Kinetic theory for electron dynamics near a positive ion

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Received 21 August 2008
Accepted 4 October 2008
Published 28 October 2008

Abstract. A theoretical description of time correlation functions for electron properties in the presence of a positive ion of charge number $Z$ is given. The simplest case of an electron gas distorted by a single ion is considered. A semi-classical representation with a regularized electron–ion potential is used to obtain a linear kinetic theory that is asymptotically exact at short times. This Markovian approximation includes all initial (equilibrium) electron–electron and electron–ion correlations through renormalized pair potentials. The kinetic theory is solved in terms of single-particle trajectories of the electron–ion potential and a dielectric function for the inhomogeneous electron gas. The results are illustrated by a calculation of the autocorrelation function for the electron field at the ion. The dependence on charge number $Z$ is shown to be dominated by the bound states of the effective electron–ion potential. On this basis, a very simple practical representation of the trajectories is proposed and shown to be accurate over a wide range including strong electron–ion coupling. This simple representation is then used for a brief analysis of the dielectric function for the inhomogeneous electron gas.

Keywords: correlation functions
Kinetic theory for electron dynamics near a positive ion

1. Introduction

Electron dynamics in a rigid uniform neutralizing background is a well-studied problem (jellium in quantum mechanics [1], one-component plasma in classical mechanics [2]). More realistically, point ions lead to a polarization of the electron density (e.g. in a hydrogen plasma) and the dynamics of the non-uniformly distributed electrons is radically changed. The objective here is to provide a practical theory for the description of equilibrium time correlation functions for electrons in the simplest case of a single point ion of charge number \( Z \). If the charge is positive, essential quantum diffraction effects must be accounted for even at high temperatures and low densities to avoid the electron–ion Coulomb singularity. A classical Hamiltonian description is used here, with a regularized electron–ion interaction that accounts for such effects [3]. This study is an outgrowth of recent investigations based on molecular dynamics simulations for this system [4]. The qualitative features observed for the electron field autocorrelation function from simulation were captured by a simple mean-field kinetic theory. Such a kinetic theory is obtained here from the asymptotically exact short-time limit for the generator of the dynamics, providing both context and a generalization of the analysis in [4] to strong electron–electron coupling conditions.
The kinetic theory is solved exactly to express the correlation functions in terms of effective single-electron trajectories about the ion and collective excitations via a dielectric function for the non-uniform electron fluid. For \( Z = 0 \) the results reduce to the familiar random phase approximation (RPA) with local field effects (the generalized Vlasov approximation of [5]; see also [6] for a related nonlinear kinetic equation for dusty plasmas). More generally it constitutes a generalization of the RPA to a non-uniform electron gas, with both ion–electron and electron–electron interactions renormalized by correlations (the Vlasov equation for an electron gas in a periodic potential is discussed in [7]). The only required input is the time-independent correlations for one or two electrons and the ion. For the calculations here the hypernetted chain approximation (HNC) integral equations are used for these static correlations. The correlation functions are further decomposed into contributions from the bound and free (positive and negative energy) states of the effective single-particle dynamics in section 3.

As a special case, the electric field autocorrelation function is considered in section 4 with the objective of providing a clear interpretation for the \( Z \) dependence observed in simulations. For increasing \( Z \) this dependence includes (1) an increasing covariance of the field (initial value of the correlation function), (2) a decreasing correlation time and (3) the development of a strong domain of anti-correlation at intermediate times [4]. It is shown here that all three features can be attributed to an increasing contribution from the bound states of the single-particle effective dynamics representing actual metastable trapped trajectories of the \( N \)-particle dynamics. With this understanding of the active mechanisms, a simple analytic and accurate model for the bound and free state contributions is proposed and tested. The dynamics is restricted to circular and straight line trajectories and the electron–ion charge correlation is represented by a nonlinear Debye distribution. Somewhat surprisingly, the model reproduces all of the above \( Z \) dependences with remarkable accuracy. This provides the basis for a practical representation of more general correlation functions, such as the dynamic structure factor, and more complex state conditions required for plasma spectroscopy in hot, dense matter [8, 9].

To illustrate the practical utility of the model, collective excitations are explored briefly in section 6 using the model to evaluate the dielectric function for this non-uniform electron distribution about the ion. For weakly non-uniform conditions (small \( Z \)) the results are suggestive of a local density approximation whereby the modes are similar to those of a uniform electron gas, but with the density replaced by the actual local density near the ion. However, this simple approximation fails for larger \( Z \) where the bound states dominate and long wavelength plasmons are replaced by local excitations at the circular orbit frequencies. Finally, some future directions are discussed in the last section.

2. Correlation functions and Markovian approximation

Consider a system of \( N_e \) electrons of charge \(-e\), an infinitely massive positive ion of charge \( Ze \) placed at the origin and a rigid uniform positive background for overall charge neutrality contained in a large volume \( V \). The Hamiltonian is

\[
H = \sum_{\alpha=1}^{N_e} \left( \frac{1}{2} m v_\alpha^2 + V_{ei}(r_\alpha) + V_{eb}(r_\alpha) \right) + \frac{1}{2} \sum_{\alpha,\gamma}^{N_e} V_{ee}(r_{\alpha\gamma}),
\]
where \( \mathbf{r}_\alpha \) and \( \mathbf{v}_\alpha \) are the position and velocity of electron \( \alpha \). The Coulomb interaction between electrons \( \alpha \) and \( \gamma \) is denoted by \( V_{ee}(\mathbf{r}_{\alpha\gamma}) \), where \( \mathbf{r}_{\alpha\gamma} \equiv |\mathbf{r}_\alpha - \mathbf{r}_\gamma| \). Also, \( V_{ei}(\mathbf{r}_\alpha) \) is the electron–ion interaction for electron \( \alpha \) and \( V_{eb}(\mathbf{r}_\alpha) \) is the Coulomb interaction for electron \( \alpha \) with the uniform neutralizing background. In a quantum description, \( V_{ei}(\mathbf{r}_\alpha) \) is also a Coulomb interaction but in the classical case the short range attractive divergence must be ‘regularized’ within a distance \( \delta \) of the order of the de Broglie wavelength [3]. The simplest such form is [10]

\[
V_{ei}(r_\alpha) = -\frac{Ze^2}{r_\alpha} \left(1 - e^{-r_\alpha/\delta}\right). \tag{2}
\]

In the remainder of this presentation such a semi-classical description is assumed. Comments on the corresponding quantum analysis are given in section 7.

The typical response functions characterizing dynamical excitations in a plasma are the charge density or current autocorrelation functions, which are sums of single-particle functions. More generally, the correlation functions of this type are defined by

\[
C_{AB}(t) = \langle A(t)B \rangle = \int d\Gamma A(\Gamma_t)B(\Gamma) \rho_e(\Gamma), \tag{3}
\]

where \( \Gamma = \{x_1, \ldots, x_{N_e}\} \) is a point in the \( 6N_e \)-dimensional phase space and \( x_\alpha = \mathbf{r}_\alpha, \mathbf{v}_\alpha \) denotes a point in the phase space of particle \( \alpha \). The notation \( \Gamma_t \) denotes the evolution of the point \( \Gamma \) to a time \( t \) later under the dynamics generated by the Hamiltonian of (1). The role of the central fixed ion is suppressed in this notation and it acts as an external potential for the electrons. The phase functions \( A(\Gamma) \) and \( B(\Gamma) \) denote some observables of interest, composed of sums of single-particle functions:

\[
A = \sum_{\alpha=1}^{N_e} a(x_\alpha), \quad B = \sum_{\alpha=1}^{N_e} b(x_\alpha). \tag{4}
\]

Finally, the average is over an equilibrium ensemble (e.g. Gibbs), \( \rho_e(\Gamma) \). Because of the special form (4), the \( N \)-particle average can be reduced to a corresponding average in the single-electron subspace by partial integration over \( N_e - 1 \)-electron degrees of freedom (see appendix B):

\[
C_{AB}(t) = \int dx \ n(r) \phi(v) a(x) \overline{b}(x,t). \tag{5}
\]

Here, \( n(r) \) is the equilibrium number density for electrons at a distance \( r \) from the ion (the precise definition as a partial integral of \( \rho_e(\Gamma) \) is given in appendix A) and \( \phi(v) \) is the Maxwell–Boltzmann velocity distribution. The function \( \overline{b}(x,t) \) at \( t = 0 \) is linearly related to the single-particle phase function \( b(x) \) in (4):

\[
\overline{b}(x,0) = \overline{b}(x) = b(x) + \int dx' n(r') \phi(v') h(r,r') b(x'). \tag{6}
\]

The correlation function \( h(r,r') \) is related to the joint number density \( n(r,r') \) for two electrons at \( r \) and \( r' \) with the ion at the origin by

\[
n(r)n(r')h(r,r') \equiv n(r,r') - n(r)n(r'). \tag{7}
\]
The precise definition for \( n(r, r') \) as a partial integral of \( \rho_e(\Gamma) \) is given in appendix A. The time evolution of \( \overline{b}(x, t) \) in the single-particle phase space is governed by a linear equation of the form

\[
\partial_t \overline{b}(x, t) + \int dx' \mathcal{L}(x, x'; t) \overline{b}(x', t) = 0.
\]

(8)

All of the results up to this point are still exact.

