Introduce the two-time ensemble distribution, say $f(\Gamma', \Gamma; t + \tau, t)$, where $\Gamma' = (1', 2', \cdots, N')$ and $\Gamma = (1, 2, \cdots, N)$. We use k to denote arguments $(\boldsymbol{x}_k, \boldsymbol{p}_k)$ and k' to denote arguments $(\boldsymbol{x}'_k, \boldsymbol{p}'_k)$. The well-known continuing equation and the measure preserving yield

$$\left(\frac{\partial}{\partial \tau} + \sum_{k=1}^{N} \boldsymbol{v}'_k \cdot \boldsymbol{\nabla}_{\boldsymbol{x}'_k} + \sum_{k=1}^{N} \boldsymbol{F}'_k \cdot \boldsymbol{\nabla}_{\boldsymbol{p}'_k}\right) f(\Gamma', \Gamma; t + \tau, t) = 0. \quad (1)$$

The initial condition is

$$f(\Gamma', \Gamma; t, t) = f(\Gamma; t)\delta(1' - 1) \cdots \delta(N' - N). \quad (2)$$

$\boldsymbol{F}'_k$ is the force exerted on particle k at time $(t + \tau)$. The current-current correlation is

$$\langle \boldsymbol{j}_e(t)\boldsymbol{j}_e(t + \tau)\rangle = \left(\frac{Ze}{Vm}\right)^2 \int \sum_{j=1}^{N} \sum_{k=1}^{N} \boldsymbol{p}_j \boldsymbol{p}'_k f(\Gamma', \Gamma; t + \tau, t) \mathrm{d}1' \cdots \mathrm{d}N' \mathrm{d}1 \cdots \mathrm{d}N$$

$$= \left(\frac{Ze}{Vm}\right)^2 \int \boldsymbol{p}_1 \boldsymbol{p}'_1 f_1(1', 1; t + \tau, t) \mathrm{d}1' \mathrm{d}1 + \left(\frac{Ze}{Vm}\right)^2 \int \boldsymbol{p}_2 \boldsymbol{p}'_1 f_1(1', 2; t + \tau, t) \mathrm{d}1' \mathrm{d}2. \quad (3)$$

Here the distributions $f_1(1', 1; t + \tau, t)$ and $f_1(1', 2; t + \tau, t)$ have been introduced

$$f_1(1', 1; t + \tau, t) = N \int f(\Gamma', \Gamma; t + \tau, t) \mathrm{d}2' \cdots \mathrm{d}N' \mathrm{d}2 \cdots \mathrm{d}N \,, \tag{4}$$

$$f_1(1', 2; t + \tau, t) = N(N - 1) \int f(\Gamma', \Gamma; t + \tau, t) \mathrm{d}2' \cdots \mathrm{d}N' \mathrm{d}1 \mathrm{d}3 \cdots \mathrm{d}N \,. \tag{5}$$

The Green–Kubo formula for the electric conductivity is expressed as[4,6]

$$\bar{\bar{\sigma}} = \beta \int_0^\infty \mathrm{d}\tau \langle \boldsymbol{j}_e \boldsymbol{j}_e(\tau) \rangle_{\mathrm{eq}} \,, \tag{6}$$

where

$$\boldsymbol{j}_e = V^{-1} \sum_{n=1}^N (Ze/m) \boldsymbol{p}_n$$

is the microscopic electric current density with V being the volume of the system.

The problem remains unsolved how to calculate both the $f_1(1', 1; t+\tau, t)$ and $f_1(1', 2; t+\tau, t)$. This will be performed in the following section. For the purpose of illustrating the technique, we are restricted to the case of weak-coupling Coulombian plasmas.

