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Kinetic Theory for Metallic Clusters II. Klimontovich Equation Approach

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Abstract. The classical Klimontovich equation for the microsocopic phase space density is given a Weyl quantization. As an example of its application, a simple nonequilibrium jellium-type model for metallic clusters in strong fields is considered and the corresponding quantum kinetic equation is discussed. The treatment of collective excitations in such an inhomogeneous plasma is described briefly.

1. Introduction

A central feature of the many contributions of Klimontovich to many-body physics [1, 2, 3] is his emphasis on the microscopic phase space density as the fundamental variable in terms of which all other properties, microscopic and macroscopic, could be expressed. In classical mechanics this density obeys an exact nonlinear Vlasov equation. Remarkably, this constitutes an exact mapping of Hamiltonian particle dynamics onto a "simpler" field theory. All of non-equilibrium statistical mechanics is comprised of a solution to this nonlinear field equation, the Vlasov equation, and averages over an ensemble for initial values of these fields. The difficult many-body problem is hidden in this final averaging process [4].

In quantum mechanics a similar mapping is accomplished by the second quantization representation. The creation and annihilation fields obey Heisenberg equations of motion that can be expressed as closed equations for the fields and their conjugates. Again, a simple field theory is supplemented by a difficult averaging over initial conditions. In both classical and quantum mechanics a formalism for constructing average values and correlation functions has been developed (e.g., loop or diagram expansion), as a practical means for implementing the microscopic field equations and averages.

Here, in honor of the memory of Yuri Klimontovich's innovative contributions to theoretical physics, we present some of our current studies of metallic clusters in strong electromagnetic fields [5, 6] in the language of his microsopic phase space density. As the problem is inherently quantum mechanical, that formalism must be translated to the corresponding quantum version. In many respects, it will be recognized as an awkward reinvention of second quantization. On the other hand, the reader will see that many important physical features are exposed more directly

in this form and perhaps its exposition provides some additional insight for new approximations in the future. Furthermore, this comparison shows clearly that the classical limit of second quantization is indeed given by Klimontovich's microscopic phase space densities which is of importance for theories of weakly degenerate systems.

The first section below is a translation of the Klimontovich formalism to quantum mechanics and quantum statistics, using the Weyl quantization rules [9]. Next, our simplified nonequilibrium model of a metallic cluster is introduced and the class of problems to be addressed are outlined. The quantum Klimontovich formalism is then applied to write a formal kinetic theory for electrons in a strong electromagnetic field. Since the confining potential provides an inherent inhomogeneity, it is appropriate to formulate the kinetic theory in a gauge invariant representation that will not be sensitive to subsequent spatial gradient expansions. The ensemble average of this quantum Klimontovich equation provides the basis for a kinetic theory. The Hartree-Fock contributions are extracted explicitly. The equation is then linearized about a stationary inhomogeneous solution and its dielectric properties are identified. Some aspects of collective excitations in the inhomogeneous plasma of the valence electrons are then discussed briefly.

2. Klimontovich Formalism in Quantum Theory

The most remarkable of the many contributions of Klimontovich was his analysis of transport and fluctuations in terms of the classical phase space density

$$f(\mathbf{r},\mathbf{p};t)=\sum_{\alpha=1}\delta\left[\mathbf{r}-\mathbf{r}_{\alpha}(t)\right]\delta\left[\mathbf{p}-\mathbf{p}_{\alpha}(t)\right]. \tag{1}$$

Here $\Gamma\equiv\{\mathbf{r}_{\alpha},\mathbf{p}_{\alpha}\}$, $\alpha=1\ldots N$, denote all positions and momenta of the particles of the system which are the solutions of Hamilton's equations, while $\{\mathbf{r},\mathbf{p}\}$ denote arbitrary single particle field points. Such highly singular quantities are familiar from classical electrodynamics where they are used for a continuum representation of the charge density and current density of point particles. It was Klimontovich's idea to add here also the momentum delta functions which has allowed him to develop an extremely powerful formalism in many-particle physics.

The function f is equivalent to the solution of the full mechanical N-body problem and depends on the precise knowledge of all initial data which, for a macroscopic system, is not available. The average of $f(\mathbf{r},\mathbf{p};t)$ over any initial ensemble $\rho(\Gamma)$ gives the one particle reduced distribution function

$$F(\mathbf{r},\mathbf{p},t)=\langle f(\mathbf{r},\mathbf{p};t)\rangle=\int d\Gamma\,\rho(\Gamma)\,f(\mathbf{r},\mathbf{p};t). \tag{2}$$

Similarly, products of the microscopice phase space density provide all information about fluctuations in the system considered. It is remarkable that the phase space density obeys an exact equation of the same form as the nonlinear Vlasov equation, that follows directly from Hamilton's equations (here, for simplicity, we consider the case without external fields),

$$\left(\partial_t+\frac{1}{m}\mathbf{p}\cdot\nabla\right)f(\mathbf{r},\mathbf{p},t)=\int d\mathbf{r}'\,n(\mathbf{r}',t)\,\nabla_{\mathbf{r}}V(\mathbf{r}-\mathbf{r}')\cdot\nabla_{\mathbf{p}}f(\mathbf{r},\mathbf{p},t), \tag{3}$$

where V ist the binary interaction potential and the number density $n(\mathbf{r},t)$ is a functional of f

$$n(\mathbf{r},t)=\int d\mathbf{p}\,f(\mathbf{r},\mathbf{p},t). \tag{4}$$

At first thought, this is a surprising result. It appears that one needs only to solve the field equation (3) to obtain $f(\mathbf{r},\mathbf{p};t)$, and that then all other properties are in hand. The flaw in this

assumption is that the nonlinearity of the field equations makes the final average over initial data very complicated (fluctuations). Nevertheless, it is a representation that separates nicely the deterministic dynamics from the effects of fluctuations and which has allowed Klimontovich to develop a rigorous kinetic theory of nonideal gases and nonideal plasmas, of relativistic systems, a microscopic theory of fluctuations and so on, e.g. [7].

The quantum version of the microscopic phase space density [8] can be constructed by the Weyl quantization rules [9]. The recipe is to first Fourier transform the classical function of coordinates and momenta to be quantized. Then this Fourier transform is inverted with the coordinates and momenta in a single exponent. To this end, the phase space variables are replaced by their quantum-mechanical operators, $\{\mathbf{r}_\alpha, \mathbf{p}_\alpha\} \longrightarrow \{\widehat{\mathbf{r}}_\alpha, \widehat{\mathbf{p}}_\alpha\}$. Functions of $\mathbf{r}_\alpha$ and $\mathbf{p}_\alpha$ become functions of the corresponding operators, and it must be assured that the result does not depend on the ordering of the (non-commuting) coordinate and momentum operators. Specifically for the phase space density

$$\widehat{f}\,(\mathbf{r},\mathbf{p},t) = (2\pi)^{-6}\int d\lambda d\eta \sum_{\alpha=1} e^{-i\left[\lambda\cdot\widehat{\mathbf{r}}_\alpha(t)+\eta\cdot\widehat{\mathbf{p}}_\alpha(t)\right]}\,\widetilde{f}_\alpha\,(\mathbf{r},\mathbf{p};\lambda,\eta,t)\,, \tag{5}$$

$$\widetilde{f}_\alpha\,(\mathbf{r},\mathbf{p};\lambda,\eta,t) = \int d\mathbf{r}_\alpha d\mathbf{p}_\alpha\, e^{i\lambda\cdot\mathbf{r}_\alpha} e^{i\eta\cdot\mathbf{p}_\alpha} f\,(\mathbf{r},\mathbf{p}) = e^{i\lambda\cdot\mathbf{r}} e^{i\eta\cdot\mathbf{p}}, \tag{6}$$

where operators are denoted by a caret on top. The identities

$$e^{-i\left[\lambda\cdot\widehat{\mathbf{r}}_\alpha(t)+\eta\cdot\widehat{\mathbf{p}}_\alpha(t)\right]} = e^{-i\frac{1}{2}\hbar\lambda\cdot\eta} e^{-i\lambda\cdot\widehat{\mathbf{r}}_\alpha(t)} e^{-i\eta\cdot\widehat{\mathbf{p}}_\alpha(t)} = e^{i\frac{1}{2}\hbar\lambda\cdot\eta} e^{-i\eta\cdot\widehat{\mathbf{p}}_\alpha(t)} e^{-i\lambda\cdot\widehat{\mathbf{r}}_\alpha(t)}, \tag{7}$$

which follow trivially by series expansion of the exponents, lead to several equivalent forms of the quantum operator for the phase space density

$$\widehat{f}\,(\mathbf{r},\mathbf{p},t) = e^{i\frac{1}{2}\hbar\nabla_\mathbf{r}\cdot\nabla_\mathbf{p}} \sum_{\alpha=1} \delta\,(\mathbf{r}-\widehat{\mathbf{r}}_\alpha)\,\delta\,(\mathbf{p}-\widehat{\mathbf{p}}_\alpha) = e^{-i\frac{1}{2}\hbar\nabla_\mathbf{r}\cdot\nabla_\mathbf{p}} \sum_{\alpha=1} \delta\,(\mathbf{p}-\widehat{\mathbf{p}}_\alpha)\,\delta\,(\mathbf{r}-\widehat{\mathbf{r}}_\alpha)\,. \tag{8}$$

The second equality also establishes $\widehat{f}\,(\mathbf{r},\mathbf{p},t)$ as a Hermitian operator which guarantees that the definition of the quantum phase space density does not depend on the ordering of coordinate and momentum operators.