The difficult many-body problem is encountered in the determination of \( \mathcal{L}(x, x'; t) \). Weak coupling and perturbation expansions are not appropriate for high \( Z \) ions or conditions for strongly coupled electrons, so instead a Markovian approximation is proposed:

\[
\mathcal{L}(x, x'; t) \rightarrow \mathcal{L}(x, x'; t = 0) \equiv \mathcal{L}(x, x') .
\]

(9)

This approximation assumes that the exact generator for the initial dynamics persists as the dominant form for later times as well. In this way the exact initial correlations among electrons and with the ion are included. The detailed form for \( \mathcal{L}(x, x') \) is obtained in appendix B with the result

\[
\mathcal{L}(x, x') = (\mathbf{v} \cdot \nabla_r - m^{-1} \nabla_r \mathcal{V}_{ie}(r) \cdot \nabla_v) \delta(x - x') + \mathbf{v} \cdot \nabla_r \mathcal{V}_{ee}(r, r') \phi(v') n(r') ,
\]

(10)

where \( \mathcal{V}_{ie}(r) \) and \( \mathcal{V}_{ee}(r, r') \) are ‘renormalized’ electron–ion and electron–electron interactions:

\[
\mathcal{V}_{ie}(r) \equiv -\beta^{-1} \ln n(r), \quad \mathcal{V}_{ee}(r, r') = -\beta^{-1} c(r, r') .
\]

(11)

The direct correlation function \( c(r, r') \) is defined in terms of \( h(r, r') \) by

\[
c(r, r') = h(r, r') - \int dr'' h(r, r'') n(r'') c(r'', r') .
\]

(12)

At \( Z = 0 \) this becomes the usual Ornstein–Zernicke equation [2].

To interpret (10), substitute this approximation into (8) to get the Markovian linear kinetic equation for \( \overline{b}(x, t) \):

\[
(\partial_t + \mathbf{v} \cdot \nabla_r - m^{-1} \nabla_r \mathcal{V}_{ie}(r) \cdot \nabla_v) \overline{b}(x, t) = -\mathbf{v} \cdot \nabla_r \beta \int dx' \mathcal{V}_{ee}(r, r') \phi(v') n(r') \overline{b}(x', t).
\]

(13)

At weak electron–electron coupling \( \mathcal{V}_{ee}(r, r') \rightarrow \mathcal{V}_{ee}(|r - r'|) \) and at weak electron–ion coupling \( \mathcal{V}_{ie}(r) \rightarrow \mathcal{V}_{ie}(r) \), and (13) is recognized as the linear Vlasov equation. More generally, the Markov approximation (13) upgrades this mean-field result to include the effects of equilibrium correlations on all interaction potentials. Thus it is suitable for a discussion of the strong coupling conditions that occur for \( Z > 1 \). The left side of (13) describes single-electron motion about the ion in the effective potential \( \mathcal{V}_{ie} \), while the right side describes dynamical screening of this motion.

In summary, the description of electron dynamical correlations and fluctuations has been reduced in the Markovian approximation to

\[
C_{AB}(t) = \int \! dx n(r) \phi(v) a(x) e^{-\mathcal{L}t} \overline{b}(x),
\]

(14)

doi:10.1088/1742-5468/2008/10/P10021
where $\mathcal{L}$ is the operator whose kernel is (10). This operator requires as input the equilibrium electron density $n(r)$ and the equilibrium direct correlation function. The kinetic equation can be solved exactly in terms of the single-particle trajectories about the ion and the dielectric function for an inhomogeneous electron gas, describing the dynamical screening due to interactions among the electrons in the presence of the ion. The details are carried out in appendix C and the correlation functions are obtained from that solution in appendix D. For the class of correlation functions for which $a(x) = a(r)$ (i.e. is independent of the velocity), the Laplace transform of (14) takes the simpler form

$$
\int_0^\infty dt \, e^{-zt} C_{AB}(t) = \int dr \, dv \, n(r) \phi(v) a(r; z) G_0(z) \overline{\theta}(x).
$$

(15)

The dynamics is governed by the resolvent operator

$$
G_0(z) = (z + \mathcal{L}_0)^{-1}, \quad \mathcal{L}_0 = v \cdot \nabla_r - m^{-1} \nabla_r V_{ie}(r) \cdot \nabla_v.
$$

(16)

The generator for the dynamics, $\mathcal{L}_0$, is seen to be that for a single electron interacting with the ion via the effective mean-field potential $V_{ie}(r)$. The function $a(r; z)$ is the given function $a(r)$, modified by dynamical screening

$$
a(r; z) = \int dr' a(r') \epsilon^{-1}(r', r; z),
$$

(17)

where $\epsilon(r, r'; z)$ is the ‘dielectric function’ for the electrons in the presence of the ion$^1$:

$$
\epsilon(r, r'; z) = \delta(r - r') - \int dr'' \pi(r, r''; z) V_{ee}(r'', r'),
$$

(18)

and $\pi(r, r''; z)$ is

$$
\pi(r, r''; z) = -\beta n(r) \int dv \phi(v) G_0(z) v \cdot \nabla_r \delta(r - r'').
$$

(19)

### 2.1. Dynamic structure factor

An important example is the autocorrelation function for the electron density near the ion. In the absence of the ion this is referred to as the dynamic structure factor and that terminology will be used here in the presence of the ion as well. The correlation function $C_{AB}(t) = C(q, q'; t)$ is constructed from the local densities of (4) with $a(x_\alpha) = \delta(q - r_\alpha)$ and $b(x_\alpha) = \delta(q' - r_\alpha)$. Then (15) becomes

$$
\int_0^\infty dt \, e^{-zt} C(q, q'; t) = \int dr \, dv \, n(r) \phi(v) \epsilon^{-1}(q, r; z) G_0(z) s(r, q').
$$

(20)

Here $s(r, q')$ is the static structure factor

$$
s(r, q') = \delta(r - q') + n(q') h(r, q') = \delta(r - q') + n(q') h(q', r) = \epsilon^{-1}(q', r; 0),
$$

(21)

$^1$ Strictly speaking the dielectric function is defined in terms of the response function and is different in general from that given here. They agree only in the weak electron–electron limit. However, it is a convenient terminology as the function considered here does determine the collective modes.
representing the exact initial correlations. The last equality of (21) is proved in appendix D.

Equation (20) is the exact short time (Markovian) form for the dynamic structure factor. For \( Z = 0 \) it becomes the usual random phase approximation (RPA) with ‘local field corrections’; this means that the bare electron–electron potential has been replaced by \( V_{ee} \) (the corresponding direct correlation function) to account for exact initial correlations. The \( Z = 0 \) case has been studied in detail for the hydrogen plasma, where this approximation is found to be very good up to moderate plasma coupling strengths over a wide range of space and timescales [5]. Equation (16) extends this approximation to include the presence of the ion for \( Z \neq 0 \), corresponding to an inhomogeneous RPA.

