Kinetic theory for strongly coupled Coulomb systems

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The calculation of dynamical properties for matter under extreme conditions is a challenging task. The popular Kubo-Greenwood model exploits elements from equilibrium density-functional theory (DFT) that allow a detailed treatment of electron correlations, but its origin is largely phenomenological; traditional kinetic theories have a more secure foundation but are limited to weak ion-electron interactions. The objective here is to show how a combination of the two evolves naturally from the short-time limit for the generator of the effective single-electron dynamics governing time correlation functions without such limitations. This provides a theoretical context for the current DFT-related approach, the Kubo-Greenwood model, while showing the nature of its corrections. The method is to calculate the short-time dynamics in the single-electron subspace for a given configuration of the ions. This differs from the usual kinetic theory approach in which an average over the ions is performed as well. In this way the effective ion-electron interaction includes strong Coulomb coupling and is shown to be determined from DFT. The correlation functions have the form of the random-phase approximation for an inhomogeneous system but with renormalized ion-electron and electron-electron potentials. The dynamic structure function, density response function, and electrical conductivity are calculated as examples. The static local field corrections in the dielectric function are identified in this way. The current analysis is limited to semiclassical electrons (quantum statistical potentials), so important quantum conditions are excluded. However, a quantization of the kinetic theory is identified for broader application while awaiting its detailed derivation.

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I. INTRODUCTION

Recent interest in matter under extreme conditions (e.g., high-pressure materials, warm dense matter, and high-temperature plasmas) has been stimulated in part by new experimental access to such states [1]. Thermodynamic properties can be addressed in a controlled way by finite-temperature density-functional theory (DFT) for the electrons [2] in conjunction with *ab initio* molecular dynamics (AIMD) for the ions [3]. The two tools of DFT and MD are appropriate for such states since strong coupling and bound states can be treated with well-developed approximations. Dynamical phenomena are more problematical, particularly for the electrons which require quantum dynamics in general. Current many-body theories of condensed matter physics or plasma physics have questionable applicability. Kinetic theories, classical or quantum, are typically limited to free electrons and weak ion-electron correlations. Models which utilize DFT quantities (such as the Kubo-Greenwood model [4] below) remove this restriction at the price of phenomenology and unknown context. The objective here is to demonstrate a kinetic theory for electrons in a given configuration of ions, obtained in a limit that incorporates the DFT model and well-known many-body effects of electron dynamics. The derivation is semiclassical but makes no explicit restrictions regarding coupling among the ions and electrons or bound and free electron states.

The system of interest here is that of electrons in equilibrium with a frozen disordered configuration of ions in the grand-canonical ensemble. In applications, properties for this system are found by averaging over different ionic configurations. The properties of interest are time correlation functions that determine transport coefficients, scattering cross sections, and other equilibrium dynamic electron fluctuations of linear response. The state conditions include possible strong coupling and other effects of correlations such as dynamical fluctuations. These are the types of difficult cases that are handled well by DFT for thermodynamic calculations, and it is tempting to think (hope) that such detailed information can be exploited somehow for the analysis of dynamics as well. A practical implementation of this idea, the Kubo-Greenwood model (KG) [4], is obtained by replacing the many-body electron-ion Hamiltonian by a sum of single-particle Hamiltonians. Though in principle arbitrary, invariably they are chosen to be noninteracting particles governed by the Kohn-Sham potential which includes the external ion field. This potential appears in the variational Euler equation of DFT and is determined from the exchange-correlation free energy as a functional of the equilibrium density [2]. In the KG model the Kohn-Sham Hamiltonian, originally defined to determine the equilibrium density, is promoted to a generator for the dynamics. Furthermore, it is assumed to represent in a mean-field way the effects of the true Coulomb interactions which it replaces. The origin of this picture of Kohn-Sham quasiparticles and the conditions for its validity have not been established. Doing so is a primary objective of the present work.