3 Calculating $f_1(1', 1; t + \tau, t)$

Due to the similarity of Eq. (1) to ordinary Liouville's equation, the subdynamic theory also applies.[5,6] The great advantage of the theory is that it provides a systematic technique of obtaining kinetic equation based on perturbation theory. Adopting the notations of Ref. [6] and simply following the technique, we can expand Eq. (1) up to the second order (i.e., the weak-coupling approximation) in the interaction parameter λ as

$$\begin{aligned}
\frac{\partial}{\partial \tau} \boldsymbol{V} \bar{f}(\Gamma', \Gamma; t + \tau, t) &= \boldsymbol{V} \Gamma^* \boldsymbol{V} \bar{f}(\Gamma', \Gamma; t + \tau, t) \\
&= \boldsymbol{V} \mathcal{L}_0 \bar{f}(\Gamma', \Gamma; t + \tau, t) + \lambda \boldsymbol{V} \mathcal{L}' \bar{f}(\Gamma', \Gamma; t + \tau, t) \\
&\quad + \lambda^2 \int_0^\infty \mathrm{d}s \boldsymbol{V} \mathcal{L}' \boldsymbol{C} \mathcal{U}^0(s) \mathcal{L}' \mathcal{U}^0(-s) \boldsymbol{V} \bar{f}(\Gamma', \Gamma; t + s, t) \,.
\end{aligned} \tag{7}$$

Since Γ and t play only the role of parameters, we drop them from now on for convenience. Then in the realization of specific correlation pattern, equation (1) can be written as

$$\begin{aligned}
\frac{\partial}{\partial \tau} \bar{f}_1(1'; t + \tau) &= L_1^{0'} \bar{f}_1(1'; t + \tau) + \lambda \int \mathrm{d}x_2' L_{12}'' \bar{f}_1(1'; t + \tau) \bar{f}_1(2'; t + \tau) \\
&\quad + \lambda^2 \int_0^\infty \mathrm{d}s \int \mathrm{d}x'' L_{12}'' U_{12}^{0'}(s) L_{12}'' U_{12}^{0'}(-s) \bar{f}_1(1'; t + \tau) \bar{f}_1(2'; t + \tau) \,.
\end{aligned} \tag{8}$$

Before further processing, some words are in order. It is well known that the regression of macroscopic small fluctuation can be described through linear hydrodynamics, which is the nucleus of Onsager's hypothesis.[7] The technique here presents its understanding at the microscopic level. That is, in our opinion, the kinetic equation resulting in the evolution of macroscopic fluctuation preserves the same form of the one resulting in hydrodynamics. For the dispersive case, it has been put into practice in the previous work.[5] The present paper is dedicated to exploring how to generalize it to the dissipative case.

Taking the above discussions into account, we reduce Eq. (8) into the formal Landau equation straightforward

$$\begin{aligned}
&\frac{\partial}{\partial \tau} \bar{f}_1(1'; t + \tau) + \boldsymbol{v}_1' \cdot \boldsymbol{\nabla}_1' \bar{f}_1(1'; t + \tau) - \frac{e\boldsymbol{E}'}{m} \cdot \boldsymbol{\nabla}_{\boldsymbol{v}_1'} \bar{f}_1(1'; t + \tau) \\
&= B \int \mathrm{d}\boldsymbol{v}_2' \partial_{12}'^r \frac{g'^2 \delta^{rs} - g'^r g'^s}{g'^3} \partial_{12}'^s \bar{f}_1(\boldsymbol{x}_1', \boldsymbol{v}_1'; t + \tau) \bar{f}_1(\boldsymbol{x}_1', \boldsymbol{v}_2'; t + \tau)
\end{aligned} \tag{9}$$

with the self-consistent fluctuating static electric field $\boldsymbol{E}'$ satisfying

$$\boldsymbol{\nabla}' \cdot \boldsymbol{E}' = -4\pi e \int \mathrm{d}\boldsymbol{v}_1' [\bar{f}_1(1'; t + \tau) - Zn_+] \,, \tag{10}$$

where $B = 8\pi^5 \int_0^\infty \mathrm{d}k k^3 V_k^2$ with V_k being the Fourier component of the interaction potential $V(r)$, and we also take into account neutral ion background. Combined with the initial condition $\bar{f}_1(1', 1; t, t) = f_1(1; t)\delta(1' - 1)$, equations (9) and (10) yield $\bar{f}_1(1'; t + \tau)$.