2.2. Electric field autocorrelation function

A second important example is the autocorrelation function \( C(t) \) for the electron electric field at the ion, where

\[
A = B = \sum_{\alpha=1}^{N_e} \mathbf{e}(\mathbf{r}_\alpha), \quad \mathbf{e}(\mathbf{r}_\alpha) = \frac{1}{Z e} \nabla_{\mathbf{r}_\alpha} V_{ei}(\mathbf{r}_\alpha).
\]  

This correlation function is also obtained from the dynamic structure factor \( C(\mathbf{r}, \mathbf{r}'; t) \) by integration:

\[
C(t) = \int d\mathbf{r} d\mathbf{r}' \mathbf{e}(\mathbf{r}) C(\mathbf{r}, \mathbf{r}'; t) \mathbf{e}(\mathbf{r}'),
\]

so

\[
\int_0^\infty dt \ e^{-zt} C(t) = \int d\mathbf{r} d\mathbf{v} \ n(\mathbf{r}) \phi(\mathbf{v}) \mathbf{e}(\mathbf{r}; z) \cdot G_0(z) \mathbf{e}_s(\mathbf{r}).
\]

Interestingly, one of the fields is dynamically screened while the other is statically screened:

\[
\mathbf{e}(\mathbf{r}; z) = \int d\mathbf{r}' \mathbf{e}(\mathbf{r}') e^{-1}(\mathbf{r}', \mathbf{r}; z), \quad \mathbf{e}_s(\mathbf{r}) = \int d\mathbf{r}' \mathbf{e}(\mathbf{r}') s(\mathbf{r}', \mathbf{r}) = \mathbf{e}(\mathbf{r}; z = 0).
\]

3. Bound and free contributions

The trajectories of the mean-field generator \( \mathcal{L}_0 \) do not represent the dynamics of any given electron, but rather their effective collective representation. Thus, the interactions among many electrons appears in the mean-field theory only through their modification of the potentials. The bound states of the effective potential \( V_{ee}(\mathbf{r}) \) are representations of real metastable states in the MD simulation. At weak coupling there are few such metastable states and their lifetimes are short compared to the correlation time for the field autocorrelation function. As \( Z \) increases the stronger coupling gives rise to more metastable states with longer lifetimes. There is a crossover of these lifetimes to values larger than the correlation time at which point they behave essentially as bound states for the relevant timescales. To isolate the effects of such bound states it is useful to divide the phase space integral of (14) into contributions from bound and free parts of that phase space. The decomposition is defined by the negative and positive energy states for the
effective potential $\mathcal{V}_{ie}(r)$. For a given position $r$ there is a maximum velocity $v_m(r)$ above which the total energy is positive:

$$v_m(r) = \sqrt{-2\mathcal{V}_{ie}(r)/m}.$$  \hfill (26)

The single-particle equilibrium density for the position and velocity can therefore be divided into two contributions:

$$n(r)\phi(v) = \Theta (v_m(r) - v)n(r)\phi(v) + \Theta (v - v_m(r))n(r)\phi(v)$$

$$= (n(r)\phi(v))_b + (n(r)\phi(v))_f.$$  \hfill (27)

For example, integration over the velocity gives the relative contribution of bound states to the density $n(r)$:

$$n_b(r) \equiv \int dv (n(r)\phi(v))_b \approx n(r)4\pi^{-1/2}v_0^{-3} \int_0^{v_m(r)} dv v^2 e^{-(v/v_0)^2}$$

$$= n(r) \left( \text{erf}\left(\frac{v_m(r)}{v_0}\right) - \frac{2}{\sqrt{\pi}} \frac{v_m(r)}{v_0} e^{-(v_m(r)/v_0)^2} \right),$$  \hfill (28)

where $v_0 = \sqrt{2k_BT/m_e}$ is the thermal velocity of the electron and erf$(x)$ is the error function. Since $v_m(r)$ is proportional to $\sqrt{Z}$, $n_b(r)$ is an increasing function of $Z$ for all $r$.

The decomposition (27) provides the identification of contributions to the correlation functions from bound and free states:

$$C_{AB}(t) = C_{AB}^b(t) + C_{AB}^f(t).$$  \hfill (29)

The analysis of the following sections shows that the interesting $Z$ dependence of electron dynamics can be understood in terms of the relative sizes of these two contributions.

4. Example: electric field autocorrelation function

The dielectric function $\epsilon(r, r'; z)$ describes a crossover from no screening at short times (large $z$) to static screening at large times ($z \to 0$). In the next two sections, the short-time form with $\epsilon(r, r'; z) \to \delta(r - r')$ will be considered. In that case the correlation functions in (15) become the effective single-particle functions:

$$C_{AB}(t) \to \int dr dv n(r)\phi(v)a(r)e^{-L_0 t}\bar{b}(x),$$  \hfill (30)

which are asymptotically exact at short times. The effects of dynamical screening at longer times are discussed briefly in section 6.

The electric field autocorrelation function is particularly instructive since the field is sensitive to configurations closest to the ion. Also, its time integral determines the dominant contribution to the half-width of spectral linewidths broadened by electrons in many practical cases [11]. The short-time form of (24) is

$$C(t) \to \int dr dv n(r)\phi(v)e(r)\cdot e^{-L_0 t}\bar{e}(r).$$  \hfill (31)
It is shown in appendix A that the statically screened field of (25) simplifies further to
\[ e_s(r) = \frac{1}{Ze} \nabla_r V_{ie}(r). \] (32)

Thus, the number density \( n(r) \) determines all of the ingredients needed for calculation of \( C(t) \). It is calculated here in the HNC approximation described in appendix A. The electron–electron coupling strength is measured by the dimensionless ratio \( \Gamma = \beta e^2 / r_0 \), where \( r_0 \) is the average distance between electrons, determined from the density by \( 4\pi n_e r_0^3 / 3 = 1 \). The ion–electron coupling is measured by \( \sigma = -\beta V_{ie}(0) = \beta Ze^2 / \delta = Z\Gamma (r_0 / \delta) \). The results presented here are for \( \Gamma = 0.1 \) and \( \sigma = 0.25Z \) for values of \( Z \leq 40 \). The corresponding quantum regularization length is \( \delta / r_0 = 0.4 \). The electron–electron coupling is therefore weak, but the ion–electron coupling can be very strong, \( \sigma \leq 10 \). These conditions were chosen because previous molecular dynamics studies have been performed at these values [4].

It is useful to anticipate the increasing role of bound states with increasing \( Z \) by considering first the time-independent covariance \( C(0) \). This is shown in figure 1. The sharp increase above \( Z \sim 5 \) is seen to be entirely due to the appearance of the bound states. Similar strong effects on dynamical structure are observed. Figure 2 shows the results for \( C(t) \) calculated from (31) for \( Z = 1, 4, 8, 20, 30, 40 \). The development of a strong anti-correlation and the decreasing initial correlation time with increasing \( Z \) is evident. These are the effects noted above, first observed in MD simulations [4]. The interpretation of this twofold dependence on \( Z \) is provided by figures 3 and 4, showing the contributions from bound and free state contributions for \( Z = 4, 30 \). For \( Z = 4 \) the dominant contribution is from free states, which have a monotonic positive decay. In contrast, for \( Z = 30 \) the dominant contribution is from bound states which provide the negative anti-correlation as the sign of the field changes along each trajectory when
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Figure 2. Autocorrelation function for an electron field at an ion of charge number $Z = 1, 4, 8, 20, 30$ and $40$.

Figure 3. Bound and free state contributions to $C(t)$ for $Z = 4$.

it passes through apsidal distances. The time for this change can be estimated by half the period for a circular orbit at position $r$, which is proportional to $(r^3/Z)^{1/2}$. This is consistent with the observed decrease in correlation time in figure 2. Further elaboration and explanation is provided by the simple model of the next section.

The results of this section demonstrate the utility of the kinetic theory for conditions of strong ion–electron coupling. Although only weak electron–electron coupling was considered, the theory is applicable to strong coupling among electrons as well. Also, while attention in this section has been limited to the electric field autocorrelation function
it is clear that the analysis applies with equal ease to the dynamic structure factor as well, with only the additional complication of more parameters (i.e. two position vectors) characterizing that function. The decomposition of the correlation function into bound and free contributions demonstrates that the interesting features associated with increasing $Z$ can be attributed entirely to the increasing contribution from bound states.