This is the desired generalization of Klimontovich's microscopic phase space density to the quantum case. It is instructive to rewrite this result as a series

$$\widehat{f}\,(\mathbf{r},\mathbf{p},t) = \sum_{l=0}^{\infty} \left(\frac{i\hbar}{2}\nabla_\mathbf{r}\cdot\nabla_\mathbf{p}\right)^l f\,(\mathbf{r},\mathbf{p},t)\,, \tag{9}$$

from which the classical limit is recovered as the first term ($l = 0$), and quantum effects arise from the non-zero l-values as gradient corrections to the classical limit.

The important properties of the classical phase space density are preserved in this quantum representation. For example, integration over one field variable leads to the expected density operator for the remaining variable

$$\int d\mathbf{r}\,\widehat{f}\,(\mathbf{r},\mathbf{p},t) = \sum_{\alpha=1} \delta\,(\mathbf{p}-\widehat{\mathbf{p}}_\alpha)\,, \tag{10}$$

$$\int d\mathbf{p}\,\widehat{f}\,(\mathbf{r},\mathbf{p},t) = \sum_{\alpha=1} \delta\,(\mathbf{r}-\widehat{\mathbf{r}}_\alpha) = \widehat{n}\,(\mathbf{r},t)\,. \tag{11}$$

Finally, the ensemble average of $\widehat{f}\,(\mathbf{r},\mathbf{p},t)$ is the usual Wigner phase space density in quantum mechanics [10] where $\widehat{\rho}$ is the density operator of the system in the initial state

$$F(\mathbf{r},\mathbf{p},t) = \left\langle \widehat{f}\,(\mathbf{r},\mathbf{p};t)\right\rangle = \mathrm{Tr}\,\widehat{\rho}\widehat{f}\,(\mathbf{r},\mathbf{p};t)\,. \tag{12}$$

This is easily established by writing (8) in second quantization representation

$$\widehat{f}\left(\mathbf{r},\mathbf{p},t\right)=\left(2\pi\hbar\right)^{-3}\int d\mathbf{x}\,e^{\frac{i}{\hbar}\mathbf{x}\cdot\mathbf{p}}\,\psi^{\dagger}\left(\mathbf{r}-\frac{1}{2}\mathbf{x},t\right)\psi\left(\mathbf{r}+\frac{1}{2}\mathbf{x},t\right), \tag{13}$$

as is shown in Appendix A. The average of this operator gives the usual definition of the Wigner function.

The Heisenberg equations of motion for $\widehat{f}\left(\mathbf{r},\mathbf{p},t\right)$ can be transformed into field equations, i.e. defined over the field variables with the result

$$\left(\partial_t+\frac{1}{m}\mathbf{p}\cdot\nabla\right)\widehat{f}\left(\mathbf{r},\mathbf{p},t\right)=\int d\mathbf{r}'\,\widehat{n}\left(\mathbf{r}',t\right)\,\frac{2}{\hbar}\sin\left(\frac{\hbar}{2}\nabla_{\mathbf{r}}\cdot\nabla_{\mathbf{p}}\right)V\left(\mathbf{r}-\mathbf{r}'\right)\widehat{f}\left(\mathbf{r},\mathbf{p},t\right), \tag{14}$$

which is the quantum Vlasor (or Hartree) equation. Clearly, the classical Vlasov equation (3) is recovered in the limit $\hbar\to 0$, whenever this limit exists. A more practical form without the differential operators on the right side of (3) is obtained in Appendix A

$$\left(\partial_t+\frac{1}{m}\mathbf{p}\cdot\nabla\right)\widehat{f}\left(\mathbf{r},\mathbf{p},t\right)=\int d\mathbf{r}''d\mathbf{p}''\int d\mathbf{p}'\,\widehat{f}\left(\mathbf{r}'',\mathbf{p}'',t\right)K(\mathbf{r}-\mathbf{r}'',\mathbf{p}-\mathbf{p}')\widehat{f}\left(\mathbf{r},\mathbf{p}',t\right), \tag{15}$$

with

$$K(\mathbf{r},\mathbf{p})=\frac{2}{\hbar}\left(2\pi\hbar\right)^{-3}\int d\mathbf{r}'V\left(\mathbf{r}+\frac{\mathbf{r}'}{2}\right)\sin\left(\frac{\mathbf{r}'\cdot\mathbf{p}}{\hbar}\right). \tag{16}$$

In summary, the formal structure of the classical Klimontovich formalism in terms of the microscopic phase space density extends naturally to quantum mechanics and quantum statistics as well. The analysis of transport and fluctuations can be accomplished in much the same way. The next few sections illustrate an application of those ideas.

3. A Simple Model for Metallic Clusters in an External Field

3.1. Model Hamiltonian

The following model for metallic clusters has been described in more detail elsewhere, in the context of a Green's function formulation of the kinetic theory [6]. Only an outline of the model is presented here. The system of interest is a bound collection of ions and electrons, neutral or charged, comprising the cluster. It is assumed that the constituents are such that the bound electronic distribution is comprised of tightly bound electrons with the ions and weakly bound "valence" electrons [11, 12, 13]. Our interest here is to describe the dynamical response of these weakly bound electrons to an external laser field. Accordingly, the ions and tightly bound electrons are replaced by a model confining potential for the valence electrons, and no further attention is given to possible transitions or response of the tightly bound subsystem. The model therefore is a collection of N electrons in a local weakly-confining potential plus a possibly strong, time dependent, external photon field. The Hamiltonian for this system is

$$H=\sum_{\alpha=1}^{N}\left(\frac{1}{2m_e}\left(\mathbf{p}_\alpha-\frac{e}{c}\mathbf{A}\left(\mathbf{r}_\alpha,t\right)\right)^2+\phi\left(\mathbf{r}_\alpha,t\right)+V_c\left(\mathbf{r}_\alpha\right)\right)+\frac{1}{2}\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N}V\left(|\mathbf{r}_\alpha-\mathbf{r}_\beta|\right) \tag{17}$$

The first term is the Hamiltonian for the electrons coupling to the external vector and scalar electromagnetic fields, $\mathbf{A}$ and ϕ, and to the confining potential V_c. The second term describes the Coulomb interactions among the electrons.

The objective here is to describe the response of the electrons to strong external laser fields via a kinetic equation for their distribution in position and momentum. An appropriate starting point therefore is the Klimontovich equation (2). The initial formal analysis does not require

specification of the confining potential. However, it is useful to have in mind the simplest case of a uniformly distributed ion charge density within a sphere of size determined by the overall cluster density. This is the familiar jellium model, for which the ground state valence electron distribution can be calculated to good approximation. The excited state dynamics of this distribution is the problem addressed here.

3.2. Gauge Invariant Klimontovich Equation

The clusters of interest can be quite large, extending to several hundred ions. In that case the confining potential is extended in space and in some cases the cluster approaches a bulk solid of finite geometry. The spatial inhomogeneity is then weak and approximations based on gradient expansion can be considered. However, such expansions depend on the particular gauge chosen for the external electromagnetic field. Consequently, it is desirable to formulate the analysis in a gauge invariant representation [14, 15].