In earlier work the authors considered time correlation functions for a semiclassical electron gas in the presence of a single fixed ion and derived a kinetic equation whose form is obtained from the short-time limit [5]. It has a single-particle dynamics with a "renormalized" external potential

from the electron-ion interaction. In addition, there is a collective Vlasov (random-phase approximation) dynamics with a renormalized electron-electron interaction. Both of these effective interactions are determined from derivatives of the semiclassical exchange-correlation free energy. In particular, the electron-ion interaction is precisely the Kohn-Sham potential of the KG model. Here, that description is extended to time correlation functions for electrons in a disordered many-ion background with configurations sampled from an equilibrium ensemble. An important distinguishing feature of this kinetic equation relative to others is that only electron degrees of freedom are averaged out to define the single-electron subspace. No ion average is performed. This allows a detailed description of the average electron interaction with each ion, setting the framework for connection with DFT. A brief summary of these ideas is given in Ref. [6].

The reduction of the generator for the dynamics at short times to a practical form at present has been established only for semiclassical electrons. Thus strong degeneracy and other extreme quantum effects are not captured in the analysis here. This limits the conditions for applicability, as described briefly in Sec. VI. However, the primary objective here is to show by example how the many-body problem can be controlled and to indicate a pathway to the basis for the KG model. In Sec. V a straightforward quantization of this semiclassical result is given as a temporary "placeholder" for the detailed quantum derivation paralleling that given here.

In the next section, the time correlation functions and their representation in terms of linear kinetic theory are introduced. The formal definition of the generator for the electron dynamics in the single-electron subspace is defined. While generally time dependent, its form is evaluated at $t = 0$ in Appendix A. No limitations are placed on the strength of correlations or coupling. This gives a Markov dynamics for the time correlation functions in which the generator is taken to have the same form at later times as well. The result has the structure of a kinetic theory in the random-phase approximation, extended to an inhomogeneous system due to the external forces of the ions. However, that force is renormalized to be derived from the Kohn-Sham potential (the ion field plus the first functional derivative of the excess free energy), and the electron-electron Coulomb potential is renormalized to the electron-electron direct correlation function (second functional derivative of the excess free energy). As illustrations, the dynamical structure function, density response function, and frequency-dependent electrical conductivity are determined from this kinetic equation. The dielectric function is considered, and the associated static local field corrections are identified. In the last section these results are summarized and discussed.

II. TIME CORRELATION FUNCTIONS FROM KINETIC THEORY

Consider a system of N_e electrons in equilibrium with N_i fixed ions. The Hamiltonian is

$$H = \sum_{\alpha=1}^{N_e}\left[\frac{1}{2}mv_\alpha^2 + V_{ei}(\mathbf{r}_\alpha,\{\mathbf{R}\})\right] + \frac{1}{2}\sum_{\alpha\neq\gamma=1}^{N_e} V_{ee}(r_{\alpha\gamma}), \quad (1)$$

where the interaction potential for the electrons with the N_i fixed ions is

$$V_{ei}(\mathbf{r}_\alpha,\{\mathbf{R}\}) \equiv \sum_{\gamma=1}^{N_i} V_{ei}(|\mathbf{r}_\alpha - \mathbf{R}_\gamma|). \quad (2)$$

The notation $\{\mathbf{R}\}$ denotes a dependence on the collection of N_i fixed ion coordinates $\mathbf{R}_\gamma$. Also, $\mathbf{r}_\alpha$ and $\mathbf{v}_\alpha$ are the position and velocity of electron α. In the quantum case all interactions are pure Coulomb. However, the analysis below is entirely within classical mechanics for both ions and electrons. Residual quantum effects must be retained to prevent collapse due to the electron-ion singularity at zero separation. In the quantum case such collapse is avoided due to diffraction effects. These can be accounted for in the classical representation by regularizing the Coulomb potential within a distance of the order of the thermal de Broglie wavelength. Similar effects occur for the electron-electron interaction, which also has an additional effect due to Pauli exclusion. The use of such modified potentials has a long history, leading to many different forms originating from different contexts for their derivation [7]. The resulting classical representation allows MD simulation of opposite charge components. One of the first was an application to hydrogen plasmas [8]; a more recent simulation in the current context is that of Refs. [9,10]. The specific forms, or their limitations, are not central to the discussion here. Instead, the objective is to demonstrate how the many-body physics can be analyzed in a controlled way to make contact with current phenomenology and to clarify its context.