5. A simple, analytic and accurate model

Consider again the electric field autocorrelation function given by (31) explicitly decomposed into its bound and free contributions:

$$C(t) = C^b(t) + C^f(t),$$

$$C^{b,f}(t) \rightarrow \int \! dr \, d\mathbf{v} \, (n(r) \phi(v))^{b,f} \mathbf{e}(r) \cdot e^{-L_0 t} \mathbf{e}_s(r).$$

The objective here is to capture the qualitative features of the bound and free contributions in a very simple model that allows further elaboration of their relative roles and the mechanisms involved. This is accomplished by assuming circular trajectories for the bound states and straight line trajectories for the free states:

$$C^f(t) \rightarrow \int \! dr \, d\mathbf{v} \, (n(r) \phi(v))^f \mathbf{e}(r) \cdot \mathbf{e}_s(r - vt),$$

$$C^b(t) \rightarrow \int \! dr \, d\mathbf{v} \, (n(r) \phi(v))^b \mathbf{e}(r) e_s(r) \cos \left( \frac{v_e(r)t}{r} \right).$$
Here $\cos(v_e(t)/r) = \mathbf{r} \cdot \mathbf{r}(t)$ and $r(t) = r$ for circular orbits. In this case the velocity must be orthogonal to $\mathbf{r}$ with the specified magnitude

$$ v_e(r) = \sqrt{\frac{r}{m} \frac{dV_n(r)}{dr}}, \quad (37) $$

for consistency with Newton’s equations. The Maxwellian in $(n(r)\phi(v))_b$ must therefore be replaced by this restriction on the velocities:

$$ (n(r)\phi(v))_b = \frac{1}{2\pi} n_b(r) \Theta(v_m(r) - v) \delta(\mathbf{v} \cdot \mathbf{r}) \delta(u - v_e(r)), \quad (38) $$

where $\mathbf{u}$ is the component of $\mathbf{v}$ orthogonal to $\mathbf{r}$. The factor $n_b(r)$ is given by (28) and is required by the correct normalization on integration over all velocities. Equation (36) then becomes

$$ C^b(t) = 4\pi \int_0^\infty dr \ r^2 n_b(r) e(r) e_u(r) \cos(\omega_e(r)t), \quad (39) $$

where $\omega_e(r) = v_e(r)/r$. Note that these modifications of the trajectories do not affect the initial value, $C(0)$, which is still exact.

One further simplification is made to complete the model. The effective potential $V_{ie}(r)$ is replaced by its weak coupling Debye form:

$$ V_{ie}(r) = -\frac{Z e^2}{(1 - \delta/\lambda)^2} \frac{1}{r} \left( e^{-r/\lambda} - e^{-r/\delta} \right), \quad (40) $$

where $\lambda = r_0/\sqrt{3\Gamma}$ is the Debye length and $\delta$ is the quantum regularization length of (2). The corresponding electron density is now the nonlinear Debye form:

$$ n(r) = n_e \exp \left( \beta \frac{Ze^2}{(1 - \delta/\lambda)^2} \frac{1}{r} \left( e^{-r/\lambda} - e^{-r/\delta} \right) \right). \quad (41) $$

This is exact in the weak coupling limit, with $Z \to Z$. More generally, $Z$ is chosen to give the correct value of $C(0)$ using (40) and (41) in the exact equation for $C(0)$ and adjusting $Z$ to fit the values obtained from HNC:

$$ C^*(0) = \frac{r_0^4}{6\Gamma} C(0) = \frac{3}{Z} \int_0^\infty dy \ y^e \ e^{-y} \left( e^{\sqrt{3\Gamma} y} - 1 \right), \quad (42) $$

with

$$ f(y) = \frac{1}{y} \frac{\Gamma}{y} \delta^*(1 - (\sqrt{3\Gamma} \delta^*)^2) \left( e^{-\delta^*\sqrt{3\Gamma} y} - e^{-y} \right), \quad \delta^* = \frac{\delta}{r_0}. \quad (43) $$

Table 1 gives the values obtained using $C^*(0)$ from the HNC approximation for the case $\Gamma = 0.1$ and $\sigma = 0.25Z$.

Figure 5 shows again the results of figures 3 and 4 for $Z = 4$ and 30, now including as well the results from the simple model of this section. Remarkably, the use of the Debye form with the straight line and circular trajectories gives an accurate representation of the kinetic theory results. This provides the basis for a practical tool for use in more complex conditions, as discussed in the last section, and for other correlation functions, as illustrated in the next section.

doi:10.1088/1742-5468/2008/10/P10021
6. Dielectric function

The last two sections addressed the short-time form (30) of the correlation functions for which the dielectric function behaves as $\epsilon(r, r'; z) \to \delta(r - r')$. For very long times (small $z$) $\epsilon(r, r'; z)$ crosses over to represent static screening. At intermediate times there are contributions from collective excitations. Their description is more complex than for the uniform electron gas for which the space dependence of the dielectric function occurs only through $r - r'$. To simplify the discussion here consider the weak electron–electron limit (but possibly strong ion–electron coupling) for which $\mathcal{V}_{ee}(r, r') \to \mathcal{V}_{ee}(|r - r'|)$ and define the partial transform

$$
\tilde{\epsilon}(r, k; z) \equiv \int dr' e^{ik(r'-r)} \epsilon(r, r'; z) = 1 + \beta n(r) \mathcal{V}_{ee}(k) \int_0^\infty dt e^{-zt} \int dv \phi(v) i\mathbf{k} \cdot \mathbf{v} (-t) e^{ik(r(-t)-r)}. \tag{44}
$$

Collective excitations for the non-uniform system, $z(k, r)$, are defined by $\tilde{\epsilon}(r, k; z(k, r)) = 0$. For zero charge number on the ion, $Z = 0$, $\tilde{\epsilon}(r, k; z) \to 0$ reduces to the familiar RPA.
dielectric function of the uniform electron gas:

\[
\tilde{\epsilon}(r, k; z) \rightarrow \tilde{\epsilon}_{\text{RPA}}(n_e, k; z) = 1 + \beta n_e \tilde{\nu}_{ee}(k) \int_0^\infty dt \, e^{-zt} \int d\mathbf{v} \, \phi(v) i\mathbf{k} \cdot \mathbf{v} e^{-i\mathbf{k} \cdot \mathbf{v} t},
\]  

(45)

identifying the excitation spectrum \(z(k)\).

For \(Z \neq 0\) the modes, \(z(k, r)\), depend on \(r\) due to the inhomogeneity caused by the ion. As an example, consider the solutions with very large \(z\). Expanding \(\tilde{\epsilon}(r, k; z)\) to order \(1/z^2\) gives

\[
z^2(k, r) = -\frac{n(r)\tilde{V}_{ee}(k)k^2}{m} + ik_{||} n(r)\tilde{V}_{ee}(k) \frac{\beta m \omega_p^2(r)}{m} + \cdots,
\]

(46)

where \(k_{||} = k \cdot r/r\) is the component of \(k\) along \(r\). For small \(k\) the first term goes to the square of the local plasma frequency:

\[
\frac{n(r)k^2\tilde{V}_{ee}(k)}{m} \rightarrow \frac{4\pi n(r)e^2}{m} \equiv \omega_p^2(r),
\]

(47)

and (46) simplifies to

\[
z^2(k, r) = -\omega_p^2(r) + ik_{||} \frac{r}{(k\lambda_D(r))^2} + \cdots.
\]

(48)

Here \(\lambda_D^2(r) = 1/\beta m \omega_p^2(r)\) is the corresponding local Debye length. Therefore, if \(k_{||} = 0\) the system supports plasmons with frequencies defined in terms of the local density. This is suggestive of a more general ‘local density approximation’ [12] where the dielectric function for the uniform electron gas is modified by replacing the uniform density with the actual non-uniform density:

\[
\tilde{\epsilon}(r, k; z) \rightarrow \tilde{\epsilon}_{\text{RPA}}(n_e, k; z)\big|_{n_e = n(r)}.
\]

(49)

However, this is not correct in general, as is evident from (46) for \(k_{||} \neq 0\) and the following.

To continue with the evaluation of (44), separate into bound and free contributions

\[
\tilde{\epsilon}(r, k; z) = 1 + \beta n(r)\tilde{\nu}_{ee}(k) \int_0^\infty dt \, e^{-zt} \frac{d}{dt} \left[ \int d\mathbf{v} \phi(v) \Theta(v - v_{m}(r)) e^{i\mathbf{k} \cdot (\mathbf{v} - \mathbf{v}_t)} \right] + \frac{1}{2\pi} \int d\mathbf{v} \Theta(v_{m}(r) - v) \delta(\mathbf{v} \cdot \mathbf{r}) \delta(u - v_{c}(r)) e^{i\mathbf{k} \cdot (\mathbf{v} - \mathbf{v}_t)} \right] \bigg|_{n_e = n(r)}.
\]

(50)

Next, introduce the approximate trajectories of the last section. The analysis is straightforward but lengthy so only the final result is given here:

\[
\tilde{\epsilon}(r, k; z) = 1 + \beta \tilde{\nu}_{ee}(k) \left( n_f(r) I_f(k, r, z) + n_b(r) I_b(k, r, z) \right).
\]

(51)

The first term in the brackets, proportional to \(n_f(r) \equiv n(r) - n_b(r)\), is the contribution from free states, while the second term proportional to \(n_b(r)\) is that from bound states (recall (38) for the bound state contribution \(n_b(r)\)). The functions \(I_f(k, r, z)\) and
the leading order contributions to (52) and (53) gives

\[ I_b(k, r, z) = k v_0 \int_0^\infty dt \frac{e^{-t f(r/v_0)}}{t f(r/v_0)} \frac{x^2 e^{-x^2}}{x^2 e^{-x^2}} j_1(k v_0 t) \]  

(52)

\[ I_b(k, r, z) = \int_0^\infty dt e^{-t f(r/\omega_c(r) t)} \left[ -i k_{||} v_c(r) \sin(\omega_c(r) t) J_0(k_{||} v_c(r) \sin(\omega_c(r) t)) \right] \]

\[ + \frac{d}{dt} J_0(k_{||} v_c(r) \sin(\omega_c(r) t)) \]  

(53)

The Bessel functions \( j_1(x) \) and \( J_0(x) \) are

\[ j_1(x) = \frac{1}{x^2} (\sin x - x \cos x), \quad J_0(x) = \frac{1}{2\pi} \int_0^{2\pi} d\phi e^{i x \cos \phi}. \]  

(54)

The free state contribution depends only on the magnitudes \( k, r \) while the bound state contribution depends on the directions as well, where \( k_{||} \) and \( k_{\perp} \) are the components of \( k \) parallel and perpendicular to \( r \).

