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ABSTRACT

The relaxation processes and fluctuations of charged simple fluids is studied theoretically. We use the memory function formalism and calculate analytic expressions for the charge-charge and mass-mass second-order memory functions. We assume a markovian memory function whose amplitude is calculated in terms of a wave vector power series, the coefficients of this series are directly related to the transport coefficients, in terms of these coefficients we obtain the correlation functions. The physical conditions obtained in the procedure of calculating the random force self-correlation, enable us to write the expressions of the hydrodynamic coefficients in the form of the Green-Kubo relations. By comparing the expressions of the charge self-correlation, obtained by using a markovian and an exponential memory functions, with the obtained from the hydrodynamics formalism, we discuss the form which the memory function must adopt in the hydrodynamic regime.

Keywords: Fluctuations, memory function, hydrodynamic, transport coefficients.

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1. INTRODUCTION

The relaxation processes in charged fluids exhibit two characteristic stages. Related to each one of these stages, at least qualitatively, there exist one characteristic time. One of these times, which related to rapid processes, describes the stage in which dissipative processes dominate the time evolution of the system. The other time is related to slow processes. In this later stage, the transport phenomena are the main characteristic of the relaxation process [1]. In charged fluids the electrostatic interaction and the fluctuations of physical quantities which interact through this potential determine importantly both stages of the relaxation processes. Some theoretical approaches and techniques have been used in studying the dielectric properties of simple charged fluids [2]. In particular the memory function formalism has been applied successfully to investigate the dynamic structure of ionic-solutions, colloid dispersions, and other complex fluids [3]-[4].

Due to their wide variety of applications and to the important fundamental physical problems involved in their phenomenology, molten salts have been among the charged fluids one of the most extensively studied in the last decades [5]. The understanding of these Colomb systems has a great relevance for several branches of natural sciences. In this paper we focus our attention in the analysis of symmetric molten salts. These are composed of two types of ions that are identical except for the signs of their charges. A real typical system of this kind is molten NaF. This is a fluid of ions with low ionic polarizabilities, having almost equal size and masses. The dynamics of this system has been studied numerically by Hansen *et al* [6].

In a previous paper we have reported an analysis of the fluctuations in a charged simple fluid [7]. In that paper we considered an exponential memory function depending on a single relaxation time. This is a suitable approximation for the memory in the long-times regime [8]. In that paper we have found that the results for the charge-charge fluctuations obtained within that scheme, are qualitatively good compared with results obtained by molecular dynamics (MD) for the moderately high-frequency regime. However, the results obtained for the low-frequency regime of the charge fluctuations spectrum exhibit a poor agreement with the MD ones. We conclude in that analysis that this deficient description can be associated with the intrinsic limitations of mean spherical approximation (MSA) which was used in that paper. Mean field theories are not capable to properly describe the physics of charged fluids in the hydrodynamic limit. Then, more detailed information about nearest-neighbours interactions and associated fluctuations is needed to describe the system collective modes and its corresponding dynamic response [7].

In the present paper we are mainly concerned with other of the important aspects which determine the relaxation processes in charged fluids, namely the general characteristics of the memory function. It has been shown that an exponential memory, depending on one relaxation time, provides a suitable description for the fluctuations in the long-times regime [8]. It is also well-known that in the short-times regime, a Gaussian form for the second-order memory provides better results than an exponential one. In charged fluids the memory function has the same basic structure for the several relevant dynamical quantities. It consists of a short-lived initial decay and a long-lived quasi-exponential tail. The inclusion of this tail is necessary in order to achieve quantitative agreement of the

calculated results with the measured spectra. It is particularly important for small wavenumbers.

In the theoretical description of molten salts dynamics, it is possible to distinguish between a specifically acoustic-type mode and a specifically optic-type mode, corresponding respectively to the fluctuations of mass and charge densities [9].

One of the aspects we study in this paper is the relation between the memory function and the hydrodynamic coefficients of a charged fluid. In particular we analyze the simple case of a markovian memory function and obtain expressions for the hydrodynamic coefficients and for the correlation functions, after that, we discuss the form which the memory function must adopt in the hydrodynamic regime. We do it by comparing the expressions of the charge-charge self correlation function obtained by using a markovian and an exponential memory functions, with those obtained from the hydrodynamics formalism [10]. We analyze the behaviour of the fluctuations at short and long times and their symmetry properties. We find that an exponential memory depending on a single relaxation time is not a suitable assumption because there exist an influence of the behaviour of the system at short times on the behaviour at long times.