Consider the fundamental solution of Eqs (9) and (10): $G(\boldsymbol{x}', \boldsymbol{v}', \boldsymbol{x}, \boldsymbol{v}; t+\tau, t)$. For simplicity, we rewrite Eq. (9) as

$$\frac{\partial}{\partial \tau} G + \varepsilon \widehat{\mathcal{A}} G = \widehat{\mathcal{K}} G \,, \tag{11}$$

where

$$\widehat{\mathcal{K}} G = -\boldsymbol{v}_1' \cdot \boldsymbol{\nabla}_1' G + B \int \mathrm{d}\boldsymbol{v}_2' \partial_{12}'^r \frac{g'^2 \delta^{rs} - g'^r g'^s}{g'^3} \partial_{12}'^s G(\boldsymbol{x}_1', \boldsymbol{v}_1', \boldsymbol{x}, \boldsymbol{v}; t + \tau) G(\boldsymbol{x}_1', \boldsymbol{v}_2', \boldsymbol{x}, \boldsymbol{v}; t + \tau) \tag{12}$$

and

$$\varepsilon \widehat{\mathcal{A}} G = -\frac{e\boldsymbol{E}'}{m} \cdot \boldsymbol{\nabla}_{\boldsymbol{v}_1'} G = \frac{4\pi e^2}{m} \left\{ \boldsymbol{\nabla}_{\boldsymbol{x}_1'} \int \mathrm{d}\boldsymbol{x}_1'' \frac{1}{|\boldsymbol{x}_1' - \boldsymbol{x}_1''|} \int \mathrm{d}\boldsymbol{v}_1'' [G(\boldsymbol{x}_1'', \boldsymbol{v}_1'', \boldsymbol{x}_1, \boldsymbol{v}_1; t + \tau) - Z n_+] \right\}$$
$$\cdot \boldsymbol{\nabla}_{\boldsymbol{v}_1'} G(\boldsymbol{x}_1', \boldsymbol{v}_1', \boldsymbol{x}_1, \boldsymbol{v}_1; t + \tau) \,. \tag{13}$$

Here ε is a small parameter being characteristic of the perturbation by the mean field. In Eq. (11), $\widehat{\mathcal{K}} G$ can be regarded as the counterpart of the regression hypothesis of fluctuations. While $\widehat{\mathcal{A}} G$ implies the relation between dispersion and fluctuation.[5] Generally $\widehat{\mathcal{K}} G$, or collision, dominates so that the perturbative technique can be made used of.

Expand the solution G with respect to ε,

$$G = G^{(0)} + \sum_{n=1}^\infty \varepsilon^n G^{(n)} \tag{14}$$

with $G^{(0)}$ satisfying

$$\frac{\partial}{\partial \tau} G^{(0)} = \widehat{\mathcal{K}} G^{(0)} \tag{15}$$

and

$$G^{(0)}|_{\tau=0} = \delta(\boldsymbol{x}_1' - \boldsymbol{x})\delta(\boldsymbol{v}_1' - \boldsymbol{v}) \,. \tag{16}$$

Below we will find that the linear transport results from linearized $\widehat{\mathcal{K}}$, hence we expand Eq. (11) up to the first order in ε (that is, fluctuations are small) after linearizing $\widehat{\mathcal{K}}$, and obtain

$$G = G^{(0)} + \varepsilon \int_0^\tau \mathrm{d}s \, \mathrm{e}^{(\tau-s)\widehat{\mathcal{K}}^*} (-\widehat{\mathcal{A}} G^{(0)}|_{\tau=s}) \,. \tag{17}$$