Consider the small-\( k \), long wavelength limit of this expression for \( \tilde{\epsilon}(r, k; z) \). Retaining the leading order contributions to (52) and (53) gives

\[ \tilde{\epsilon}(r, k; z) \to 1 + \frac{\omega^2_p(r)}{z^2} \left( \frac{n_{l}(r)}{n(r)} \right) + \frac{4}{3\sqrt{\pi}} \left( \frac{v_m(r)}{v_0} \right)^3 e^{-\left(\frac{v_m(r)}{v_0}\right)^2} \]

\[ + \frac{\omega^2_c(r)}{z^2 + \omega^2_c(r) (k \lambda_D)^2} \frac{m_b(r)}{n(r)}. \]  

(55)

The limiting forms for these long wavelength excitations as functions of the ion charge number \( Z \) are

\[ z^2 \to \begin{cases} 
-\omega^2_p(r), & Z < 1 \\
-\omega^2_c(r) \left( 1 + \frac{i k_{||} r}{(k \lambda_D)^2} \right), & Z \gg 1.
\end{cases} \]  

(56)

The local plasmons are recovered for small charge numbers, while for large charge numbers the local circular frequencies \( \omega^2_c(r) \) dominate. The complex coefficient in (56) implies that these excitations are damped.

The dielectric function \( \tilde{\epsilon}(r, k; z) \) is quite complex, but it is seen that the simple model of straight line and circular orbits simplifies this considerably. Further analysis of the collective modes for the inhomogeneous electron gas will be given elsewhere.

7. Discussion

A very general description of time correlation functions for electron properties near a positive ion has been given by the Markovian approximation (15). The time dependence has two contributions: an effective single-particle dynamics that dominates for short and intermediate times, and a modification of that dynamics due to collective modes. The
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doi:10.1088/1742-5468/2008/10/P10021
Acknowledgments

The research was supported by the NSF/DOE Partnership in Basic Plasma Science and Engineering under the Department of Energy award DE-FG02-07ER54946.

Appendix A. Equilibrium BBGKY hierarchy

Consider a point ion of charge number \( Z \) in an electron gas of average density \( n_e \) with a positive uniform neutralizing background of density \( n_b = n_e \). The equilibrium structure of the electrons in the presence of the ion is given by the one- and two-particle distribution functions, defined for the equilibrium ensemble by

\[
 f_{ie} (r_{10}, v_0, v_1) \equiv N_e \int dx_2 \cdots dx_{N_e} \rho_e (\Gamma), \tag{A.1}
\]

\[
 f_{i ee} (r_{10}, r_{20}, v_0, v_1, v_2) \equiv N_e^2 \int dx_3 \cdots dx_{N_e} \rho_e (\Gamma), \tag{A.2}
\]

where \( r_{10} = r_1 - r_0 \) is the position of an electron at \( r_1 \) relative to the ion at \( r_0 \). This position dependence reflects the fluid symmetry (rotational invariance) about the ion. The distribution function \( f_{ie}(r_{10}, v_0, v_1) \) obeys the equilibrium BBGKY hierarchy equation:

\[
 (v_1 \cdot \nabla_1 + v_0 \cdot \nabla_0 + m_0^{-1} F_{ie}(r_{10}) \cdot \nabla_{v_0} + m_e^{-1} F_{ei}(r_{10}) \cdot \nabla_{v_1} ) f_{ie} (r_{10}, v_0, v_1) = - \int dr_2 dv_2 \left( m_0^{-1} F_{ie}(r_{20}) \cdot \nabla_{v_0} + m_e^{-1} F_{ei}(r_{21}) \cdot \nabla_{v_1} \right) f_{ie} (r_{20}, v_0, v_1) + \int dr_2 (m_0^{-1} F_{ie}(r_{20}) \cdot \nabla_{v_0} + m_e^{-1} F_{ee}(r_{21}) \cdot \nabla_{v_1}) f_{ie} (r_{20}, v_0, v_1) n_b. \tag{A.3}
\]

The last term on the right-hand side is due to the interaction of the ion and electron with the uniform neutralizing background whose density is \( n_b = n_e \). Also, \( F_{ie}(r_{10}) \) is the force of the electron on the ion, \( F_{ei} = -F_{ie} \) is the reaction force of the ion on the electron and \( F_{ee}(r_{21}) \) is the force between electrons. These forces are derived from the corresponding potentials

\[
 F_{ei} = -F_{ie} = -\nabla_1 V_{ei} (r_{10}), \quad F_{ee} (r_{21}) = -\nabla_1 V_{ee} (r_{21}).
\]

The solutions to (A.3) have the forms

\[
 f_{ie} (r_0, v_0, r_1, v_1) = \phi_i (v_0) \phi_e (v_1) n(r_{10}), \tag{A.4}
\]

\[
 f_{i ee} (r_0, v_0, r_1, v_1, r_2, v_2) = \phi_i (v_0) \phi_e (v_1) \phi_e (v_2) n (r_{10}, r_{20}). \tag{A.5}
\]

Here \( \phi_i (v_0) \) and \( \phi_e (v_1) \) are the Maxwellians for the ion and electron:

\[
 \phi_\alpha (v) = \left( \frac{m_\alpha}{2 \pi k_B T} \right)^{3/2} e^{-m_\alpha v^2/(2 k_B T)}, \tag{A.6}
\]
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and \( n(r_{10}), n(r_{10}, r_{20}) \) are the one- and two-particle electron number densities (relative to the ion) normalized to \( N_e \) and \( N_e^2 \), respectively. Use of these forms in (A.3) gives directly

\[
0 = v_0 \cdot \left( -\nabla n(r_{10}) - \beta n(r_{10}) \nabla V_{ei}(r_{10}) \right)
- \beta \int dr_2 \left[ n(r_{10}, r_{20}) - n(r_{10}) n_e \right] \nabla V_{ei}(r_{20})
+ v_1 \cdot \left( \nabla n(r_{10}) + \beta n(r_{10}) \nabla V_{ei}(r_{10}) \right)
- \beta \int dr_2 \left[ n(r_{10}, r_{20}) - n(r_{10}) n_e \right] \nabla V_{ee}(r_{21}).
\]  

(A.7)

Since the velocities of the ion and electron are independent, the following two equations hold:

\[
\nabla \ln n(r_{10}) = -\beta \nabla V_{ei}(r_{10}) - \beta n_e \int dr_2 \left[ \frac{n(r_{10}, r_{20})}{n(r_{10}) n_e} - 1 \right] \nabla V_{ei}(r_{20}),
\]  

(A.8)

\[
\nabla \ln n(r_{10}) = -\beta \nabla V_{ei}(r_{10}) + \beta n_e \int dr_2 \left[ \frac{n(r_{10}, r_{20})}{n(r_{10}) n_e} - 1 \right] \nabla V_{ee}(r_{21}).
\]  

(A.9)

This provides two, seemingly independent, equations for the same electron density around the ion \( n_{ie}(r_{10}) \). Their equivalence implies

\[
\int dr_2 \left( F_{ie}(r_{20}) + F_{ee}(r_{12}) \right) [n(r_{10}, r_{20}) - n(r_{10}) n_e] = 0,
\]  

(A.10)

which means that the total external force on the system of two selected particles, the ion and the one electron, is zero at equilibrium. In other words, the distortion of \( n(r_{10}, r_{20}) \) is just such as to enforce this condition. Both equations (A.8) and (A.9) are useful, as illustrated in the following two subsections.