The equilibrium time correlation functions for two observables A and B in the grand-canonical ensemble are

$$\langle A(t)\delta B;\{\mathbf{R}\}\rangle = \sum_{N_e}\int d\{x\}\rho_e(\{\mathbf{R}\},\{x\})A(t,\{\mathbf{R}\},\{x\})\delta B(\{\mathbf{R}\},\{x\}), \quad (3)$$

$$\rho_e(\{\mathbf{R}\},\{x\}) = e^{\beta\Omega(\{\mathbf{R}\})}e^{-\beta(H(\{\mathbf{R}\},\{x\})-\mu)}, \quad (4)$$

where $\delta B = (B - \langle B\rangle)$. The set of phase variables $\{x\} = \{x_1,\ldots,x_{N_e}\}$ denote the positions and velocities of each electron, e.g., $x_1 \Longleftrightarrow \mathbf{r}_1,\mathbf{v}_1$. The passive dependence on the ion coordinates has been made explicit here but will be suppressed in the following for simplicity of notation, except where needed.

The time dependence of $A(t,\{x\})$ is generated by the Hamiltonian (1) from the initial value $A(\{x\})$. The phase functions $A(\{x\})$ and $B(\{x\})$ denote some observables of interest, composed of sums of single-particle functions

$$A = \sum_{\alpha=1}^{N_e} a(x_\alpha), \quad B = \sum_{\alpha=1}^{N_e} b(x_\alpha). \quad (5)$$

The special form (5) allows reduction of the N_e electron average to a corresponding average in the single-electron subspace by partial integration over $N_e - 1$ degrees of freedom (see Appendix A),

$$\langle A(t)\delta B\rangle = \int dx n(\mathbf{r})\phi(v)a(x)\overline{b}(x,t). \quad (6)$$

Here $n(\mathbf{r})$ is the equilibrium number density for electrons at a position $\mathbf{r}$, and $\phi(v)$ is the Maxwell-Boltzmann velocity

distribution. The function $\bar{b}(x,t)$ is

$$\bar{b}(x,t) = \frac{1}{n(\mathbf{r})\phi(v)} \int dx' G(x,x';t) b(x'), \tag{7}$$

where the phase-space density autocorrelation function is

$$G(x,x';t) = \langle f(x,t)(f(x') - \langle f(x')\rangle)\rangle,$$
$$f(x) = \sum_{\alpha=1}^{N_e} \delta(x - x_\alpha). \tag{8}$$

The time derivative of $\bar{b}(x,t)$ is

$$\partial_t \bar{b}(x,t) = \frac{1}{n(\mathbf{r})\phi(v)} \int dx' \partial_t G(x,x';t) b(x'). \tag{9}$$

Both (7) and (8) are linear maps of $b(x')$. Eliminating the latter gives the formal kinetic equation in the single-particle phase space

$$\partial_t \bar{b}(x,t) + \int dx' L(x,x';t) \bar{b}(x',t) = 0, \tag{10}$$

with

$$L(x,x';t) \equiv -\frac{1}{n(\mathbf{r})\phi(v)} \int dx''(\partial_t G(x,x'';t)) \times G^{-1}(x'',x';t) n(\mathbf{r}')\phi(v'). \tag{11}$$

The initial value for this equation is

$$\bar{b}(x,0) = \bar{b}(x) = b(x) + \int dx' n(\mathbf{r}')\phi(v')(g(\mathbf{r},\mathbf{r}') - 1) b(x'), \tag{12}$$

and $g(\mathbf{r},\mathbf{r}')$ is the pair correlation function for two electrons at $\mathbf{r}$ and $\mathbf{r}'$ in the presence of the ion configuration $\{\mathbf{R}\}$. Note that the equation is inherently linear. An elaboration of this approach to time correlation functions via a formal linear kinetic theory is given in Ref. [11].