A change of gauge corresponds to the replacements

$$\mathbf{A}'(\mathbf{r},t) = \mathbf{A}(\mathbf{r},t) + \nabla\chi(\mathbf{r},t), \qquad \phi'(\mathbf{r},t) = \phi(\mathbf{r},t) - \frac{1}{c}\partial_t\chi(\mathbf{r},t), \tag{18}$$

where $\chi(\mathbf{r},t)$ is arbitrary. As Maxwell's equations are invariant under this transformation the physical state is unchanged. This gauge transformation is generated in quantum theory by the unitary transformation

$$\widehat{G}' = e^{i\frac{e}{\hbar c}\chi}\,\widehat{G}\,e^{-i\frac{e}{\hbar c}\chi}, \qquad \chi = \sum_{\alpha=1}^{N}\chi(\mathbf{r}_\alpha,t), \tag{19}$$

where $\widehat{G}$ is an arbitrary operator not explicitly dependent on $\mathbf{A}$ or ϕ. Now consider first a different unitary transformation described by

$$\widehat{\mathcal{G}} = e^{-i\frac{e}{\hbar c}B[\mathbf{A}]}\,\widehat{G}\,e^{i\frac{e}{\hbar c}B[\mathbf{A}]}, \qquad B[\mathbf{A}] = \int_0^1 d\lambda \sum_{\alpha=1}^{N}\mathbf{r}_\alpha\cdot\mathbf{A}(\lambda\mathbf{r}_\alpha,t). \tag{20}$$

Under a gauge transformation this becomes

$$\widehat{\mathcal{G}}' = e^{i\frac{e}{\hbar c}\chi}e^{-i\frac{e}{\hbar c}B[\mathbf{A}']}\,\widehat{G}\,e^{i\frac{e}{\hbar c}B[\mathbf{A}']}e^{i\frac{e}{\hbar c}\chi}, \tag{21}$$

where

$$\begin{aligned} B[\mathbf{A}'] &= \int_0^1 d\lambda\sum_{\alpha=1}^{N}\mathbf{r}_\alpha\cdot\mathbf{A}'(\lambda\mathbf{r}_\alpha,t) = \int_0^1 d\lambda\sum_{\alpha=1}^{N}\mathbf{r}_\alpha\cdot\left(\mathbf{A}(\lambda\mathbf{r}_\alpha,t) + \nabla_{\lambda\mathbf{r}_\alpha}\chi(\lambda\mathbf{r}_\alpha,t)\right) \\ &= B[\mathbf{A}] + (\chi - N\chi(\mathbf{0},t)). \end{aligned} \tag{22}$$

Therefore, the operator $\widehat{\mathcal{G}}$ is seen to be invariant under the gauge transformation

$$\widehat{\mathcal{G}}' = e^{-i\frac{e}{\hbar c}B[\mathbf{A}]}\,\widehat{G}\,e^{i\frac{e}{\hbar c}B[\mathbf{A}]} = \widehat{\mathcal{G}}. \tag{23}$$

A special case of this is the gauge invariant Klimontovich phase space density operator

$$\widehat{\mathcal{F}}(\mathbf{r},\mathbf{p},t) \equiv e^{-i\frac{e}{\hbar c}B(A)}\,\widehat{f}(\mathbf{r},\mathbf{p},t)\;e^{i\frac{e}{\hbar c}B(A)}. \tag{24}$$

The Klimontovich equation for $\widehat{\mathcal{F}}$ follows directly from that for $\widehat{f}$ by the unitary transformation in (3). In the remainder of this discussion attention will be limited to spatially homogeneous

fields (more precisely, the dimensions of the cluster are small compared to the wavelength of the laser field). Since gauge is no longer a concern, it is convenient to use the Coulomb gauge

$$\phi = 0, \qquad \mathbf{E}(t) = -\frac{1}{c}\partial_t \mathbf{A}\,(t)\,, \tag{25}$$

where $\mathbf{E}(t)$ is the external electric field. The Klimontovich equation for $\widehat{\mathcal{F}}$ then becomes

$$\begin{aligned}
&\left(\partial_t + e\mathbf{E}(t)\cdot\nabla_{\mathbf{p}} + \frac{1}{m}\mathbf{p}\cdot\nabla_{\mathbf{r}}\right)\widehat{\mathcal{F}}\,(\mathbf{r},\mathbf{p},t) - \int d\mathbf{p}'\,K_c(\mathbf{r},\mathbf{p}-\mathbf{p}')\,\widehat{\mathcal{F}}\,(\mathbf{r},\mathbf{p}',t) \\
= &\int d\mathbf{r}''d\mathbf{p}''d\mathbf{p}'\,K(\mathbf{r}-\mathbf{r}'',\mathbf{p}-\mathbf{p}')\,\widehat{\mathcal{F}}\,(\mathbf{r}'',\mathbf{p}'',t)\,\widehat{\mathcal{F}}\,(\mathbf{r},\mathbf{p}',t)\,.
\end{aligned} \tag{26}$$

The effects of the confinement potential and the Coulomb interactions induce momentum changes through the functions $K_c(\mathbf{r},\mathbf{p})$ and $K(\mathbf{r},\mathbf{p})$, respectively

$$K_c(\mathbf{r},\mathbf{p}) = \frac{2}{\hbar}\,(2\pi\hbar)^{-3}\int d\mathbf{r}'\,V_c\left(\mathbf{r}+\frac{\mathbf{r}'}{2}\right)\sin\left(\frac{\mathbf{r}'\cdot\mathbf{p}}{\hbar}\right), \tag{27}$$

$$K(\mathbf{r},\mathbf{p}) = \frac{2}{\hbar}\,(2\pi\hbar)^{-3}\int d\mathbf{r}'\,V\left(\mathbf{r}+\frac{\mathbf{r}'}{2}\right)\sin\left(\frac{\mathbf{r}'\cdot\mathbf{p}}{\hbar}\right). \tag{28}$$

Equation (26) is formally exact and fully equivalent to the N particle Heisenberg equations of motion. The left side of this equation describes the dynamics of non-interacting electrons confined locally and in the presence of the homogeneous, time dependent external field. The Coulomb interactions among these electrons is described by the bilinear functional of $\widehat{\mathcal{F}}$ on the right side. All correlations and quantum statistics result from averages of this equation, as illustrated in the next section.

4. Kinetic Theory

The kinetic equation for the gauge invariant Wigner function follows directly from an ensemble average of the Klimontovich equation (26). However, while the Klimontovich equation is closed and deterministic its average does not provide a closed equation for the Wigner function. This is due to the nonlinearity inducing correlations. The bilinear average can be analysed to obtain approximate kinetic equations and correlation functions, as has been described in the books of Klimontovich. The mean field or Hartree-Fock contributions, can be isolated explicitly to characterize screening and dielectric response as described in the next section.

The average of (26) over some initial ensemble gives

$$\begin{aligned}
&\left(\partial_t + e\mathbf{E}(t)\cdot\nabla_{\mathbf{p}} + \frac{1}{m}\mathbf{p}\cdot\nabla_{\mathbf{r}}\right)\mathcal{F}\,(\mathbf{r},\mathbf{p},t) - \int d\mathbf{p}'\,K_c(\mathbf{r},\mathbf{p}-\mathbf{p}')\mathcal{F}\,(\mathbf{r},\mathbf{p}',t) \\
= &\int d\mathbf{r}''d\mathbf{p}''\int d\mathbf{p}'\,K(\mathbf{r}-\mathbf{r}'',\mathbf{p}-\mathbf{p}')\left\langle\widehat{\mathcal{F}}\,(\mathbf{r}'',\mathbf{p}'',t)\,\widehat{\mathcal{F}}\,(\mathbf{r},\mathbf{p}',t)\right\rangle,
\end{aligned} \tag{29}$$

where

$$\mathcal{F}\,(\mathbf{r},\mathbf{p},t) \equiv \left\langle\widehat{\mathcal{F}}\,(\mathbf{r},\mathbf{p},t)\right\rangle. \tag{30}$$