In the remainder of the appendices and in the text, only the special case of a massive ion fixed at the origin is considered.

**A.1. Screened electric field**

The electric field due to one electron at the ion is defined by

\[
e(r) = \frac{1}{Ze} \nabla V_{ei}(r).
\]  

(A.11)

The electric field autocorrelation function of (24) depends on the associated statically screened field

\[
e_s(r) = \int dr' e(r') s(r', r) = e(r) + \frac{1}{n(r)} \int dr' e(r') (n(r, r') - n(r) n(r')).
\]  

(A.12)

This dependence on the two-electron density \( n(r, r') \) can be eliminated using (A.8) to get

\[
e_s(r) = -\frac{1}{Ze} \nabla \ln n(r).
\]  

(A.13)

doi:10.1088/1742-5468/2008/10/P10021
An effective potential is defined in terms of the density $n(r)$ in (11):
\[
\mathcal{V}_e (r) \equiv -\beta^{-1} \ln n (r),
\] (A.14)
so the screened electric field is given in terms of the gradient of this effective potential:
\[
e_s (r) = \frac{1}{Ze} \nabla_1 \mathcal{V}_e (r).
\] (A.15)

### A.2. Hypernetted chain approximation

A simple and accurate method to determine the density is given by the hypernetted chain (HNC) integral equations [2]. They can be obtained from the usual form for a three-component plasma of electrons, protons and ions of charge number $Z$. Then the limit is taken of uniform proton distribution and dilute concentration for the ions of charge $Z$. Instead, it is useful here to state the result as an approximation to (A.9). Consider the mean-field limit of no electron–electron correlations:
\[
\int \! \mathrm{d} \mathbf{r}_2 \left[ \frac{n (\mathbf{r}_1, \mathbf{r}_2)}{n (\mathbf{r}_1) n_e} - 1 \right] \nabla_2 V_{ee} (r_{21}) \to \int \! \mathrm{d} \mathbf{r}_2 \left[ \frac{n (\mathbf{r}_1) n (\mathbf{r}_2)}{n (\mathbf{r}_1) n_e} - 1 \right] \nabla_2 V_{ee} (r_{21}).
\] (A.16)

Then equation (A.9) simplifies to
\[
\nabla_1 \left[ \ln n (\mathbf{r}_1) + \beta V_{ei} (\mathbf{r}_1) + \beta n_e \int \! \mathrm{d} \mathbf{r}_2 \left( \frac{n (\mathbf{r}_2)}{n_e} - 1 \right) V_{ee} (r_{21}) \right] = 0,
\] (A.17)
or
\[
\ln \frac{n (\mathbf{r}_1)}{n_e} = -\beta V_{ei} (\mathbf{r}_1) - \beta n_e \int \! \mathrm{d} \mathbf{r}_2 \left( \frac{n (\mathbf{r}_2)}{n_e} - 1 \right) V_{ee} (r_{21}).
\] (A.18)

An arbitrary constant has been used to ensure the limit $n(\mathbf{r}_1) \to n_e$ when $V_{ei}(\mathbf{r}_1) \to 0$. Equation (A.18) is an integral form of the Boltzmann–Poisson equation.

The HNC approximation is similar, but retains electron–electron correlations in the absence of the ion:
\[
-\beta \int \! \mathrm{d} \mathbf{r}_2 \left[ \frac{n (\mathbf{r}_1, \mathbf{r}_2)}{n (\mathbf{r}_1) n_e} - 1 \right] \nabla_2 V_{ee} (r_{21}) \to \int \! \mathrm{d} \mathbf{r}_2 \left[ \frac{n (\mathbf{r}_1) n (\mathbf{r}_2)}{n (\mathbf{r}_1) n_e} - 1 \right] \nabla_2 c_{ee} (r_{21}).
\] (A.19)

The function $c_{ee}(r_{21})$ is the electron direct correlation function defined in terms of the electron–electron pair correlation function (without the ion), $n_{ee}(r_{21})$, by the Ornstein–Zernicke equation
\[
c_{ee} (r) = h_{ee} (r) - n_e \int \! \mathrm{d} \mathbf{r}' h_{ee} (r') c_{ee} (|\mathbf{r} - \mathbf{r}'|), \quad h_{ee} (r) = \frac{n_{ee} (r)}{n_e^2} - 1.
\] (A.20)

The approximation (A.19) in (A.9) gives the HNC approximation for $n(r)$:
\[
\ln \frac{n (\mathbf{r}_1)}{n_e} = -\beta V_{ei} (\mathbf{r}_1) + n_e \int \! \mathrm{d} \mathbf{r}_2 \left( \frac{n (\mathbf{r}_2)}{n_e} - 1 \right) c_{ee} (r_{21}).
\] (A.21)

This is the same as (A.18) except that $V_{ee}(r_{21})$ has been replaced by $-\beta^{-1}c_{ee}(r_{21})$.

The electron–electron direct correlation function is determined independently from the Ornstein–Zernicke equation (A.20) and the HNC approximation:
\[
\ln \frac{n_{ee} (r)}{n_e^2} = -\beta V_{ee} (\mathbf{r}_1) + h_{ee} (r) - c_{ee} (r).
\] (A.22)

Equations (A.20)–(A.22) are the HNC equations used for the numerical calculations presented here.

doi:10.1088/1742-5468/2008/10/P10021
Appendix B. Evaluation of \( \mathcal{L}(x, x'; t = 0) \)

The dynamics of \( C_{AB}(t) \) is conveniently expressed in terms of the fundamental correlation function \( G(x, x'; t) \):

\[
C_{AB}(t) = \int dx \, dx' a(x) G(x, x'; t) b(x'), \quad \text{(B.1)}
\]

\[
G(x, x'; t) = \langle f(x, t) (f(x') - \langle f(x') \rangle) \rangle, \quad f(x) = \sum_{\alpha=1}^{N_e} \delta(x - x_{\alpha}). \quad \text{(B.2)}
\]

The initial value \( G(x, x'; 0) \) is easily calculated, with the result

\[
G(x, x'; 0) = n(r) \phi(v) (\delta(x - x') + \phi(v') \, n(r') \, h(r, r')). \quad \text{(B.3)}
\]

In the last equality the two-electron correlation function \( h(r, r') \) has been identified from (7). Comparison with (6) shows that \( \overline{b}(x) \) can be written

\[
\overline{b}(x) = \frac{1}{n(r) \phi(v)} \int dx \, G(x, x'; 0) b(x'). \quad \text{(B.4)}
\]

This leads to the representation (5) for \( C_{AB}(t) \):

\[
C_{AB}(t) = \int dx \, n(r) \phi(v) a(x) \overline{b}(x, t), \quad \text{(B.5)}
\]

with

\[
\overline{b}(x, t) = \int dx' U(x, x'; t) \overline{b}(x'), \quad \text{(B.6)}
\]

\[
U(x, x'; t) = \frac{1}{n(r) \phi(v)} \int dx'' G(x, x'', t) G^{-1}(x'', x'; 0) n(r') \phi(v'). \quad \text{(B.7)}
\]

The inverse of \( G(x, x'; 0) \) has been introduced by the definition

\[
\delta(x - x') = \int dx'' G(x, x'', 0) G^{-1}(x'', x'; 0). \quad \text{(B.8)}
\]

It is verified that

\[
G^{-1}(x, x'; 0) = \frac{1}{n(r) \phi(v)} \delta(x - x') - c(r, r'), \quad \text{(B.9)}
\]

if \( c(r, r') \) obeys the equation

\[
c(r, r') = h(r, r') - \int dr'' h(r, r'') n(r'') c(r'', r'), \quad \text{(B.10)}
\]

which is a generalization of the Ornstein–Zernicke equation [2].