The initial condition $G^{(1)}|_{\tau=0} = 0$ implied by Eq. (16) has been employed. $\widehat{\mathcal{K}}$ is linearized as $\widehat{\mathcal{K}}^*$. Equivalently, equation (17) can be expressed as

$$G(\boldsymbol{x}_1', \boldsymbol{v}_1', \boldsymbol{x}, \boldsymbol{v}; t + \tau) = G^{(0)}(\boldsymbol{x}_1', \boldsymbol{v}_1', \boldsymbol{x}, \boldsymbol{v}; t + \tau) + \varepsilon \int_0^\tau \mathrm{d}s \, \mathrm{e}^{(\tau-s)\widehat{\mathcal{K}}^*}$$
$$\times \left\{ \int \mathrm{d}\boldsymbol{u} \mathrm{d}\boldsymbol{w} \delta(\boldsymbol{x}_1' - \boldsymbol{u})\delta(\boldsymbol{v}_1' - \boldsymbol{w})[-\widehat{\mathcal{A}} G^{(0)}(\boldsymbol{u}, \boldsymbol{w}, \boldsymbol{x}, \boldsymbol{v}; t + s)] \right\}$$
$$= G^{(0)}(\boldsymbol{x}_1', \boldsymbol{v}_1', \boldsymbol{x}, \boldsymbol{v}; t + \tau) + \varepsilon \int_0^\tau \mathrm{d}s \int \mathrm{d}\boldsymbol{u} \mathrm{d}\boldsymbol{w} \, \mathrm{e}^{(\tau-s)\widehat{\mathcal{K}}^*} \{\delta(\boldsymbol{x}_1' - \boldsymbol{u})\delta(\boldsymbol{v}_1' - \boldsymbol{w})$$
$$\times [-\widehat{\mathcal{A}} G^{(0)}(\boldsymbol{u}, \boldsymbol{w}, \boldsymbol{x}, \boldsymbol{v}; t + s)] \} \,. \tag{18}$$

In the above equation, the linear property of $\mathrm{e}^{\tau\widehat{\mathcal{K}}^*}$ has been used. $\mathrm{e}^{(\tau-s)\widehat{\mathcal{K}}^*} \delta(\boldsymbol{x}_1' - \boldsymbol{u})\delta(\boldsymbol{v}_1' - \boldsymbol{w})$ is the fundamental solution of linearized Eq. (15).

From Eq. (12) we notice that Landau collision operator is a nonlinear Fokker–Planck operator,[6]

$$\widehat{\mathcal{K}} G(\boldsymbol{x}_1', \boldsymbol{v}_1', \boldsymbol{x}, \boldsymbol{v}; t + \tau) = B m^{-2} \partial_1'^r \left[-A^r(\boldsymbol{v}_1') + \frac{1}{2} \partial_1'^s [B^{rs}(\boldsymbol{v}_1')] \right] G(\boldsymbol{x}_1', \boldsymbol{v}_1', \boldsymbol{x}, \boldsymbol{v}; t + \tau) \,, \tag{19}$$

where

$$A^r(\boldsymbol{v}_1') = \int \mathrm{d}\boldsymbol{v}_2' \left[(\partial_1'^s - \partial_2'^s) \frac{g'^2 \delta^{rs} - g'^r g'^s}{g'^3} \right] G(\boldsymbol{x}_1', \boldsymbol{v}_2', \boldsymbol{x}, \boldsymbol{v}; t + \tau) \,, \tag{20}$$

$$B^{rs}(\boldsymbol{v}_1') = 2 \int \mathrm{d}\boldsymbol{v}_2' \frac{g'^2 \delta^{rs} - g'^r g'^s}{g'^3} G(\boldsymbol{x}_1', \boldsymbol{v}_2', \boldsymbol{x}, \boldsymbol{v}; t+\tau), \tag{21}$$