The correlation function on the right side can be written as

$$\begin{aligned}
&\left\langle\widehat{\mathcal{F}}\,(\mathbf{r}_1,\mathbf{p}_1,t)\,\widehat{\mathcal{F}}\,(\mathbf{r}_2,\mathbf{p}_2,t)\right\rangle = \mathcal{F}\,(\mathbf{r}_1,\mathbf{p}_1,t)\,\mathcal{F}\,(\mathbf{r}_2,\mathbf{p}_2,t) \\
&- (2\pi\hbar)^{-3}\int d\mathbf{Y}\int d\mathbf{p}_3 d\mathbf{p}_4\,\delta\,(\mathbf{p}_1+\mathbf{p}_2-\mathbf{p}_3-\mathbf{p}_4)\,e^{\frac{i}{2\hbar}\mathbf{Y}\cdot(\mathbf{p}_2-\mathbf{p}_1)}e^{\frac{i}{\hbar}(\mathbf{r}_1-\mathbf{r}_2)\cdot(\mathbf{p}_3-\mathbf{p}_4)} \\
&\times\mathcal{F}\left[\frac{1}{2}\left(\mathbf{r}_1+\mathbf{r}_2-\frac{\mathbf{Y}}{2}\right),\mathbf{p}_3,t\right]\mathcal{F}\left[\frac{1}{2}\left(\mathbf{r}_1+\mathbf{r}_2+\frac{\mathbf{Y}}{2}\right),\mathbf{p}_4,t\right] \\
&+\mathcal{C}\,(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t)\,.
\end{aligned} \tag{31}$$

The first term on the right results from neglecting all correlations and gives rise to the Hartree mean field contributions. The second term is due to exchange correlations alone and gives the Fock contributions. Finally, $\mathcal{C}\left(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2,t\right)$ represents the remaining correlations due to the interactions among the electrons (scattering effects).

The exact kinetic equation therefore has the form

$$\begin{aligned}\left(\partial_t + e\mathbf{E}(t)\cdot\nabla_{\mathbf{p}} + \frac{1}{m}\mathbf{p}\cdot\nabla_{\mathbf{r}}\right)\mathcal{F}\left(\mathbf{r},\mathbf{p},t\right) &- \int d\mathbf{p}'\, K_{\text{eff}}(\mathbf{r},\mathbf{p}-\mathbf{p}';\mathcal{F})\mathcal{F}\left(\mathbf{r},\mathbf{p}',t\right) \\ &= I^F\left(\mathbf{r},\mathbf{p},t;\mathcal{F}\right) + I^C\left(\mathbf{r},\mathbf{p},t';\mathcal{F}\right), \end{aligned} \tag{32}$$

where $K_{\text{eff}}(\mathbf{r},\mathbf{p})$ describes the contributions from both the confining potential and the Hartree Coulomb terms

$$K_{\text{eff}}(\mathbf{r},\mathbf{p}) = \frac{2}{\hbar}\left(2\pi\hbar\right)^{-3}\int d\mathbf{r}'\sin\left(\frac{\mathbf{r}'\cdot\mathbf{p}}{\hbar}\right)V_{\text{eff}}\left(\mathbf{r}+\frac{1}{2}\mathbf{r}'\right), \tag{33}$$

$$V_{\text{eff}}(\mathbf{r}) \equiv V_c(\mathbf{r}) + \int d\mathbf{r}''\, n\left(\mathbf{r}'',t\right)V(\mathbf{r}-\mathbf{r}''). \tag{34}$$

The remaining two terms, $I^F\left(\mathbf{r},\mathbf{p},t\right)$ and $I^C\left(\mathbf{r},\mathbf{p},t\right)$ are the correlation effects due to Fock exchange and Coulomb correlations. The Fock exchange term can be given explicitly

$$I^F\left(\mathbf{r},\mathbf{p},t;\mathcal{F}\right) = -\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{p}_1 d\mathbf{p}_2 G(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)\mathcal{F}\left(\mathbf{r}_1+\mathbf{r},\mathbf{p}_1+\mathbf{p},t\right)\mathcal{F}\left(\mathbf{r}_2+\mathbf{r},\mathbf{p}_2+\mathbf{p},t\right), \tag{35}$$

where the kernel $G(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)$ is given in Appendix C. Finally, the Coulomb correlation contributions require further analysis to describe collisional effects. This can be accomplished in the Klimontovich formalism through closures analogous to those used in the classical case, or via more systematic Green's function methods. These results are still formally exact. In particular no compromise has been made with respect to the quantum diffraction, degeneracy, or exchange effects.

5. Linear Kinetic Theory

5.1. Equilibrium States

In the absence of a time dependent driving field Eq. (32) supports a stationary (equilibrium) distribution

$$\frac{1}{m}\mathbf{p}\cdot\nabla_{\mathbf{r}}\mathcal{F}_0\left(\mathbf{r},\mathbf{p}\right) - \int d\mathbf{p}'\, K_{0\text{eff}}(\mathbf{r},\mathbf{p}-\mathbf{p}')\,\mathcal{F}_0\left(\mathbf{r},\mathbf{p}'\right) = I^F\left(\mathbf{r},\mathbf{p};\mathcal{F}_0\right) + I^C\left(\mathbf{r},\mathbf{p};\mathcal{F}_0\right), \tag{36}$$

$$K_{0\text{eff}}(\mathbf{r},\mathbf{p}) = \frac{2}{\hbar}\frac{1}{\left(2\pi\hbar\right)^3}\int d\mathbf{r}'\sin\left(\frac{\mathbf{r}'\mathbf{p}}{\hbar}\right)\left\{V_c\left(\mathbf{r}+\frac{\mathbf{r}'}{2}\right) + \int d\mathbf{r}'' n_0\left(\mathbf{r}'',t\right)V\left(\mathbf{r}+\frac{\mathbf{r}'}{2}-\mathbf{r}''\right)\right\}. \tag{37}$$

This equilibrium state is inhomogeneous due to the confining potential and possibly inhomogeneous initial conditions. The solution to this equation is a formidable task except in the high temperature classical limit. The mean field approximation, obtained by neglecting $I^C\left(\mathbf{r},\mathbf{p};\mathcal{F}_0\right)$ is indeterminate with many solutions. In that case additional information must be supplied (e.g., the known limiting form for non-interacting particles). In the following it is assumed that $I^C\left(\mathbf{r},\mathbf{p};\mathcal{F}_0\right)$ has been specified to good approximation and that the solution $\mathcal{F}_0$ is known.

5.2. Excitations About Equilibrium

Consider the case of small perturbations of the equilibrium state due to a (weak) external field and/or initial perturbations. The system response is then described by the linearization of (32) about this equilibrium state

$$\left(\partial_t + \frac{1}{m}\mathbf{p}\cdot\nabla_{\mathbf{r}} - I_0\right)\delta\mathcal{F}\left(\mathbf{r},\mathbf{p},t\right) \;-\; \int d\mathbf{p}'\, K_{0\text{eff}}(\mathbf{r},\mathbf{p}-\mathbf{p}')\,\delta\mathcal{F}\left(\mathbf{r},\mathbf{p}',t\right) \tag{38}$$

$$-\int d\mathbf{p}'\, K_1(\mathbf{r},\mathbf{p}-\mathbf{p}'\,\delta\mathcal{F})\,\mathcal{F}_0\left(\mathbf{r},\mathbf{p}',t\right) \;=\; -e\mathbf{E}(t)\cdot\nabla_{\mathbf{p}}\mathcal{F}_0\left(\mathbf{r},\mathbf{p}\right), \tag{39}$$

where I_0 is an operator representing the linearized contributions from $I^F\left(\mathbf{r},\mathbf{p},t;\mathcal{F}\right)$ and $I^C\left(\mathbf{r},\mathbf{p},t';\mathcal{F}\right)$, and

$$K_1(\mathbf{r},\mathbf{p}) = \frac{2}{\hbar}\left(2\pi\hbar\right)^{-3}\int d\mathbf{r}'\,\sin\left(\frac{\mathbf{r}'\cdot\mathbf{p}}{\hbar}\right)\int d\mathbf{r}''\,\delta n\left(\mathbf{r}'',t\right)V\left(\mathbf{r}+\frac{1}{2}\mathbf{r}'-\mathbf{r}''\right). \tag{40}$$

This equation is linear and therefore its formal solution can be written directly. However, translational invariance is broken by the confining potential so the physics of this inhomogeneous electron gas is quite complex.