The formal equation for \( \overline{b}(x, t) \), (8), follows from differentiation of (B.6) with respect to time and the identification

\[
\mathcal{L}(x, x'; t) = - \int dx'' (\partial_t U(x, x''; t)) U^{-1}(x'', x'; t). \quad \text{(B.11)}
\]
This provides the desired result for identifying the Markovian approximation
\[ \mathcal{L}(x, x') \equiv \mathcal{L}(x, x'; t = 0) = -\partial_t U(x, x'; 0), \]  
where the property \( U(x, x'; t = 0) = \delta(x - x') \) has been used. Equation (B.7) gives finally
\[ \mathcal{L}(x, x') = -\frac{1}{n(r)\phi(v)} \int \mathrm{d}x'' \partial_t G(x, x''; t) \bigg|_{t=0} G^{-1}(x'', x'; 0)n(r')\phi(v'). \]  

It only remains to calculate the initial derivative \( \partial_t G(x, x''; t)|_{t=0} \) to determine \( \mathcal{L}(x, x') \). To simplify the notation it is useful to denote the force on the electron due to both the ion and the uniform positive background by \( \mathbf{F}_0(r) \):
\[
\partial_t G(x, x'; t)|_{t=0} = -\int \mathrm{d}x_1 \delta(x_1 - x)(\mathbf{v}_1 \cdot \nabla_{r_1} + m^{-1}\mathbf{F}_0(r_1) \cdot \nabla_{v_1}) \left[ \delta(x_1 - x')n(r_1)\phi(v_1) \right. \\
+ \int \mathrm{d}x_2 \delta(x_2 - x') \phi(v_1) \phi(v_2) (n(r_1, r_2) - n(r_1) n(r_2)) \\
- \int \mathrm{d}x_2 \mathrm{d}x_2 \delta(x_1 - x) m^{-1}\mathbf{F}_{ee}(r_{12}) \cdot \nabla_{v_1} \\
\times \left[ (\delta(x' - x_1) + \delta(x' - x_2)) \phi(v_1) \phi(v_2) n(r_1, r_2) \\
+ \int \mathrm{d}x_3 \delta(x' - x_3) \phi(v_1) \phi(v_2) \phi(v_3) (n(r_1, r_2, r_3) - n(r_1, r_2) n(r')) \right] \\
= - (\mathbf{v} \cdot \nabla_r + m^{-1}\mathbf{F}_0(r) \cdot \nabla_v) G(x, x'; 0) \\
- \nabla_v \cdot \delta(x' - x) \phi(v) m^{-1} \int \mathrm{d}r_2 \mathbf{F}_{ee}(|r - r_2|) n(r, r_2) \\
+ \beta\phi(v) \phi(v') \mathbf{v} \cdot \left[ \mathbf{F}_{ee}(|r - r'|) n(r, r') \right. \\
+ \int \mathrm{d}r_2 \mathbf{F}_{ee}(|r - r_2|) n(r_1, r_2, r') - n(r_1, r_2) n(r') \right].
\]  
The two integrals on the right can be performed using the hierarchy equation (A.9) for \( n(r) \) and the corresponding next-order hierarchy equation for \( n(r_1, r_2) \). In the current notation these are
\[ \int \mathrm{d}r_2 \mathbf{F}_{ee}(|r - r_2|) n(r, r_2) = \beta^{-1} \nabla_1 n(r_{10}) - n(r_{10}) \mathbf{F}_0(r), \]  
\[ \int \mathrm{d}r_2 \mathbf{F}_{ee}(|r - r_2|) n(r_1, r_2, r') = \beta^{-1} \nabla_1 n(r_1, r') - (\mathbf{F}_0(r_1) + \mathbf{F}_{ee}(r_1 - r')) n(r_1, r'). \]  

Then (A.19) becomes
\[
\partial_t G(x, x'; t)|_{t=0} = - (\mathbf{v} \cdot \nabla_r + m^{-1}\mathbf{F}_0(r) \cdot \nabla_v) G(x, x'; 0) \\
- (m^{-1} (\beta^{-1} \nabla_1 \ln n(r) - m^{-1}\mathbf{F}_0(r)) \cdot \nabla_v \delta(x' - x) n(r) \phi(v) \\
+ \beta\phi(v) \phi(v') (n(r_1, r_2) - n(r_1) n(r_2)) \mathbf{v} \\
\cdot (\beta^{-1} \nabla_r \ln (n(r_1, r_2) - n(r_1) n(r_2)) - \mathbf{F}_0(r)).
\]
Next, eliminate the delta function using (B.3):
\[
\frac{\partial}{\partial \tau} G(x, x'; t) \bigg|_{t=0} = - (v \cdot \nabla_r + m^{-1} F_0(r) \cdot \nabla_v) G(x, x'; 0)
- (m^{-1} (\beta^{-1} \nabla_r \ln n(r)) - m^{-1} F_0(r)) \cdot \nabla_v G(x, x'; 0)
+ (m^{-1} (\beta^{-1} \nabla_r \ln n(r)) - m^{-1} F_0(r))
\cdot \nabla_v \phi(v) \phi(v') (n(r, r') - n(r) n(r'))
+ \beta \phi(v) \phi(v') (n(r_1, r_2) - n(r_1) n(r_2)) \nabla_v
+ (\beta^{-1} \nabla_r \ln (n(r_1, r_2) - n(r_1) n(r_2)) - F_0(r))
\]
\[
= - (v \cdot \nabla_r + m^{-1} (\beta^{-1} \nabla_r \ln n(r)) \cdot \nabla_v) G(x, x'; 0)
+ \phi(v) \phi(v') n(r) n(r') v \cdot \nabla_r h(r, r'). \tag{B.18}
\]

Substitution of this result into (B.13) gives the generator for initial dynamics:
\[
\mathcal{L}(x, x') = (v \cdot \nabla_r + m^{-1} (\beta^{-1} \nabla_r \ln n(r)) \cdot \nabla_v) \delta(x - x')
- v \cdot \nabla_r \int dx'' \phi(v'') n(r'') h(r, r'') G^{-1}(x'', x'; 0) \phi(v') n(r')
= (v \cdot \nabla_r + m^{-1} (\beta^{-1} \nabla_r \ln n(r)) \cdot \nabla_v) \delta(x - x')
- v \cdot \nabla_r \left[h(r, r') - \int dr'' n(r'') h(r, r'') c(r'', r') \right] \phi(v') n(r'). \tag{B.19}
\]

Finally, using (B.10) the result (10) is obtained:
\[
\mathcal{L}(x, x') = (v \cdot \nabla_r + m^{-1} (\beta^{-1} \nabla_r \ln n(r)) \cdot \nabla_v) \delta(x - x')
- v \cdot \nabla_r c(r, r') \phi(v') n(r'). \tag{B.20}
\]

Appendix C. Solution to kinetic equation

The solution to (13) can be obtained in terms of an effective single-electron dynamics by direct integration:
\[
\tilde{b}(x, t) = e^{-\mathcal{L}_0 \tau} \tilde{b}(x) - \int_0^t d\tau e^{-\mathcal{L}_0 (t-\tau)} v \cdot \nabla_r \int dr' \beta \mathcal{V}_{ee}(r, r') I(r', \tau), \tag{C.1}
\]
where the generator for the effective single-particle dynamics is
\[
\mathcal{L}_0 \equiv v \cdot \nabla_r - m^{-1} \nabla_r \mathcal{V}_{ee}(r) \cdot \nabla_v, \tag{C.2}
\]
and the source term \( I(r, t) \) is
\[
I(r, t) \equiv \int dv \phi(v) n(r) \tilde{b}(x, t). \tag{C.3}
\]

The initial condition \( \tilde{b}(x) \) is given by (6). It is convenient at this point to introduce the corresponding Laplace transform:
\[
\tilde{b}(x, z) = \int_0^\infty dt e^{-z t} \tilde{b}(x, t). \tag{C.4}
\]
Then the Laplace transformation of (C.1) gives the equation for $\tilde{b}(x, z)$

$$
\tilde{b}(x, z) = G_0 \tilde{b}(x) - G_0 v \cdot \nabla_r \int dr' \beta \nu_{ee}(r, r') \tilde{I}(r', z),
$$

(C.5)

and

$$
\tilde{I}(r, z) = \int dv \phi(v) n(r) \tilde{b}(x, z), \quad G_0 = (z + L_0)^{-1}.
$$

(C.6)

An equation for $\tilde{I}(r, z)$ follows from substitution of (C.5) into (C.6):

$$
\tilde{I}(r, z) = \int dv \phi(v) n(r) G_0 \tilde{b}(x, 0) - \int dv \phi(v) n(r) G_0 v \cdot \nabla_r \int dr' \beta \nu_{ee}(r, r') \tilde{I}(r', z)
$$

$\equiv \tilde{I}_0(r, z) + \int dr'' \pi(r, r'', z) \int dr' \beta \nu_{ee}(r'', r') \tilde{I}(r', z),

(C.7)

where $\pi(r, r''; z)$ is

$$
\pi(r, r''; z) \equiv -\beta n(r) \int dv \phi(v) G_0 v \cdot \nabla_r \delta(r - r''),
$$

(C.8)

and

$$
\tilde{I}_0(r, z) \equiv n(r) \int dv \phi(v) G_0 \tilde{b}(x).
$$

(C.9)

This is an integral equation for $I(r, t)$ which can be written

$$
\int dr' \epsilon(r, r'; z) \tilde{I}(r', z) = \tilde{I}_0(r, z).
$$

(C.10)

The dielectric function $\epsilon(r, r'; z)$ is defined by

$$
\epsilon(r, r'; z) = \delta(r - r') - \int dr'' \pi(r, r''; z) \nu_{ee}(r'', r').
$$

(C.11)

With these results (C.5) becomes

$$
\tilde{b}(x, z) = G_0 \left[ \tilde{b}(x) - v \cdot \nabla_r \int dr'' \beta \nu_{ee}(r, r'') \int dr' \epsilon^{-1}(r'', r'; z) \tilde{I}_0(r', z) \right].
$$

(C.12)

The inverse dielectric function is defined by

$$
\int dr'' \epsilon(r, r''; z) \epsilon^{-1}(r'', r'; z) = \delta(r - r') = \int dr'' \epsilon^{-1}(r, r''; z) \epsilon(r'', r'; z).
$$

(C.13)

Equation (C.12) is the desired solution to the kinetic equation, in terms of the single-particle dynamics of $G_0$, since all terms on the right-hand side are now explicit.