and the dummy indices r, s run from 1 to 3. Here a key issue must be addressed. That is, although the time in Green–Kubo formula runs over the positive axis, it is reasonable to assume that the integration is dominated by the time of hydrodynamic scale since in the smaller scale, the regular correlation is not formed, consequently leading to the counteraction of transient correlation.[1] Moreover, we believe that Onsager's hypothesis about the evolution of small fluctuation implies the great similarity between the kinetic equations describing fluctuation and hydrodynamics. Since the linear Landau equation yields hydrodynamic modes, naturally we linearize Eqs (19) $\sim$ (21) also. Thus $G(\boldsymbol{v}_2')$ in Eqs (20) and (21) can be substituted by the stationary solution of $\delta(\boldsymbol{x}_1' - \boldsymbol{x}_1'')\delta(\boldsymbol{v}_1' - \boldsymbol{v}_1'')$, i.e., the well-known Maxwell–Boltzmann distribution

$$G(\boldsymbol{v}_2') = n\Big(\frac{m}{2\pi k_B T}\Big)^{3/2} \mathrm{e}^{-m\boldsymbol{v}_2'^2/2k_B T}. \tag{22}$$

With the approximation of the small angle head-on collision introduced, $\boldsymbol{A}$ and $\bar{\bar{B}}$ are further simplified as

$$A^r(\boldsymbol{v}_1') = -\gamma(\boldsymbol{v}_1')\boldsymbol{v}_1^{r\prime}, \tag{23}$$

$$B^{rs}(\boldsymbol{v}_1') = \alpha(\boldsymbol{v}_1')\delta^{rs} + \beta(\boldsymbol{v}_1')\boldsymbol{v}_1'^r \boldsymbol{v}_1'^s - \boldsymbol{\Delta}^{rs}(\boldsymbol{v}_1') \tag{24}$$

with

$$\gamma(\boldsymbol{v}_1') = \Big(\frac{4n^2}{\pi^{3/2}}\Big)\Big(\frac{mv_1'^2}{2k_B T}\Big)\Big(\frac{\triangle\Omega}{v_1'^3}\Big) \int_{\sqrt{mv_1'^2/2k_B T}}^{\infty} \mathrm{d}x\, \mathrm{e}^{-(x-\sqrt{mv_1'^2/2k_B T})^2} = \Big(\frac{2\sqrt{2}n^2}{\pi}\Big)\Big(\frac{mv_1'^2}{2k_B T}\Big)\Big(\frac{\triangle\Omega}{v_1'^3}\Big), \tag{25}$$

$$\alpha(\boldsymbol{v}_1') = \Big(\frac{2n^2}{\pi^{3/2}}\Big)\Big(\frac{mv_1'^2}{2k_B T}\Big)^{1/2}\Big(\frac{\triangle\Omega}{v_1'}\Big) \int_{\sqrt{mv_1'^2/2k_B T}}^{\infty} \mathrm{d}x\, x\, \mathrm{e}^{-(x-\sqrt{mv_1'^2/2k_B T})^2} = \Big(\frac{1+\sqrt{2\pi}}{\pi^{3/2}}n^2\Big)\Big(\frac{mv_1'^2}{2k_B T}\Big)^{1/2}\Big(\frac{\triangle\Omega}{v_1'}\Big), \tag{26}$$

$$\beta(\boldsymbol{v}_1') = -\gamma(\boldsymbol{v}_1') + \Big(\frac{2n^2}{\pi^{3/2}}\Big)\Big(\frac{mv_1'^2}{2k_B T}\Big)^{3/2}\Big(\frac{\triangle\Omega}{v_1'^3}\Big) \int_{\sqrt{mv_1'^2/2k_B T}}^{\infty} \mathrm{d}x\, \frac{1}{x}\, \mathrm{e}^{-(x-\sqrt{mv_1'^2/2k_B T})^2} \tag{27}$$

and

$$\bar{\bar{\boldsymbol{\Delta}}}(\boldsymbol{v}_1') = \begin{pmatrix} I_1 & & 0 \\ & I_2 & \\ 0 & & I_3 \end{pmatrix}. \tag{28}$$