To expose some of the inherent collective effects a special solution is sought by separating the dependence on space through the reference density $n_0(\mathbf{r})$ from the remaining spatial variations. The basic assumption in this is that the primary direct effect of the confining potential is to establish the localization of the valence electrons in the cluster. Accordingly, the solution is written in the form

$$\delta\mathcal{F}\left(\mathbf{r},\mathbf{p},t\right) = \delta\mathcal{F}\left[\mathbf{r},\mathbf{p},t;n_0(\mathbf{r})\right], \tag{41}$$

and the kinetic equation becomes

$$\frac{\delta}{\delta n_0}\delta\mathcal{F}\left(\mathbf{r},\mathbf{p},t;n_0\right)\frac{1}{m}\mathbf{p}\cdot\nabla_{\mathbf{r}}n_0(\mathbf{r}) - \int d\mathbf{p}'\,\delta\mathcal{F}\left[\mathbf{r},\mathbf{p},t;n_0(\mathbf{r})\right]K_{0\text{eff}}(\mathbf{r},\mathbf{p}-\mathbf{p}')$$

$$+\left(\partial_t + \frac{1}{m}\mathbf{p}\cdot\nabla_{\mathbf{r}}\mid_{n_0} - I_0\right)\delta\mathcal{F}\left(\mathbf{r},\mathbf{p},t\right)$$

$$-\int d\mathbf{p}'\,K_1(\mathbf{r},\mathbf{p}-\mathbf{p}';\delta\mathcal{F})\mathcal{F}_0\left(\mathbf{r},\mathbf{p}'\right) = -e\mathbf{E}(t)\cdot\nabla_{\mathbf{p}}\mathcal{F}_0\left(\mathbf{r},\mathbf{p}\right). \tag{42}$$

The first two terms involve the direct dependence on the reference density $n_0(\mathbf{r})$, and the confining potential V_c. In the case of long wavelength perturbations these two terms cancel approximately,

$$\frac{\delta}{\delta n_0}\mathcal{F}\left(\mathbf{r},\mathbf{p},t;n_0\right)\frac{1}{m}\mathbf{p}\cdot\nabla_{\mathbf{r}}n_0(\mathbf{r}) - \int d\mathbf{p}'\delta\mathcal{F}\left(\mathbf{r},\mathbf{p},t;n_0(\mathbf{r})\right)K_{0\text{eff}}(\mathbf{r},\mathbf{p}-\mathbf{p}') \approx 0. \tag{43}$$

The remaining space dependence is determined from

$$\left(\partial_t + \frac{1}{m}\mathbf{p}\cdot\nabla_{\mathbf{r}}\mid_{n_0} - I_0\right)\delta\mathcal{F}\left(\mathbf{r},\mathbf{p},t\right)$$

$$-\int d\mathbf{p}'K_1(\mathbf{r},\mathbf{p}-\mathbf{p}';\delta\mathcal{F})\mathcal{F}_0\left(\mathbf{r},\mathbf{p}',t\right) = -e\mathbf{E}(t)\cdot\nabla_{\mathbf{p}}\mathcal{F}_0\left(\mathbf{r},\mathbf{p}\right). \tag{44}$$

Since the space derivative now is taken at constant n_0 (the space dependence appears only as a parameter) this equation is formally similar to that for a homogeneous electron gas, which

may be solved by Fourier-Laplace transformation. The result is given by (D.6) and (D.7) of Appendix D,

$$\begin{aligned}\delta\widetilde{n}\left(\mathbf{k},z\right) &= \epsilon^{-1}\left(z,\mathbf{k};\mathbf{r}\right)\int d\mathbf{p}\left(z+\frac{1}{m}i\mathbf{k}\cdot\mathbf{p}-I_0\right)^{-1}\left[\delta\widetilde{\mathcal{F}}\left(\mathbf{k},\mathbf{p},t=0\right)\right.\\ &\left.-e\left(2\pi\right)^3\delta\left(\mathbf{k}\right)\widetilde{\mathbf{E}}_z\cdot\nabla_{\mathbf{p}}\mathcal{F}_0\left(\mathbf{r},\mathbf{p}\right)\right]. \qquad (45)\end{aligned}$$

The dielectric function $\epsilon\left(z,\mathbf{k};\mathbf{r}\right)$ is given in terms of the polarization function $\Pi\left(z,\mathbf{k};\mathbf{r}\right)$

$$\epsilon\left(z,\mathbf{k};\mathbf{r}\right)=1-\widetilde{V}\left(k\right)\Pi\left(z,\mathbf{k};\mathbf{r}\right), \qquad (46)$$

where

$$\Pi\left(z,\mathbf{k};\mathbf{r}\right)=\int d\mathbf{p}\left(z+\frac{1}{m}i\mathbf{k}\cdot\mathbf{p}-I_0\right)^{-1}\frac{i}{\hbar}\left\{\mathcal{F}_0\left(\mathbf{r},\mathbf{p}+\frac{1}{2}\hbar\mathbf{k},t\right)-\mathcal{F}_0\left(\mathbf{r},\mathbf{p}-\frac{1}{2}\hbar\mathbf{k},t\right)\right\}, \qquad (47)$$

resembles the Lindhard (RPA) polarization function [16] which, in fact, was derived by Klimontovich and Silin before [17]. The result (47), however, is more general than the RPA polarization since it contains collision effects via the linearized collision integral I_0, a formal expression also obtained by Klimontovich. The use of such a linearized term has recently been demonstrated to preserve conservation laws and sum rules [18] and allows to selfconsistently study plasma oscillations in the presence of collisions [19].

It is easily verified that the usual classical form of the polarization, i.e. the Vlasov polarization, is recovered by neglecting I_0 and expanding (47) to leading order in $\hbar k$. The effects of the confining potential are incorporated here, so the result applies for strong spatial inhomogeneity (large wavelength compared to the cluster size). Similarly, the result applies to a time-dependent stationary state if only it evolves slowly, i.e. on time scales larger than one plasma oscillation period. There is no limitation on the time dependence of the applied field; only its amplitude must be small.

6. Plasma Oscillations in an Inhomogeneous System

The normal excitations $\omega(k)$ of the plasma are obtained from the zeroes of the complex dielectric function

$$\epsilon\left(z=i\omega(k),\mathbf{k};\mathbf{r}\right)=0,$$

where, in general, $\omega(k)$ is complex, the imaginary part reflecting the damping of the oscillations, e.g. [20, 21]. For a homogeneous system the long wavelength expansion of the dielectric function leads directly to plasmon excitations with the plasma frequency which are undamped,

$$Re\,\epsilon\left(i\omega(k),\mathbf{k}\right)=1-\frac{\omega_p^2}{\omega^2},\qquad \omega_p^2=\frac{4\pi ne^2}{m_e}.$$

Before deriving such dispersion relations for general inhomogeneous systems, the result for the plasma frequency of small homogeneous spherical particles embedded in a dielectric medium is illustrated. The familiar boundary conditions are that the tangential components for the electrostatic field and the normal components of the displacement field should be continuous across the surface of the particles. In terms of the scalar electrostatic potential and a spherical particle of radius R with dielectric constant ϵ_2 embedded in another medium with dielectric constant ϵ_1 this gives

$$\phi\left(R_+\right)=\phi(R_-),\qquad \epsilon_1\frac{\partial\phi\left(r\right)}{\partial r}\mid_{R_+}=\epsilon_2\frac{\partial\phi\left(r\right)}{\partial r}\mid_{R_-}, \qquad (48)$$

where it has been assumed that no charges are accumulated on the particle surface. The solutions to Laplace's equation that are well-behaved at the origin and vanishing at infinty are

$$\phi(r) = \begin{cases} A_\ell\, r^\ell\, Y_{\ell m}(\theta,\phi), & r < R \\ B_\ell\, r^{-(\ell+1)}\, Y_{\ell m}(\theta,\phi), & r > R \end{cases}, \tag{49}$$

and correspond to dipole ($\ell = 1$), quadrupole ($\ell = 2$), and higher multipole oscillations. The boundary conditions give $B_\ell/A_\ell = R^{2\ell+1}$ and $\epsilon_2/\epsilon_1 = -(\ell+1)/\ell$. Taking as an example a rigid metal sphere with $\epsilon_2(\omega) = 1 - \frac{\omega_p^2}{\omega^2}$ embedded in a dielectric medium with $\epsilon_1 = \epsilon_d$ this gives

$$\omega^2 = \frac{\omega_p^2}{1 + \frac{(\ell+1)\epsilon_d}{\ell}}. \tag{50}$$

For the special case of $\epsilon_d = 1$ (vacuum) and $\ell = 1$ these are the Mie plasmons, $\omega^2 = \omega_p^2/3$.