2. THEORETICAL FRAMEWORK

We use the projection-operator formalism to study the dynamics of a charged symmetric fluid [11, 12], which was already described in the references [7, 17] but for better clarity it is exposed here. After Gianquinta *et al* [1], we select the following microscopic set of conserved variables: the density of mass $\rho_k(t)$, the density of longitudinal current of mass $J_k^M(t)$, the density of charge $Q_k(t)$, the density of longitudinal current of charge $J_k^Q(t)$, and the temperature $T_k(t)$ [13]. These quantities are defined as follows

$$\rho_k(t) = \sum_{j=1}^N m_j e^{i\mathbf{k}\cdot\mathbf{r}_j(t)}, \quad (1)$$

$$J_k^M(t) = \sum_{j=1}^N m_j v_j^l(t) e^{i\mathbf{k}\cdot\mathbf{r}_j(t)}, \quad (2)$$

$$Q_k(t) = \sum_{j=1}^N q_j e^{i\mathbf{k}\cdot\mathbf{r}_j(t)}, \quad (3)$$

$$J_k^Q(t) = \sum_{j=1}^N q_j v_j^l(t) e^{i\mathbf{k}\cdot\mathbf{r}_j(t)}, \quad (4)$$

$$T_k(t) = \frac{1}{C_v(k)} [E_k(t) - O_1(k)\rho_k(t) - O_2(k)Q_k(t)], \quad (5)$$

where

$$O_1(k) = \frac{\langle E_k \rho_{-k} \rangle \langle Q_k Q_{-k} \rangle - \langle E_k Q_{-k} \rangle \langle Q_k \rho_{-k} \rangle}{\langle \rho_k \rho_{-k} \rangle \langle Q_k Q_{-k} \rangle - \langle \rho_k Q_{-k} \rangle \langle Q_k \rho_{-k} \rangle}, \quad (6)$$

$$O_2(k) = \frac{\langle E_k Q_{-k} \rangle \langle \rho_k \rho_{-k} \rangle - \langle E_k \rho_{-k} \rangle \langle \rho_k Q_{-k} \rangle}{\langle \rho_k \rho_{-k} \rangle \langle Q_k Q_{-k} \rangle - \langle \rho_k Q_{-k} \rangle \langle Q_k \rho_{-k} \rangle}, \quad (7)$$

Here $E_k(t)$ is the density of energy expressed in terms of the interionic potential V_{ij} , and $C_v(k)$ is the heat capacity at constant volume. These quantities are respectively given by

$$E_k(t) = \sum_{i=1}^N \left[\frac{m_i \mathbf{v}_i^2(t)}{2} + \frac{1}{2} \sum_{j \neq i}^N V_{ij}(r_{ij}) \right] e^{i\mathbf{k} \cdot \mathbf{r}_i(t)}, \quad (8)$$

$$C_v(k) = \frac{K_B T^2}{\langle T_k^2 \rangle}. \quad (9)$$

These dynamic variables may be considered as the components of the vector

$$\mathbf{A}_k(t) = \begin{pmatrix} \rho_k(t) \\ J_k^M(t) \\ T_k(t) \\ Q_k(t) \\ J_k^Q(t) \end{pmatrix}. \quad (10)$$

The equation of motion for $\mathbf{A}_k(t)$ is the following

$$\frac{d\mathbf{A}_k(t)}{dt} - i\mathbf{\Omega}_k\mathbf{A}_k(t) + \int_0^t \mathbf{M}_k(t-s)\mathbf{A}_k(s)ds = \mathbf{R}_k(t), \quad (11)$$

where $\mathbf{\Omega}_k$ is the frequency matrix, $\mathbf{M}_k(t)$ is the memory function matrix, and $\mathbf{R}_k(t)$ is the random force vector [14]. From the above equation of motion and the Fourier-Laplace transform definition, the correlation function matrix $\tilde{\mathbf{C}}_{AA}(k, z)$ can be expressed in the form

$$(z\mathbf{I} - i\mathbf{\Omega}_k + \tilde{\mathbf{M}}(k, z))\tilde{\mathbf{C}}_{AA}(k, z) = \mathbf{C}_{AA}(k, 0). \quad (12)$$

The explicit representation of the matrices of this relation can be considerably simplified if one applies the usual symmetry operations [15]. For a symmetric molten salt, if in addition one considers the charge conjugation symmetry operation, the quantities $\rho_k(t)$, $J_k^M(t)$, and $T_k(t)$ can be decoupled of $Q_k(t)$ and $J_k^Q(t)$. From the expression (12) we obtain the various correlation functions.