III. MARKOVIAN KINETIC EQUATION AND ITS RELATION TO DFT

The generator of dynamics, $L(x,x';t)$, is an appropriate point for the introduction of approximations. Typically, matter under extreme conditions does not admit any small parameter expansions because the treatment must include possible strong Coulomb coupling. Here, a Markov approximation is chosen that does not prejudice such conditions. Furthermore there is no scattering context so that the electrons may be free or bound to the ions. A Markov kinetic equation has a generator whose form does not change in time. Hence, a practical expression can be determined from $L(x,x';t=0)$ and assumed to hold as well for all later times. One of the first developments of this idea for classical time correlation functions was given by Lebowitz, Percus, and Sykes [12] and for the quantum case by Boercker and Dufty [11]. The primary difference here is the presence of the external forces due to the ions. The analysis follows that of Ref. [5], and the details are given in Appendix B with the resulting kinetic equation,

$$(\partial_t + \mathbf{v}\cdot\nabla_\mathbf{r} - m^{-1}\nabla_\mathbf{r}\mathcal{V}_{ie}(\mathbf{r})\cdot\nabla_\mathbf{v})\bar{b}(x,t) = -\mathbf{v}\cdot\nabla_\mathbf{r}\beta \int dx' \mathcal{V}_{ee}(\mathbf{r},\mathbf{r}')\phi(v')n(\mathbf{r}')\bar{b}(x',t). \tag{13}$$

To understand this result, note that if $\mathcal{V}_{ie}$ and $\mathcal{V}_{ee}$ were their (regularized) Coulomb interactions, then (13) would be the random-phase approximation in the presence of the external ion potential. Here, however, those potentials have been renormalized by the initial equilibrium correlations. The left-hand side of (13) describes single-particle motion in an external renormalized ion-electron potential $\mathcal{V}_{ie}(r)$,

$$\mathcal{V}_{ie}(\mathbf{r},\{\mathbf{R}\}) \equiv -\beta^{-1}\ln n(\mathbf{r},\{\mathbf{R}\}). \tag{14}$$

The right-hand side of (13) describes dynamical correlations for this single-particle motion with a renormalized electron-electron potential,

$$\mathcal{V}_{ee}(\mathbf{r},\mathbf{r}',\{\mathbf{R}\}) = -\beta^{-1}c(\mathbf{r},\mathbf{r}',\{\mathbf{R}\}). \tag{15}$$

Here $c(\mathbf{r},\mathbf{r}',\{\mathbf{R}\})$ is the electron direct correlation function determined in terms of $g(\mathbf{r},\mathbf{r}',\{\mathbf{R}\})$ through the Ornstein-Zernicke equation [Eq. (A13)] [13]. For weak coupling, (14) and (15) reduce to their Coulomb forms. The explicit dependence on $\{\mathbf{R}\}$ has been restored at this point to emphasize that the electron subsystem is nonuniform due to the presence of the ions.

These renormalizations are due to static correlations of the equilibrium ensemble and provide the desired connection to DFT. To see this, note that the electron system is an inhomogeneous electron gas due to the presence of the ions. The associated equilibrium free energy F is a functional of the corresponding inhomogeneous density and is traditionally separated into a noninteracting part, $F^{(0)}$, and an interacting part, $F^{(1)}$,

$$F(\beta \mid n) = F^{(0)}(\beta \mid n) + F^{(1)}(\beta \mid n). \tag{16}$$

The equilibrium density for evaluation of these functionals is determined from the ion-electron potential by

$$\frac{\delta F(\beta \mid n)}{\delta n(\mathbf{r},\{\mathbf{R}\})} = \mu - V_{ei}(\mathbf{r},\{\mathbf{R}\}), \tag{17}$$

with $V_{ei}(\mathbf{r},\{\mathbf{R}\})$ given by (2). Equation (17) can be rearranged as

$$\frac{\delta F^{(0)}(\beta \mid n)}{\delta n(\mathbf{r},\{\mathbf{R}\})} = \mu - v_{\mathrm{KS}}(\mathbf{r},\{\mathbf{R}\}), \tag{18}$$

where $v_{\mathrm{KS}}(\mathbf{r},\{\mathbf{R}\})$ is known in DFT as the Kohn-Sham potential

$$v_{\mathrm{KS}}(\mathbf{r},\{\mathbf{R}\}) \equiv V_{ei}(\mathbf{r},\{\mathbf{R}\}) + \frac{\delta F^{(1)}(\beta \mid n)}{\delta n(\mathbf{r},\{\mathbf{R}\})}. \tag{19}$$