Here I_1, I_2 and I_3 can be explicitly expressed as

$$I_1 = I_2 = \left[\Big(\frac{2n^2}{\pi^{3/2}}\Big)\Big(\frac{mv_1'^2}{2k_B T}\Big)^{1/2}\Big(\frac{\triangle\Omega}{v_1'}\Big) \int_0^{\infty} \mathrm{d}x\, \frac{x^4\, \mathrm{e}^{-x^2}}{(x+\sqrt{mv_1'^2/2k_B T})^3}\right]\Big(\frac{\triangle\Omega}{4\pi}\Big) \tag{29}$$

and

$$I_3 = \left[\Big(\frac{2n^2}{\pi^{3/2}}\Big)\Big(\frac{mv_1'^2}{2k_B T}\Big)^{1/2}\Big(\frac{\triangle\Omega}{v_1'}\Big) \int_0^{\infty} \mathrm{d}x\, \frac{x^4\, \mathrm{e}^{-x^2}}{(x+\sqrt{mv_1'^2/2k_B T})^3}\right], \tag{30}$$

where $\triangle\Omega$ is the solid angle within which the head-on collision occurs. $\triangle\Omega/4\pi$ is a small parameter. In the limit of $\triangle\Omega/4\pi \longrightarrow 0$, I_1 and I_2 are dropped out. Moreover, the numerical calculation shows that in the regime of near equilibrium, $A^r(\boldsymbol{v}_1')$ and the first two terms of Eq. (24) are much greater than $\boldsymbol{\Delta}^{rs}(\boldsymbol{v}_1')$. Hence it is also dropped out. Notice that the $v^r v^s$ ($r \neq s$) terms involves higher-order hydrodynamic behavior (nondiagonal momentum flow or shear modes), we can drop them in the linear approximation. Finally, equation (19) reaches the standard form of linear FPE,[1]

$$\frac{\partial}{\partial\tau}G + \boldsymbol{v}_1' \cdot \boldsymbol{\nabla}_1' G = \gamma^* \nabla_{\boldsymbol{v}_1'}(\boldsymbol{v}_1' G) + \frac{1}{2}\alpha^* \nabla_{\boldsymbol{v}_1'}^2 G, \tag{31}$$

where

$$\gamma^* = 4\sqrt{2\pi}\frac{\triangle\Omega}{4\pi}\Big(\frac{m}{2k_B T}\Big)^{3/2} n^2 B m^{-2} \tag{32}$$

and

$$\alpha^* = \left[\frac{4(1+\sqrt{2\pi})}{\pi^{1/2}} - 4\sqrt{2\pi} + \frac{4}{\pi^{1/2}}\int_{\sqrt{3}}^{\infty} \mathrm{d}x\, x^{-1}\, \mathrm{e}^{-(x-\sqrt{3})^2}\right]$$
$$\times \frac{\triangle\Omega}{4\pi}\Big(\frac{m}{2k_B T}\Big)^{1/2} n^2 B m^{-2}. \tag{33}$$

Chandrasekhar obtained the exact fundamental solution of Eq. (31),

$$G = \frac{1}{8\pi(FI - H^2)^{3/2}} \exp\left[-\frac{IR^2 - 2H\boldsymbol{R}\cdot\boldsymbol{S} + FS^2}{2(FI - H^2)}\right], (34)$$

where

$$F = \frac{1}{2}\left(\frac{\alpha^*}{\gamma^{*3}}\right)[2\gamma^*t - 3 + 4\,\mathrm{e}^{-\gamma^*t} - \mathrm{e}^{-2\gamma^*t}],$$

$$I = \frac{1}{2}\left(\frac{\alpha^*}{\gamma^*}\right)[1 - 2\,\mathrm{e}^{-2\gamma^*t}], \quad H = \frac{1}{2}\left(\frac{\alpha^*}{\gamma^{*2}}\right)[1 - 2\,\mathrm{e}^{-\gamma^*t}]^2,$$

$$\boldsymbol{R} = \boldsymbol{x} - \boldsymbol{x}_1 - \boldsymbol{v}_1\frac{1 - \mathrm{e}^{-\gamma^*t}}{\gamma^*},$$

and $\boldsymbol{S} = \boldsymbol{v} - \boldsymbol{v}_1\,\mathrm{e}^{-\gamma^*t}$. It should be clarified that the starting point here substantially differs from that of Ref. [1], although the exact solution of Ref. [1] is employed. The latter is based on the stochastic model describing Brownian motion.