The dynamic charge self-correlation $\tilde{S}_{QQ}(k, z)$ is given by

$$\tilde{S}_{QQ}(k, z) = \frac{\langle Q_k Q_{-k} \rangle}{z + \frac{k^2 \langle J_k^Q J_{-k}^Q \rangle / \langle Q_k Q_{-k} \rangle}{z + \tilde{R}_{55}(k, z) / \langle J_k^Q J_{-k}^Q \rangle}}, \quad (13)$$

where, $\tilde{R}_{55}(k, z)$ is the second-order memory in the continued fraction representation for the charge self-correlation. This memory is associated with the electric conduction during the relaxation process. The dynamic mass-mass correlation function is given by

$$\tilde{S}_{\rho\rho}(k, z) = \frac{\langle \rho_k \rho_{-k} \rangle}{z + \frac{k^2 \langle J_k^M J_{-k}^M \rangle / \langle \rho_k \rho_{-k} \rangle}{z + \tilde{R}_{22}(k, z) / \langle J_k^M J_{-k}^M \rangle - \tilde{F}(k, z)}}, \quad (14)$$

with

$$\tilde{F}(k, z) = \frac{[\tilde{R}_{23}(k, z) - \langle \dot{J}_k^M T_{-k} \rangle][\tilde{R}_{32}(k, z) + \langle T_{-k} \dot{J}_{-k}^M \rangle]}{\langle J_k^M J_{-k}^M \rangle [\tilde{R}_{33}(k, z) + z \langle T_k T_{-k} \rangle]}, \quad (15)$$

where, $\tilde{R}_{22}(k, z)$ is the second-order memory function in its continued fraction representation for the mass density. This can be associated with viscosity effects in the relaxation process. The memory functions $\tilde{R}_{23}(k, z)$ and $\tilde{R}_{32}(k, z)$ are associated to the coupling between the momentum current J_k^M and the heat flux T_k . Finally, the memory function $\tilde{R}_{33}(k, z)$ is associated to the relaxation process through thermal conduction. Obviously, explicit expressions for these quantities cannot be obtained from this formalism.

3. MARKOVIAN MEMORY

We analyze the simple case of a markovian memory function and obtain expressions for the hydrodynamic coefficients and for the correlation functions. In the memory functions formalism one selects a set of independent microscopic variables whose relaxation time τ_r satisfies the relation $\tau_r \gg \tau_c$, where τ_c is the largest characteristic time of the other relevant variables of the system. With the set of slow variables, the vector \mathbf{A} is constructed in such a way that the components span the subspace (A_1, A_2, \dots, A_r) . In this case \mathbf{A} is given by the expression (10). The projection operator \mathcal{P} is defined such that this projects in the Liouville subspace which contains the slowly relaxing variables, and the operator \mathcal{Q} projects in the orthogonal complement which, by construction, contains all the variables which are rapidly damped. The rapidly damping variables originate the so-called random force which, consequently, is a rapid damping quantity in the sense that its self-correlation *ie.* the memory function, relaxes in a characteristic time of the order of τ_c . In this way there is a clear separation in the time scales in which \mathbf{A} and \mathbf{R} relax. In these conditions, for times $t \gg \tau_c$ we may write

$$\mathbf{M}(k, t - t') = \mathbf{\Gamma}(k)\delta(t - t'). \quad (16)$$

By the substitution of (16) in the movement equation for the vector \mathbf{A} , expression (12), one obtains

$$[z\mathbf{I} - i\mathbf{\Omega}_k + \mathbf{\Gamma}(k)] \tilde{\mathbf{C}}_{AA}(k, z) = \tilde{\mathbf{C}}_{AA}(k, 0), \quad (17)$$

where the memory matrix is given by

$$\mathbf{\Gamma}(k) = \langle \mathbf{A}_k \mathbf{A}_{-k} \rangle^{-1} \int_0^\infty d\tau \langle \mathbf{R}_{-k}(\tau) \mathbf{R}_{-k} \rangle. \quad (18)$$

By definition the self-correlation of the random force is given by

$$R_{ij}^0(k) = \int_0^\infty d\tau \langle R_k^i(\tau) R_{-k}^j \rangle. \quad (19)$$

By using the operation of inversion of symmetry $(\mathbf{q}, \mathbf{p}) \rightarrow (-\mathbf{q}, -\mathbf{p})$, see Ref. [14], the self-correlation of the random force, can be transformed into

$$\langle R_\mu(k, t) R_\nu(-k) \rangle = \epsilon_\mu \epsilon_\nu \langle R_\mu(-k, t) R_\nu(k) \rangle. \quad (20)$$

Here ϵ_μ is the parity of R_μ , under the inversion of symmetry transformation. The self-correlation of the random force is an odd function of k , if $\epsilon_\mu \neq \epsilon_\nu$, and is an even function of k , if $\epsilon_\mu = \epsilon_\nu$.