Return now to the description of plasma oscillations in media with a general spatial dependence on the dielectric properties. Only longitudinal excitations will be considered. The electrostatic potential can be written

$$\phi(\mathbf{r},t) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} = \phi_{ext}(\mathbf{r},t) - \int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \nabla' \cdot \mathbf{P}(\mathbf{r}',t), \tag{51}$$

where $\phi_{ext}(\mathbf{r},t)$ is the potential due to external charges, and $\mathbf{P}(\mathbf{r},t)$ is the macroscopic polarization

$$\mathbf{P}(\mathbf{r},t) = \frac{1}{4\pi}\{\epsilon(\mathbf{r},t) - 1\}\mathbf{E}(\mathbf{r},t) = -\frac{1}{4\pi}\{\epsilon(\mathbf{r},t) - 1\}\nabla\phi(\mathbf{r},t). \tag{52}$$

Substitution of (52) into (51) and integration by parts twice leads to [22]

$$\epsilon(\mathbf{r},t)\,\phi(\mathbf{r},t) = \phi_{ext}(\mathbf{r},t) - \frac{1}{4\pi}\int d\mathbf{r}' \phi(\mathbf{r}',t)\left(\nabla' \frac{1}{|\mathbf{r}-\mathbf{r}'|}\right) \cdot \nabla' \epsilon(\mathbf{r}',t), \tag{53}$$

which makes explicit the dependence on the spatial variation of the dielectric properties.

In the long wavelength limit $\epsilon(\mathbf{r},t)$ for the model here of electrons in a metal cluster can be estimated from

$$\epsilon(\mathbf{r},t) \to 1 - \lim_{k\to 0} \widetilde{V}(k)\,\Pi(i\omega,\mathbf{k};\mathbf{r},t) \approx 1 - \frac{\omega_p^2(\mathbf{r},t)}{\omega^2}, \tag{54}$$

$$\omega_p^2(\mathbf{r},t) = \frac{4\pi n_0(\mathbf{r},t)\,e^2}{m_e}. \tag{55}$$

In the absence of external charges (53) now gives the general dispersion relation [23]

$$\left(\omega^2 - \omega_p^2(\mathbf{r},t)\right)\phi(\mathbf{r},t) - \frac{e^2}{m_e}\int d\mathbf{r}' \phi(\mathbf{r}',t)\left(\nabla' \frac{1}{|\mathbf{r}-\mathbf{r}'|}\right) \cdot \nabla' n_0(\mathbf{r}',t) = 0. \tag{56}$$

This result is quite general, without any assumptions regarding the electron density profile $n_0(\mathbf{r},t)$. An expansion of $\phi(\mathbf{r},t)$ in spherical harmonics gives the various multipole excitations. In particular, for a profile with a sharp boundary the bulk and Mie plasmon excitations are recovered. Under nonequilibrium conditions the electron distribution may change with time leading to a time evolution of the density profile $n_0(\mathbf{r})$. Thus, equation (56) has to be solved together with the quantum kinetic equation for $\mathcal{F}(\mathbf{r},\mathbf{p},t;n_0)$.

7. Conclusions

The Klimontovich equation for the classical microscopic phase space density has been quantized for its corresponding operator equation for quantum mechanical applications. This is a suitable starting point to formulate a kinetic theory for its mean value (the Wigner function) as well as for correlation functions and fluctuations. The advantage of the exact Klimontovich equation is its structural simplicity, having the same form as the mean field approximation to its average. This complexity of the many-body problem is transferred to an analysis of averages, since the equation is nonlinear. It would be interesting to translate some of the simple approximations using the classical Klimontovich equation to the corresponding quantum case.

In this brief presentation no such detailed analysis of the fluctuations was possible. Instead, the Hartree-Fock contributions to the mean value kinetic equation were identified explicitly as a means to discuss collective excitations. The Klimontovich equation retains a classical language, being expressed in terms of the phase space variables of position and momentum. The valence electrons in metallic clusters are perhaps best described in this language, but clearly require a quantum treatment. In addition, the experimentally interesting case of probing such clusters with intense fields poses the problem of an inhomogeneous electron gas possibly driven far from equilibrium. The basis for a kinetic theory applicable to this problem follows quite simply from the Klimontovich equation, as illustrated here. In particular, the effects of spatial confinement on the collective excitations was presented as a non-trivial application.

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Appendix A. Second Quantization Representation

Consider the first form of the Weyl quantization given by Eq. (8)

$$\widehat{f}\left(\mathbf{r},\mathbf{p},t\right)=e^{i\frac{1}{2}\hbar\nabla_{\mathbf{r}}\cdot\nabla_{\mathbf{p}}}\sum_{\alpha=1}^{N}\delta\left[\mathbf{r}-\widehat{\mathbf{r}}_{\alpha}(t)\right]\delta\left[\mathbf{p}-\widehat{\mathbf{p}}_{\alpha}(t)\right]. \tag{A.1}$$

The second quantized form of this operator is

$$\begin{aligned}\sum_{\alpha=1}^{N}\delta\left(\mathbf{r}-\widehat{\mathbf{r}}_{\alpha}\right)\delta\left(\mathbf{p}-\widehat{\mathbf{p}}_{\alpha}\right) &= \int d\mathbf{r}_1 d\mathbf{r}_2\,\psi^{\dagger}\left(\mathbf{r}_1,t\right)\psi\left(\mathbf{r}_2,t\right)\left\langle\mathbf{r}_1\right|\delta\left(\mathbf{r}-\widehat{\mathbf{r}}_{\alpha}\right)\delta\left(\mathbf{p}-\widehat{\mathbf{p}}_{\alpha}\right)\left|\mathbf{r}_2\right\rangle\\ &= \sum_{\mathbf{p}'}\int d\mathbf{r}_1 d\mathbf{r}_2\,\psi^{\dagger}\left(\mathbf{r},t\right)\psi\left(\mathbf{r}_2,t\right)\delta\left(\mathbf{r}-\mathbf{r}_1\right)\left\langle\mathbf{r}|\mathbf{p}'\right\rangle\delta\left(\mathbf{p}-\mathbf{p}'\right)\left\langle\mathbf{p}'|\mathbf{r}_2\right\rangle\\ &= \frac{1}{\left(2\pi\hbar\right)^3}\int d\mathbf{r}_2\,e^{-\frac{i}{\hbar}\left(\mathbf{r}-\mathbf{r}_2\right)\cdot\mathbf{p}}\,\psi^{\dagger}\left(\mathbf{r},t\right)\psi\left(\mathbf{r}_2,t\right). \end{aligned}\tag{A.2}$$

Consequently

$$\begin{aligned}\widehat{f}\left(\mathbf{r},\mathbf{p},t\right) &= e^{i\frac{1}{2}\hbar\nabla_{\mathbf{r}}\cdot\nabla_{\mathbf{p}}}\frac{1}{\left(2\pi\hbar\right)^3}\int d\mathbf{x}\,e^{\frac{i}{\hbar}\mathbf{x}\cdot\mathbf{p}}\,\psi^{\dagger}\left(\mathbf{r},t\right)\psi\left(\mathbf{r}+\mathbf{x},t\right)\\ &= \frac{1}{\left(2\pi\hbar\right)^3}\int d\mathbf{x}\,\psi^{\dagger}\left(\mathbf{r}+i\frac{1}{2}\hbar\nabla_{\mathbf{p}},t\right)\psi\left(\mathbf{r}+i\frac{1}{2}\hbar\nabla_{\mathbf{p}}+\mathbf{r}_2,t\right)e^{\frac{i}{\hbar}\mathbf{x}\cdot\mathbf{p}}\\ &= \frac{1}{\left(2\pi\hbar\right)^3}\int d\mathbf{x}\,e^{\frac{i}{\hbar}\mathbf{x}\cdot\mathbf{p}}\psi^{\dagger}\left(\mathbf{r}-\frac{1}{2}\mathbf{x},t\right)\psi\left(\mathbf{r}+\frac{1}{2}\mathbf{x},t\right), \end{aligned}\tag{A.3}$$

which is the result (13) quoted in the text.