4 The Transport Coefficients

For normal transport, combining Eqs (3) and (6) yields

$$\sigma^{ij} = \beta\left(\frac{Ze}{Vm}\right)^2\int_0^\infty \mathrm{d}\tau\int \mathrm{d}1\,\mathrm{d}1'\,p_1^i p_1'^j f_1(1', 1; t + \tau, t)$$

$$= \beta\left(\frac{Ze}{Vm}\right)^2\int_0^\infty d\tau\int \mathrm{d}1\,\mathrm{d}1'\,p_1^i p_1'^j$$

$$\times \mathrm{e}^{-\hat{\mathcal{L}}'\tau}\delta(1' - 1)f_1(1; t), \tag{35}$$

where $\mathrm{e}^{-\hat{\mathcal{L}}'\tau}\delta(1' - 1)$ is nothing but the fundamental solution of the linearized Eqs (11) $\sim$ (13) up to the first order in ε. Thus taking Eq. (34) into it, σ^{ij} is written as

$$\sigma^{ij} = \beta\left(\frac{Ze}{Vm}\right)^2\int_0^\infty \mathrm{d}\tau\int \mathrm{d}1\,\mathrm{d}1'\,p_1'^i p_1'^j [G(\boldsymbol{x}_1', \boldsymbol{p}_1', \boldsymbol{x}_1, \boldsymbol{p}_1; \tau)$$

$$\times f_1(\boldsymbol{x}_1, \boldsymbol{p}_1; t) + \epsilon\int_0^\tau \mathrm{d}s\int \mathrm{d}\boldsymbol{u}\,\mathrm{d}\boldsymbol{w}$$

$$\times G(\boldsymbol{x}_1' - \boldsymbol{u}, \boldsymbol{v}_1', \boldsymbol{w}; \tau - s)$$

$$\times (-\hat{\mathcal{A}}G(\boldsymbol{u} - \boldsymbol{x}_1, \boldsymbol{w}, \boldsymbol{p}_1; s))f_1(\boldsymbol{x}_1, \boldsymbol{p}_1; t)]$$

$$= \frac{1}{2}\delta^{ij}\beta(Ze)^2\alpha^*/\gamma^{*2} + \epsilon\beta\left(\frac{Ze}{Vm}\right)^2\int_0^\infty \mathrm{d}\tau\int_0^\tau \mathrm{d}s\int \mathrm{d}_1\,\mathrm{d}_1'$$

$$\times \int \mathrm{d}\boldsymbol{u}\,\mathrm{d}\boldsymbol{w}\,p_1^i p_1'^j(G(\boldsymbol{x}_1' - \boldsymbol{u}, \boldsymbol{v}_1', \boldsymbol{w}'; \tau - s). \tag{36}$$

In the last line we employ the integral performed by Mclennan[1] with α^* and γ^* expressed in terms of microscopic variables. We find that the electric conductivity consists of two parts. The leading part is proportional to diffusion coefficient,[1] as one may expect. The second part arises from the first order self-consistent field correction, which can be neglected in many cases.

5 Conclusions

In this paper, we calculate Green–Kubo formula for transport coefficients through the first principle. The stochastic model has been recovered at the kinetic level. The technique gives us deep insight into the microscopic meaning of Onsager's hypothesis on fluctuations. Indeed, the present calculations are restricted to specific cases. We take into account both the weak-coupling approximation and small static electric fluctuation approximation. Besides, the neutral ion background is employed, implying that only electronic motions account for fluctuations. It is essential that the calculations are valid for equilibrium systems, however, we hope to explore whether it is possible to generalize the present technique to other cases in future work.

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