3.1 MASS-MASS MEMORY FUNCTION CALCULATION

In order to calculate the density-density memory function we need the self-correlation of the random force $R_{22}^0(k)$. We observe in the expression (20) that the quantity R_{22}^0 is an even function of k . By expanding $R_{22}^0(k)$ around $k = 0$ we obtain

$$R_{22}^0(k) = \alpha_1^{(0)} + k^2 \alpha_1^{(2)} + \dots, \quad (21)$$

from this expression it follows that

$$\alpha_1^{(0)} + k^2 \alpha_1^{(2)} + \dots = \int_0^\infty d\tau \langle R_k^2(\tau) R_{-k}^2 \rangle = \int_0^\infty d\tau \langle e^{iQL} Q t Q J_k^M Q J_{-k}^M \rangle, \quad (22)$$

with L the Liouville operator. In the limit $k \rightarrow 0$ we have

$$\alpha_1^{(0)} = \int_0^\infty d\tau \langle e^{iQL} Q t Q \lim_{k \rightarrow 0} J_k^M Q \lim_{k \rightarrow 0} J_{-k}^M \rangle. \quad (23)$$

From the expression for the microscopic density of current of mass one can obtain for J_k^M the following form [14]

$$J_{k\alpha}^M = ik \sum_{i=1}^N [m_i \dot{r}_i^\alpha \dot{r}_i^\beta - \frac{1}{2} \sum_{j \neq i}^N \frac{r_{ji}^\beta r_{ji}^\alpha}{r_{ij}^2} P_k(r_{ij})] e^{ikr_i^\beta}, \quad (24)$$

with

$$P_k(r_{ij}) = r_{ij} \frac{\partial V(r_{ij})}{\partial r_{ij}} \frac{e^{ikr_i^\beta} - 1}{ikr_{ji}^\beta}, \quad (25)$$

$$r_{ij} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}, \quad (26)$$

and

$$r_{ij}^\beta = r_i^\beta - r_j^\beta. \quad (27)$$

where we have chosen to the β -component of the position vector \mathbf{r} to be parallel to the wave-vector \mathbf{k} .

By taking $\alpha = \beta$, one obtains that $\lim_{k \rightarrow 0} J_k^M = \mathbf{0}$, then, $\alpha_1^{(0)} = \mathbf{0}$. To calculate $\alpha_1^{(2)}$, we start from the conservation equation for $J_k^M(t)$.

$$\dot{J}_k^M = iLJ_k^M = ikf_1(k), \quad (28)$$

here $f_1(k)$ is the longitudinal component of the stress tensor or the flux $J_k^M(t)$. By expanding this in k one arrives to

$$f_1(k) = \frac{1}{ik} \sum_{i=1}^N m_i \ddot{z}_i + \sum_{i=1}^N [m_i \dot{z}_i \dot{z}_i + m_i \ddot{z}_i z_i] + ik \sum_{i=1}^N [m_i \dot{z}_i \dot{z}_i z_i + \frac{m_i \ddot{z}_i z_i^2}{2}] + O(k^2). \quad (29)$$

The first term is zero because of the third Newton's law $\sum m_i \ddot{z}_i = \sum \sum_{i \neq j} F_{ij} = \mathbf{0}$. In this way we obtain

$$f_1(k) = \sum_{i=1}^N [m_i \dot{z}_i \dot{z}_i + m_i \ddot{z}_i z_i] + O(k). \quad (30)$$

On the other hand, since J_k^M is orthogonal to $J_k^M(t)$, one obtains $\mathcal{P}J_k^M = \mathbf{0}$, therefore the random force can be written in the form

$$R_2(k, t) = ik e^{iQLt} f_1(k). \quad (31)$$

Since Liouville operator is hermitian and considering the following identity

$$e^{iQLt} = e^{iLt} - \int_0^t d\tau e^{iL(t-\tau)} iPL e^{iQL\tau}, \quad (32)$$

we have

$$ike^{iQLt} f_1(k) = ik e^{iLt} f_1(k) - k^2 \int_0^t d\tau e^{iL(t-\tau)} \langle f_1(k) e^{iQL\tau} f_1(-k) \rangle \langle J_k^M J_{-k}^M \rangle^{-1} J_k^M \quad (33)$$

To the lowest-order in k we may approximate

$$e^{iQLt} \rightarrow e^{iLt}. \quad (34)$$

By using this approximation with the expressions (31) and (22), we arrive to

$$\alpha_1^{(2)} = \int_0^\infty d\tau \langle e^{iL\tau} f_1(k) f_1(-k) \rangle. \quad (35)$$