The result (A.3) can be inverted to give the operator of the density fluctuation

$$\psi^{\dagger}(\mathbf{r}_1,t)\,\psi(\mathbf{r}_2,t)=\int d\mathbf{p}\,e^{\frac{i}{\hbar}(\mathbf{r}_1-\mathbf{r}_2)\cdot\mathbf{p}}\,\widehat{f}\left(\frac{\mathbf{r}_1+\mathbf{r}_2}{2},\mathbf{p},t\right). \tag{A.4}$$

This expression is used in Appendix C to identify the Hartree-Fock approximation.

Appendix B. Alternative form of Klimontovich Equation

The operator valued Klimontovich equation given by Eq. (14) is formal due to the differential operators occurring on the right side. An alternative, equivalent form is obtained by rewriting

$$\begin{aligned}
&\sin\left(\frac{\hbar}{2}\nabla_{\mathbf{r}}\cdot\nabla_{\mathbf{p}}\,V(\mathbf{r}-\mathbf{r}')\right)\widehat{f}(\mathbf{r},\mathbf{p},t)=\mathrm{Im}\exp\left(i\frac{\hbar}{2}\nabla_{\mathbf{r}}\cdot\nabla_{\mathbf{p}}\right)V(\mathbf{r}-\mathbf{r}')\,\widehat{f}(\mathbf{r},\mathbf{p},t)\\
=\;&\mathrm{Im}V\left(\mathbf{r}+i\frac{\hbar}{2}\nabla_{\mathbf{p}}-\mathbf{r}'\right)\widehat{f}(\mathbf{r},\mathbf{p},t)\\
=\;&\mathrm{Im}\,(2\pi\hbar)^{-3}\int d\mathbf{p}'\,\widetilde{V}(p')\exp\left\{-\frac{i}{\hbar}\left(\mathbf{r}+i\frac{\hbar}{2}\nabla_{\mathbf{p}}-\mathbf{r}'\right)\cdot\mathbf{p}'\right\}\widehat{f}(\mathbf{r},\mathbf{p},t)\\
=\;&(2\pi\hbar)^{-3}\int d\mathbf{p}'d\mathbf{r}_1\,V(\mathbf{r}_1)\sin\frac{2\,(\mathbf{r}_1-\mathbf{r}+\mathbf{r}')\cdot\mathbf{p}'}{\hbar}\,\widehat{f}(\mathbf{r},\mathbf{p}+\mathbf{p}',t)\\
=\;&(2\pi\hbar)^{-3}\int d\mathbf{p}'d\mathbf{r}_1\,V\left(\frac{1}{2}\mathbf{r}_1+\mathbf{r}-\mathbf{r}'\right)\sin\frac{\mathbf{r}_1\cdot(\mathbf{p}'-\mathbf{p})}{\hbar}\,\widehat{f}(\mathbf{r},\mathbf{p}',t)\,.
\end{aligned}$$

With this result (14) becomes

$$\left(\partial_t+\frac{1}{m}\mathbf{p}\cdot\nabla\right)\widehat{f}(\mathbf{r},\mathbf{p},t)=\int d\mathbf{r}'d\mathbf{p}'d\mathbf{p}''\,K_c(\mathbf{r}-\mathbf{r}',\mathbf{p}-\mathbf{p}'')\widehat{f}(\mathbf{r}',\mathbf{p}',t)\,\widehat{f}(\mathbf{r},\mathbf{p}'',t)\,, \tag{B.1}$$

where the kernel $K_c(\mathbf{r},\mathbf{p})$ is

$$K_c(\mathbf{r},\mathbf{p})=\frac{2}{\hbar}\,(2\pi\hbar)^{-3}\int d\mathbf{r}_1 V\left(\frac{1}{2}\mathbf{r}_1+\mathbf{r}\right)\sin\left(\frac{\mathbf{r}_1\cdot\mathbf{p}}{\hbar}\right). \tag{B.2}$$

Appendix C. Hartree - Fock Approximation

The required two point function in second quantized form is

$$\begin{aligned}
&\left\langle\widehat{f}(\mathbf{r}_1,\mathbf{p}_1,t)\,\widehat{f}(\mathbf{r}_2,\mathbf{p}_2,t)\right\rangle=(2\pi\hbar)^{-6}\int d\mathbf{x}\,e^{\frac{i}{\hbar}\mathbf{x}\cdot\mathbf{p}_1}\int d\mathbf{x}'\,e^{\frac{i}{\hbar}\mathbf{x}'\cdot\mathbf{p}_2}\\
&\times\left\langle\psi^{\dagger}\left(\mathbf{r}_1-\frac{1}{2}\mathbf{x},t\right)\psi\left(\mathbf{r}_1+\frac{1}{2}\mathbf{x},t\right)\psi^{\dagger}\left(\mathbf{r}_2-\frac{1}{2}\mathbf{x}',t\right)\psi\left(\mathbf{r}_2+\frac{1}{2}\mathbf{x}',t\right)\right\rangle,
\end{aligned} \tag{C.1}$$

where (A.3) has been used. The Hartree-Fock approximation is therefore

$$\begin{aligned}
&\left\langle\psi^{\dagger}\left(\mathbf{r}_1-\frac{1}{2}\mathbf{x}\right)\psi\left(\mathbf{r}_1+\frac{1}{2}\mathbf{x}\right)\psi^{\dagger}\left(\mathbf{r}_2-\frac{1}{2}\mathbf{x}'\right)\psi\left(\mathbf{r}_2+\frac{1}{2}\mathbf{x}'\right)\right\rangle\\
\longrightarrow\;&\left\langle\psi^{\dagger}\left(\mathbf{r}_1-\frac{1}{2}\mathbf{x}\right)\psi\left(\mathbf{r}_1+\frac{1}{2}\mathbf{x}\right)\right\rangle\left\langle\psi^{\dagger}\left(\mathbf{r}_2-\frac{1}{2}\mathbf{x}'\right)\psi\left(\mathbf{r}_2+\frac{1}{2}\mathbf{x}'\right)\right\rangle\\
&\pm\left\langle\psi^{\dagger}\left(\mathbf{r}_1-\frac{1}{2}\mathbf{x}\right)\psi\left(\mathbf{r}_2+\frac{1}{2}\mathbf{x}'\right)\right\rangle\left\langle\psi^{\dagger}\left(\mathbf{r}_2-\frac{1}{2}\mathbf{x}'\right)\psi\left(\mathbf{r}_1+\frac{1}{2}\mathbf{x}\right)\right\rangle,
\end{aligned} \tag{C.2}$$

where the plus (minus) sign refers to bosons (fermions). Substitution into (C.1) and use of (A.4) gives the Klimontovich form of the Hartree-Fock approximation. In the gauge invariant representation it is

$$\left\langle \widehat{\mathcal{F}}\left(\mathbf{r}_1,\mathbf{p}_1,t\right)\widehat{\mathcal{F}}\left(\mathbf{r}_2,\mathbf{p}_2,t\right)\right\rangle = \mathcal{F}\left(\mathbf{r}_1,\mathbf{p}_1,t\right)\mathcal{F}\left(\mathbf{r}_2,\mathbf{p}_2,t\right)$$
$$\pm\left(2\pi\hbar\right)^{-3}\int d\mathbf{Y}\int d\mathbf{p}_3 d\mathbf{p}_4\,\delta\left(\mathbf{p}_1+\mathbf{p}_2-\mathbf{p}_3-\mathbf{p}_4\right)e^{\frac{i}{2\hbar}\mathbf{Y}\cdot\left(\mathbf{p}_2-\mathbf{p}_1\right)}e^{\frac{i}{\hbar}\left(\mathbf{r}_1-\mathbf{r}_2\right)\cdot\left(\mathbf{p}_3-\mathbf{p}_4\right)}$$
$$\times\mathcal{F}\left(\frac{\mathbf{r}_1+\mathbf{r}_2}{2}-\frac{1}{4}\mathbf{Y},\mathbf{p}_3,t\right)\mathcal{F}\left(\frac{\mathbf{r}_1+\mathbf{r}_2}{2}+\frac{1}{4}\mathbf{Y},\mathbf{p}_4,t\right). \tag{C.3}$$

The first term on the right is the Hartree approximation, and the second gives the Fock contributions.