The low frequency limit $(z = 0)$ of $\epsilon(r, r'; z)$ has a simple form in terms of the electron correlations. First, write $\epsilon(r, r'; z)$ as

$$
\epsilon(r, r'; z) = \delta(r - r') - \int dr'' \pi(r, r''; z) \nu_{ee}(r'', r')
$$

$$
= \delta(r - r') + \beta n(r) \int dv \phi(v) G_0 (G_0^{-1} - z) \nu_{ee}(r, r')
$$

$$
= \delta(r - r') + \beta n(r) \left( \nu_{ee}(r, r') - z \int dv \phi(v) G_0 \nu_{ee}(r, r') \right),
$$

(C.14)
where the definition of \( \pi(\mathbf{r}, \mathbf{r}'; z) \) in (C.8) and \( G_0 \) in (C.6) have been used. Then taking the real and imaginary parts of \( z \) going to zero gives
\[
\epsilon(\mathbf{r}, \mathbf{r}'; z = 0) = \delta(\mathbf{r} - \mathbf{r}') + \beta n(r) \mathcal{V}_{ee}(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') - n(r)c(\mathbf{r}, \mathbf{r}') . \tag{C.15}
\]
It follows from the generalized Ornstein–Zernicke equation (B.10) that the inverse of \( \epsilon(\mathbf{r}, \mathbf{r}'; z = 0) \) is
\[
\epsilon^{-1}(\mathbf{r}, \mathbf{r}'; z = 0) = s(\mathbf{r}', \mathbf{r}) , \tag{C.16}
\]
where the static structure factor is defined by
\[
s(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') + h(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') + h(\mathbf{r}', \mathbf{r}) n(\mathbf{r}) . \tag{C.17}
\]
The high frequency limit (\( z \to \infty \)) of \( \epsilon(\mathbf{r}, \mathbf{r}'; z) \) also has a simple form
\[
\epsilon(\mathbf{r}, \mathbf{r}'; z) \to \delta(\mathbf{r} - \mathbf{r}') + \frac{1}{z} \beta n(r) \int d\mathbf{v} \phi(v) \mathbf{v} \cdot \nabla_{\mathbf{r}} \mathcal{V}_{ee}(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') . \tag{C.18}
\]
This implies no screening at asymptotically short times.

**Appendix D. Correlation functions**

The Laplace transform of the correlation function (5) is
\[
\tilde{C}_{AB}(z) = \int dx n(r) \phi(v) a(x) \tilde{b}(x, z) . \tag{D.1}
\]
Substitution of the solution (C.12) gives
\[
\tilde{C}_{AB}(z) = \int dx n(r) \phi(v) a(x) G_0 \left[ \tilde{b}(x) - \mathbf{v} \cdot \nabla_{\mathbf{r}} \int dr'' \beta \mathcal{V}_{ee}(\mathbf{r}, \mathbf{r}'') \times \int dr' \epsilon^{-1}(\mathbf{r}'', \mathbf{r}'; z) \tilde{I}_0(\mathbf{r}', z) \right] . \tag{D.2}
\]
Considerable simplification occurs for the special case where \( a(x) = a(\mathbf{r}) \), i.e. it is independent of the velocity:
\[
\tilde{C}_{AB}(z) = \int dx n(r) \phi(v) a(\mathbf{r}) G_0 \tilde{b}(x) + \int dr a(\mathbf{r}) \int dr'' \beta \mathcal{V}_{ee}(\mathbf{r}'', \mathbf{r}) \int dr' \epsilon^{-1}(\mathbf{r}''', \mathbf{r}'; z) \tilde{I}_0(\mathbf{r}', z) \times \int dr'' \mathcal{V}_{ee}(\mathbf{r}'', \mathbf{r}'') \int dr' \epsilon^{-1}(\mathbf{r}'', \mathbf{r}'; z) \tilde{I}_0(\mathbf{r}', z) , \tag{D.3}
\]
where use has been made of the definition (C.8) for \( \pi(\mathbf{r}, \mathbf{r}''; z) \). It follows from (C.11) that

\[
\int \text{d}r'' \pi(\mathbf{r}, \mathbf{r}''; z) \int \text{d}r'' \mathcal{V}_{ee}(\mathbf{r}'', \mathbf{r}'') \epsilon^{-1}(\mathbf{r}'', \mathbf{r}''; z) = \epsilon^{-1}(\mathbf{r}, \mathbf{r}; z) - \delta(\mathbf{r} - \mathbf{r}'),
\]

so (D.3) becomes

\[
\tilde{C}_{AB}(z) = \int \text{d}x n(r) \phi(v) a(r) \mathcal{G}_0 \tilde{b}(x)
+ \int \text{d}r a(r) \int \text{d}r' [\epsilon^{-1}(\mathbf{r}, \mathbf{r}'; z) - \delta(\mathbf{r} - \mathbf{r}')] I_0(\mathbf{r}', z)
= \int \text{d}r \int \text{d}v n(r) \phi(v) \int \text{d}r' a(r') \epsilon^{-1}(\mathbf{r}', \mathbf{r}; z) \mathcal{G}_0 \tilde{b}(x),
\]

where (C.9) for \( I_0(\mathbf{r}', z) \) has been made explicit, and the dummy labels \( \mathbf{r}, \mathbf{r}' \) have been interchanged. Finally, this can be put in the simple form

\[
\tilde{C}_{AB}(z) = \int \text{d}r \text{d}v n(r) \phi(v) a_s(r; z) \mathcal{G}_0 \tilde{b}(x),
\]

where

\[
a_s(r; z) = \int \text{d}r' a(r') \epsilon^{-1}(\mathbf{r}', \mathbf{r}; z).
\]

Use has been made of the fact that \( n(r) \phi(v) \) commutes with \( \mathcal{L}_0 \).

**D.1. Dynamic structure factor and field autocorrelation function**

The dynamic structure factor is the autocorrelation function for the electron density, corresponding to

\[
a(x) = \delta(\mathbf{r} - \mathbf{q}), \quad b(x) = \delta(\mathbf{r} - \mathbf{q}').
\]

The correlation function (D.7) in this case is

\[
\tilde{C}(\mathbf{q}, \mathbf{q}; z) = \int \text{d}r \text{d}v n(r) \phi(v) \epsilon^{-1}(\mathbf{q}, \mathbf{r}; z) \mathcal{G}_0(0) s(\mathbf{r}, \mathbf{q}),
\]

where \( s(\mathbf{r}, \mathbf{q}') \) is the static structure factor of (C.17).

The electric field autocorrelation follows from (D.10) by integration:

\[
\tilde{C}(z) = \int \text{d}q \text{d}q' \mathbf{e}(\mathbf{q}) \cdot \tilde{C}(\mathbf{q}, \mathbf{q}; z) \mathbf{e}(\mathbf{q}') = \int \text{d}r \text{d}v n(r) \phi(v) \mathbf{e}_s(r; z) \mathcal{G}_0 \mathbf{e}_s(r),
\]

\[
\mathbf{e}_s(r; z) = \int \text{d}q \mathbf{e}(\mathbf{q}) \epsilon^{-1}(\mathbf{q}, \mathbf{r}; z),
\]

\[
\mathbf{e}_s(r) = \int \text{d}q \mathbf{e}(\mathbf{q}) s(\mathbf{r}, \mathbf{q}) = \int \text{d}q \mathbf{e}(\mathbf{q}) \epsilon^{-1}(\mathbf{q}, \mathbf{r}; 0).
\]
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