Thus $f_1(k)$ is given by the first term of the expression (30), therefore

$$\alpha_1^{(2)} = \lim_{\eta \rightarrow 0^+} \int_0^\infty d\tau e^{-\eta\tau} \langle f_1(\tau) f_1(0) \rangle. \quad (36)$$

The limit is needed to make sure the integral convergency. In this expression

$$f_1(\tau) = e^{iL\tau} f_1(0), \quad (37)$$

with

$$f_1(0) = \sum_{i=1}^N m_i [\dot{z}_i \dot{z}_i + \ddot{z}_i z_i]. \quad (38)$$

The self-correlation of a dynamic variable A, is given by $C_{AA}(t) = \langle A(t)A(0) \rangle$, with $\langle A \rangle = 0$. If $\langle A \rangle \neq 0$ the correct expression is [14] $C_{AA}(t) = \langle [A(t) - \langle A(0) \rangle][A(0) - \langle A(0) \rangle] \rangle$. By using this definition the expression (36) can be cast into.

$$\alpha_1^{(2)} = \lim_{\eta \rightarrow 0^+} \int_0^\infty d\tau e^{-\eta\tau} \langle [f_1(\tau) - PV][f_1(0) - PV] \rangle. \quad (39)$$

By comparison with the hydrodynamic result ref. [14], it follows

$$k_B T \left(\frac{4}{3} \eta + \xi \right) = \int_0^\infty \langle [\sigma_0^{zz}(\tau) - PV][\sigma_0^{zz} - PV] \rangle d\tau, \quad (40)$$

therefore

$$\alpha_1^{(2)} = k_B T \left(\frac{4}{3} \eta + \xi \right), \quad (41)$$

where η is the shear viscosity and ξ is the bulk viscosity. Hence, the mass-mass markovian memory $\Gamma_{22}(k)$ is given by

$$\Gamma_{22}(k) = \frac{k^2 k_B T \left(\frac{4}{3} \eta + \xi \right)}{\langle J_k^M J_{-k}^M \rangle}. \quad (42)$$

3.2 CHARGE-CHARGE MEMORY

By following a similar procedure we now calculate the $R_{55}(k)$ self-correlation. One observes in the expression (20), that the quantity $R_{55}(k)$, is an even function of k . By expanding this around $k = 0$, we obtain

$$R_{55}(k) = \alpha_2^{(0)} + k^2 \alpha_2^{(2)} + \dots = \int_0^\infty d\tau \langle e^{iQL} Q t Q J_k^Q Q J_{-k}^Q \rangle. \quad (43)$$

From the expression for the microscopic density of the longitudinal current of charge we derive for J_k^Q the following form

$$J_k^Q = -\frac{1}{2} \sum_{i \neq j}^N \sum_{j}^N \frac{(z_i - z_j)}{r_{ij}} \frac{\partial V(r_{ij})}{\partial r_{ij}} \left(\frac{q_i}{m_i} - \frac{q_j}{m_j} \right) e^{ikz_i} + ik\sigma_{zz}(k), \quad (44)$$

where

$$\sigma_{zz}(k) = \sum_i q_i \dot{z}_i \dot{z}_i e^{ikz_i} - \frac{1}{4} \sum_{i \neq j}^N \sum_{j}^N \left(\frac{q_i}{m_i} + \frac{q_j}{m_j} \right) \cdot \frac{(z_i - z_j)(z_i - z_j)}{r_{ij}} \frac{\partial V(r_{ij})}{\partial r_{ij}} \frac{(e^{ikz_i} - e^{ikz_j})}{ik(z_i - z_j)}. \quad (45)$$

Gianquinta *et. al.* [1] have discussed this situation and interpreted the first term on the right-hand side of the Eq. (44) as describing a relative acceleration of the two components, in this sense this term represents an resistive optic-like mode. Notice that there is an important difference with the previous case, we can see from Eq. (44) that $\lim_{k \rightarrow 0} J_k^Q \neq 0$, therefore, now $\alpha_2^{(0)} \neq 0$. To calculate $\alpha_2^{(0)}$ y $\alpha_2^{(2)}$, we follow again a similar procedure to that of the calculation of $\alpha_1^{(2)}$. In this case we find

$$\alpha_2^{(0)} = \int_0^\infty d\tau \langle e^{iL\tau} f_2^{(0)}(0) f_2^{(0)}(0) \rangle = \lim_{\eta \rightarrow 0^+} \int_0^\infty d\tau e^{-\eta\tau} \langle f_2^{(0)}(\tau) f_2^{(0)}(0) \rangle, \quad (46)$$

and

$$\alpha_2^{(2)} = \int_0^\infty d\tau \langle e^{iL\tau} f_2^{(2)}(0) f_2^{(2)}(0) \rangle = \lim_{\eta \rightarrow 0^+} \int_0^\infty d\tau e^{-\eta\tau} \langle f_2^{(2)}(\tau) f_2^{(2)}(0) \rangle, \quad (47)$$