The Hartree-Fock contributions to the kinetic equation are

$$I^H\left(\mathbf{r},\mathbf{p},t;\mathcal{F}\right)=\int d\mathbf{r}'d\mathbf{p}'d\mathbf{p}''\,K_c(\mathbf{r}-\mathbf{r}',\mathbf{p}-\mathbf{p}'')\mathcal{F}\left(\mathbf{r}',\mathbf{p}',t\right)\mathcal{F}\left(\mathbf{r},\mathbf{p}'',t\right), \tag{C.4}$$

$$I^F\left(\mathbf{r},\mathbf{p},t;\mathcal{F}\right)=\int d\mathbf{r}_1d\mathbf{r}_2d\mathbf{p}_1d\mathbf{p}_2\,G(\mathbf{r}_1-\mathbf{r},\mathbf{r}_2-\mathbf{r},\mathbf{p}_1-\mathbf{p},\mathbf{p}_2-\mathbf{p})\mathcal{F}\left(\mathbf{r}_1,\mathbf{p}_1,t\right)\mathcal{F}\left(\mathbf{r}_2,\mathbf{p}_2,t\right). \tag{C.5}$$

with

$$G(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)=\pm e^{\frac{i}{\hbar}(\mathbf{r}_1+\mathbf{r}_2)\cdot(\mathbf{p}_1-\mathbf{p}_2)}e^{-\frac{i}{\hbar}(\mathbf{p}_1+\mathbf{p}_2)\cdot(\mathbf{r}_1-\mathbf{r}_2)}\left(\frac{2}{\hbar\pi}\right)^3\int d\mathbf{p}'\,K_c(-\mathbf{r}_1-\mathbf{r}_2,\mathbf{p}')e^{2\frac{i}{\hbar}(\mathbf{r}_2-\mathbf{r}_1)\cdot\mathbf{p}'}. \tag{C.6}$$

Appendix D. Solution to the Linear Kinetic Equation

The Fourier-Laplace transform of Eq. (44) is

$$\left(z+\frac{1}{m}i\mathbf{k}\cdot\mathbf{p}-I_0\right)\delta\widetilde{\mathcal{F}}\left(\mathbf{k},\mathbf{p},z\right) - \int d\mathbf{r}\,e^{i\mathbf{k}\cdot\mathbf{r}}\int d\mathbf{p}'\,K_1(\mathbf{r},\mathbf{p}-\mathbf{p}';\delta\mathcal{F})\mathcal{F}_0\left(\mathbf{r},\mathbf{p}'\right)$$
$$= \delta\widetilde{\mathcal{F}}\left(\mathbf{k},\mathbf{p},t=0\right)-\frac{e}{c}\mathbf{E}_z\cdot\nabla_{\mathbf{p}}\int d\mathbf{r}\,e^{i\mathbf{k}\cdot\mathbf{r}}\mathcal{F}_0\left(\mathbf{r},\mathbf{p}\right). \tag{D.1}$$

The second term on the left side can be simplified to

$$\int d\mathbf{r}\,e^{i\mathbf{k}\cdot\mathbf{r}}\int d\mathbf{p}'\,K_1(\mathbf{r},\mathbf{p}-\mathbf{p}';\delta\mathcal{F})\mathcal{F}_0\left(\mathbf{r},\mathbf{p}',t\right)=\frac{1}{i\hbar}\left(2\pi\right)^{-3}\int d\mathbf{k}_2\,\delta\widetilde{n}\left(\mathbf{k}_2,z\right)\widetilde{V}\left(k_2\right)$$
$$\times\int d\mathbf{r}\,e^{i(\mathbf{k}-\mathbf{k_2})\cdot\mathbf{r}}\left\{\mathcal{F}_0\left(\mathbf{r},\mathbf{p}+\frac{1}{2}\hbar\mathbf{k}_2,t\right)-\mathcal{F}_0\left(\mathbf{r},\mathbf{p}-\frac{1}{2}\hbar\mathbf{k}_2,t\right)\right\}. \tag{D.2}$$

For consistency, the dominant space dependence of $\mathcal{F}_0\left(\mathbf{r},\mathbf{p}\right)$ is assumed to occur through the density field n_0. Since the spatial transform is taken with n_0 held constant, we have

$$\int d\mathbf{r}\,e^{i\mathbf{k}\cdot\mathbf{r}}\mathcal{F}_0\left(\mathbf{r},\mathbf{p}\right)\approx\left(2\pi\right)^3\delta\left(\mathbf{k}\right)\mathcal{F}_0\left(\mathbf{r},\mathbf{p}\right). \tag{D.3}$$

and (D.2) becomes

$$\int d\mathbf{r}\,e^{i\mathbf{k}\cdot\mathbf{r}}\int d\mathbf{p}'\,K_1(\mathbf{r},\mathbf{p}-\mathbf{p}';\delta\mathcal{F})\mathcal{F}_0\left(\mathbf{r},\mathbf{p}',t\right)$$
$$\approx \delta\widetilde{n}\left(\mathbf{k},z\right)\widetilde{V}\left(k\right)\frac{1}{i\hbar}\left\{\mathcal{F}_0\left(\mathbf{r},\mathbf{p}+\frac{1}{2}\hbar\mathbf{k},t\right)-\mathcal{F}_0\left(\mathbf{r},\mathbf{p}-\frac{1}{2}\hbar\mathbf{k},t\right)\right\}, \tag{D.4}$$

and the formal solution to the kinetic equation reads

$$\begin{aligned}\delta\widetilde{\mathcal{F}}\left(\mathbf{k},\mathbf{p},z\right) &= \delta\widetilde{n}\left(\mathbf{k},z\right)\widetilde{V}\left(k\right)\left(z+\frac{1}{m}i\mathbf{k}\cdot\mathbf{p}-I_0\right)^{-1} \\ &\times\left\{\frac{1}{i\hbar}\left[\mathcal{F}_0\left(\mathbf{r},\mathbf{p}+\frac{1}{2}\hbar\mathbf{k}\right)-\mathcal{F}_0\left(\mathbf{r},\mathbf{p}-\frac{1}{2}\hbar\mathbf{k}\right)\right]\right. \qquad \text{(D.5)} \\ &\left.+\delta\widetilde{\mathcal{F}}\left(\mathbf{k},\mathbf{p},t=0\right)-\frac{e}{c}\left(2\pi\right)^3\delta\left(\mathbf{k}\right)\widetilde{\mathbf{E}}_z\cdot\nabla_{\mathbf{p}}\mathcal{F}_0\left(\mathbf{r},\mathbf{p}\right)\right\}. \qquad \text{(D.6)}\end{aligned}$$

Integrating this over $\mathbf{p}$ allows explicit solution for the Fourier-Laplace transformed density

$$\begin{aligned}\delta\widetilde{n}\left(\mathbf{k},z\right) &= \epsilon^{-1}\left(z,\mathbf{k};\mathbf{r}\right)\int d\mathbf{p}\left(z+\frac{1}{m}i\mathbf{k}\cdot\mathbf{p}-I_0\right)^{-1}\left\{\delta\widetilde{\mathcal{F}}\left(\mathbf{k},\mathbf{p},t=0\right)\right. \\ &\left.-\frac{e}{c}\left(2\pi\right)^3\delta\left(\mathbf{k}\right)\widetilde{\mathbf{E}}_z\cdot\nabla_{\mathbf{p}}\mathcal{F}_0\left(\mathbf{r},\mathbf{p}\right)\right\}. \qquad \text{(D.7)}\end{aligned}$$

The dielectric function $\epsilon\left(z,\mathbf{k};\mathbf{r}\right)$ is given in terms of the polarization function $\Pi\left(z,\mathbf{k};\mathbf{r}\right)$

$$\epsilon\left(z,\mathbf{k};\mathbf{r}\right)=1-\widetilde{V}\left(k\right)\Pi\left(z,\mathbf{k};\mathbf{r}\right), \qquad \text{(D.8)}$$

where

$$\Pi\left(z,\mathbf{k};\mathbf{r}\right)=\int d\mathbf{p}\left(z+\frac{1}{m}i\mathbf{k}\cdot\mathbf{p}-I_0\right)^{-1}\frac{i}{\hbar}\left(\mathcal{F}_0\left(\mathbf{r},\mathbf{p}+\frac{1}{2}\hbar\mathbf{k},t\right)-\mathcal{F}_0\left(\mathbf{r},\mathbf{p}-\frac{1}{2}\hbar\mathbf{k},t\right)\right). \qquad \text{(D.9)}$$

Finally, substitution of (D.7) into (D.6) gives the solution to the kinetic equation.

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