In this expressions

$$f_2^{(0)} = -\frac{1}{2} \sum_{i \neq j}^N \sum_{i \neq j}^N \frac{(z_i - z_j)}{r_{ij}} \frac{\partial V(r_{ij})}{\partial r_{ij}} \left(\frac{q_i}{m_i} - \frac{q_j}{m_j} \right), \quad (48)$$

$$f_2^{(2)} = -\frac{1}{2} \sum_{i \neq j}^N \sum_{i \neq j}^N z_i \frac{(z_i - z_j)}{r_{ij}} \frac{\partial V(r_{ij})}{\partial r_{ij}} \left(\frac{q_i}{m_i} - \frac{q_j}{m_j} \right) + \sum_{i=j}^N q_i \dot{z}_i^2 - \frac{1}{4} \sum_{i \neq j}^N \sum_{i \neq j}^N \frac{(z_i - z_j)^2}{r_{ij}} \frac{\partial V(r_{ij})}{\partial r_{ij}} \left(\frac{q_i}{m_i} + \frac{q_j}{m_j} \right). \quad (49)$$

In the hydrodynamic limit we may identify

$$\Gamma_{55}(k) = \frac{\alpha_2^{(0)} + k^2 \alpha_2^{(2)}}{\langle J_k^Q J_{-k}^Q \rangle} = \frac{\omega_p^2}{4\pi\sigma(k)}, \quad (50)$$

The second equality is followed from the hydrodynamic matrix [10]. In the above expression we have

$$\sigma(k) = \sigma \left[1 + \frac{k^2}{4\pi e^2} \frac{\partial \mu}{\partial q} \Big|_{T,\rho} \right]. \quad (51)$$

Provided that $\langle J_k^Q J_{-k}^Q \rangle = \omega_p^2 k_B T / 4\pi$, we have at the second-order that

$$\alpha_2^{(0)} + k^2 \alpha_2^{(2)} = \left(\frac{\omega_p^2}{4\pi} \right)^2 \frac{k_B T}{4\pi\sigma} \left[1 - \frac{k^2}{4\pi e^2} \frac{\partial \mu}{\partial q} \Big|_{T,\rho} \right]. \quad (52)$$

Thus:

$$\alpha_2^{(0)} = \left(\frac{\omega_p^2}{4\pi} \right)^2 \frac{k_B T}{4\pi\sigma}, \quad (53)$$

and

$$\alpha_2^{(2)} = - \left(\frac{\omega_p^2}{4\pi} \right)^2 \frac{k_B T}{4\pi\sigma} \frac{1}{4\pi e^2} \frac{\partial \mu}{\partial q} \Big|_{T,\rho}. \quad (54)$$

The expressions (42) and (50) for the density-density and charge-charge second-order memories respectively, clearly exhibit that the random force fluctuations are related to the hydrodynamic coefficients. Namely, we arrive to a relationship between the hydrodynamic

coefficients and the dissipative processes. Notice that the expressions (39), (46) and (47) for the coefficients $\alpha_j^{(0)}$ have the form of the well known Green-Kubo relations. The validity of these expressions is restricted to the hydrodynamic limit. Explicit expressions for these coefficients are useful for numerical calculations of hydrodynamic transport coefficients.

3.3 COMPARISON BETWEEN MARKOVIAN AND EXPONENTIAL MEMORY FUNCTIONS.

We wish to compare the expressions of the charge self-correlation function, $\tilde{S}_{QQ}(k, z)$, obtained by the use of a markovian memory function, with the obtained by using an exponential one. From this analysis we will additionally find the form which the memory function must adopt in the hydrodynamic regime. In order to do this, it is convenient to consider as a reference expression the derived by Gianquinta *et. al.* [10] for the charge self-correlation function.

From the hydrodynamic equations, explicit expressions of the self-correlation functions were obtained by Gianquinta *et. al.* [10] Since we are interested in the charge-charge memory function, here we make use only of the expression of the charge self-correlation function in the Kubo regime $4\pi\sigma/\epsilon \gg ck$. In this regime, which is the regime of the transport processes, the charge fluctuation mode is decoupled from the mass and temperature fluctuations modes. The expression for the charge self-correlation function is the following

$$\frac{\tilde{S}_{QQ}(k, z)}{S_{QQ}(k)} = \left[\frac{A_{22}(k)}{z + z(k)} + \frac{B_{22}(k)}{z + z_2 k^2} + \frac{C_{22}(k)z + D_{22}}{z^2 + 2\Gamma k^2 z + c^2 k^2 + \Gamma^2 k^4} \right], \quad (55)$$

where

$$z(k) = \frac{4\pi\sigma}{\epsilon} + z_1 k^2, \quad (56)$$

$$z_1 = \sigma \left[\frac{4\pi}{k_s^2} + \frac{T\lambda_p^2}{\rho C_p} + \gamma K_T \rho^2 \tilde{\nu}^2 \right], \quad (57)$$

$$z_2 = \frac{\kappa}{\rho C_p}. \quad (58)$$

A detailed discussion about the above quantities and about the related modes strengths can be seen in ref. [10]. To our purposes we do not need to know the explicit form of the mode strengths. We are only interested in their dependence on the complex variable $z = -i\omega + \epsilon$. The first term of the expression (55) corresponds to a charge fluctuation mode, and the last terms can be associated to modes of a one-component neutral fluid, namely, one damping thermal mode and two acoustic-like propagating modes. The consistence of this result can be corroborated by noticing that when $k \rightarrow 0$, the frequency modes become vanish. This is the typical behavior that one finds for neutral fluids. On the other hand, the frequency mode of charge fluctuations does not vanish in this limit. This is a characteristic behavior of an optic-like mode.

From the results obtained by the use of a markovian memory function, expression (50), and from the equation (13), the charge self-correlation function in its continued fraction representation is given by

$$\frac{\tilde{S}_{QQ}(k, z)}{S_{QQ}(k)} = \frac{(\Gamma_{55}(k) + z_2^{(m)})/(z_2^{(m)} - z_1^{(m)})}{z - z_2^{(m)}} - \frac{(\Gamma_{55}(k) + z_1^{(m)})/(z_2^{(m)} - z_1^{(m)})}{z - z_1^{(m)}}, \quad (59)$$

where

$$z_{1,2}^{(m)} = \frac{-\Gamma_{55} \pm \sqrt{\Gamma_{55}^2 - 4k^2\lambda_2}}{2}, \quad (60)$$

with

$$S_{QQ}(k) = \langle Q_k Q_{-k} \rangle, \quad (61)$$

$$\lambda_2 = \frac{\langle J_k^Q J_{-k}^Q \rangle}{\langle Q_k Q_{-k} \rangle}. \quad (62)$$

In the above expressions the super index m stands for the expressions calculated by the use of a markovian memory function. Notice that in the right-hand side of the expression (59) there are only two modes. The first one is associated to charge fluctuations and the other one to a damped thermal mode. Thus, a markovian memory function predicts for the hydrodynamic regime only two modes of the four present in the expression (55).

It can be shown that assuming an exponential memory function, the charge self-correlation function can be written in the form [7].

$$\frac{\tilde{S}_{QQ}(k, z)}{S_{QQ}(k)} = \frac{a(k)}{z - z_1^{(e)}} + \frac{b(k)}{z - z_2^{(e)}} + \frac{c(k)}{z - z_3^{(e)}}, \quad (63)$$

where $z_i^{(e)}$ are the roots of the following third-degree algebraic equation

$$z^3 - 2\tau_k^{-1}z^2 + \tau_k^{-2}\alpha_1 z - \tau_k^{-2}\lambda_3 = 0, \quad (64)$$

here the super index (e) stands for the expressions obtained by using an exponential memory function. By analyzing the expression (63) one obtains that one of the roots, $z_1^{(e)}$ is real, while $z_2^{(e)}$ and $z_3^{(e)}$, are complex conjugated [7].

A simplified analysis of the roots of this equation can be done by considering the low frequency limit $\omega\tau_k \ll 1$. We make the product of the equation (64) by τ_k^2 to obtain

$$\omega = i\tau_k \left[\omega_{1l}^2 - \omega_0^2 / S_{zz}(k) \right], \quad (65)$$

this frequency corresponds to a charge relaxation mode. The quantities (63)-(65) are in detail described in reference [7]. Notice that an exponential memory predicts only three modes, however, in the hydrodynamic expression (55) there appear four.

4. SYMMETRY OPERATIONS AND MEMORY FUNCTIONS.

Since the projection operator formalism is unable to provide an explicit form for the memory functions, usually one proceeds as we have done here, *ie*, one proposes a phenomenological form for the memory function. However, there exist a theoretical formalism which allows to obtain an explicit form for the memory function, this procedure is necessarily of a more microscopic nature than the projection operators does. It includes both, the mode-coupling approach and the kinetic theories [14]. Regardless the way in which the memory function is obtained, due to the symmetry properties this function must satisfy the sum rules for frequency momenta. For a symmetric charged fluid, the hermitian nature of the Liouville operator causes that only even momenta exist. On the other hand for hard-spheres liquids the Liouville operator is non-hermitian. As a consequence of this, in this case also odd momenta appear [4], [16].

The symmetries of a system are contained in its corresponding hamiltonian. If the Hamiltonian has the form $H_N = K_N + U_N$, with a well behaved potential energy U_N , then the Liouville operator is hermitian [4, 14, 16]. In this conditions one obtains steady correlation functions *ie*, the correlations are independent of the time origen choice. It leads that only there exist even frequency momenta. Under these circumstances it is possible to approximate, in the short times regime, the correlation function by a Taylor series in the form.

$$C_{AA}(t) = C_{AA}(0) + \frac{t^2}{2!} C_{AA}^{(2)}(0) + \frac{t^4}{4!} C_{AA}^{(4)}(0) + \dots, \quad (66)$$

here the super index indicates the *j*-th derivative.

On the other hand, since the projection operator \mathcal{P} and the corresponding orthogonal one, \mathcal{Q} , are hermitian, hence, the operator $\mathcal{Q}\mathcal{L}\mathcal{Q}$ also does. Consequently the time evolution operator of the memory functions $e^{-i\mathcal{Q}\mathcal{L}\mathcal{Q}t}$ is an unitary operator. Thus, the steady memory function admits the following representation

$$M_{AA}(t) = M_{AA}(0) + \frac{t^2}{2!} M_{AA}^{(2)}(0) + \frac{t^4}{4!} M_{AA}^{(4)}(0) + \dots \quad (67)$$

The coefficients of this series and those of the expression (66), are related each other by

$$\begin{aligned} M_{AA}(0) &= -Y_{AA}^{(2)}(0) \\ M_{AA}^{(2)}(0) &= -Y_{AA}^{(4)}(0) + [M_{AA}^{(2)}(0)]^2 \\ &\vdots \end{aligned} \quad (68)$$

where $Y_{AA}(\mathbf{t}) = C_{AA}(\mathbf{t})/C_{AA}(0)$.

From the expression adopted by the memory function in the short-times regime and the comparisons made in the above section, we may conclude that a memory function depending on a single relaxation time is not capable to provide a suitable description of the behavior of a charged fluid in the hydrodynamic regime (Kubo's regime).

Thus, in order to obtain a memory function capable to reproduce the behavior in the Kubo's regime as the predicted by the expression (67), and additionally to obtain the correct number of relaxation modes, it would be necessary to consider for the memory function the following kind of combination.

$$M_{AA}(k, t) = A(k)e^{(-t/\tau_1)^2} + B(k)e^{-|t|/\tau_2}, \quad (69)$$

the absolute value is to make sure a correct time parity in such a way that when $k \rightarrow 0$, then $B(k) \rightarrow 0$ and when $k \rightarrow \infty$, then $A(k) \rightarrow 0$.

In a paper we have explored for the charge second-order memory function the following form [17],

$$M_{AA}(k, t) = m(k)e^{-t/\tau_1} + n(k)e^{-t/\tau_2}. \quad (70)$$

By using this expression we have calculated the charge-charge self-correlation and the dynamic structure factor of a symmetric molten salt [17]. We obtained a good quantitative agreement with the behavior obtained by MD in the hydrodynamic regime. However, in the regime of intermediate frequencies we obtained a deviation from the molecular dynamics results. Hence, it seems clear that this disagreement is due to the deficiency of an exponential form to describe properly the relaxation processes in the short-times regime. We would conclude that, in general the dynamics of charged fluids is poorly described by using approximations for the memory function which depend on a single characteristic time. A better description requires of two characteristic relaxation times, the short one related to individual dissipative processes and the longer one related to collective modes effects. In this theoretical framework both times are related and influence each other in a complex way.

5. CONCLUSION

In this paper we have studied the relaxation processes and fluctuations of charged simple fluids. By assuming a markovian memory function whose amplitude is calculated in terms of a wave vector power series, the coefficients of this series are directly related to the transport coefficients; in terms of these expansion coefficients we obtain the correlation functions. We have found that expansion coefficients in the hydrodynamic limit take the form of the Green-Kubo relations. On the other hand, by comparing the expressions of the charge self-correlation, obtained by using a markovian and an exponential memory functions, with the obtained from the hydrodynamics formalism, we found that in the hydrodynamic regime the markovian and exponential approaches have only two and three modes, respectively. While that, the result obtained from the hydrodynamics formalism have four modes. Finally, of the previous result and of the operations of symmetry of the system, one argues the appropriate form for the memory function of second order, which should depend on two times of relaxation, one for short times and another long times, explicitly as that given by the expression

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