Furthermore, $F^{(0)}(\beta \mid n)$ can be evaluated for the classical system considered here to give

$$\frac{\delta F^{(0)}(\beta \mid n)}{\delta n(\mathbf{r},\{\mathbf{R}\})} = \beta^{-1}\ln n(\mathbf{r},\{\mathbf{R}\}). \tag{20}$$

Consequently, the renormalized ion-electron potential (14) becomes

$$\mathcal{V}_{ie}(\mathbf{r},\{\mathbf{R}\}) = -\frac{\delta F^{(0)}(\beta \mid n)}{\delta n(\mathbf{r},\{\mathbf{R}\})} = v_{\mathrm{KS}}(r,\{\mathbf{R}\}) - \mu. \tag{21}$$

With this identification it is instructive to write the kinetic equation (13) as

$$\partial_t \overline{b}(x,t) - \{h_{\rm KS}(x),\overline{b}(x,t)\} = \frac{1}{\phi(v)n(\mathbf{r})}\int dx'\{\mathcal{V}_{ee}(\mathbf{r},\mathbf{r}'),\phi(v)n(\mathbf{r})\phi(v')n(\mathbf{r}')\overline{b}(x',t)\}. \tag{22}$$

Here $\{,\}$ denotes the Poisson bracket and $h_{\rm KS}$ is the Kohn-Sham Hamiltonian,

$$h_{\rm KS}(x) = \tfrac{1}{2}mv^2 + v_{\rm KS}(\mathbf{r}). \tag{23}$$

As noted in the Introduction a common approximation for evaluating Green-Kubo time correlation expressions for transport coefficients is the replacement of the actual Hamiltonian with Coulomb interactions by a sum of single-particle Kohn-Sham Hamiltonians [4]. The resulting kinetic theory representation is the same as (22) with zero on the right-hand side. The semiclassical analysis here provides an important context for that approximation, justifying the introduction of the Kohn-Sham dynamics, and making the connection to DFT.

In addition, the renormalized electron-electron potential (15) is related to the excess free-energy functional by

$$\begin{aligned}\beta\mathcal{V}_{ee}(\mathbf{r},\mathbf{r}',\{\mathbf{R}\}) &= -c(\mathbf{r},\mathbf{r}',\{\mathbf{R}\})\\ &= \frac{\delta^2\beta F^{(1)}(\beta,\{\mathbf{R}\}\mid n)}{\delta n(\mathbf{r},\{\mathbf{R}\})\delta n(\mathbf{r}',\{\mathbf{R}\})}\\ &= \frac{\delta\beta v_{\rm KS}(\mathbf{r},\{\mathbf{R}\})}{\delta n(\mathbf{r}',\{\mathbf{R}\})}.\end{aligned} \tag{24}$$

Thus all of the input for the kinetic equation can be obtained from DFT, even for conditions of interest for strong coupling.

IV. DYNAMIC STRUCTURE, RESPONSE, AND CONDUCTIVITY

The correlation functions for the dynamic structure factor, density response function, and electrical conductivity are closely related. The dynamic structure factor is determined from the Fourier transform of the density-density time correlation function

$$C(\mathbf{r},\mathbf{r}',t) = \langle\widehat{n}(\mathbf{r},t)\delta\widehat{n}(\mathbf{r}')\rangle, \quad \widehat{n}(\mathbf{r}) = \sum_{\alpha=1}^{N_e}\delta(\mathbf{r}_\alpha - \mathbf{r}). \tag{25}$$

The density response function is proportional to its time derivative [14]

$$\chi(\mathbf{r},\mathbf{r}',t) = \beta\partial_t C(\mathbf{r},\mathbf{r}',t). \tag{26}$$

Finally, using the continuity equation

$$\partial_t\widehat{n}(\mathbf{r},t) + \nabla\cdot\widehat{\mathbf{j}}(\mathbf{r},t) = 0, \quad \widehat{\mathbf{j}}(\mathbf{r}) = \sum_{\alpha=1}^{N_e}\delta(\mathbf{r}_\alpha - \mathbf{r})\mathbf{v}_\alpha, \tag{27}$$

the response function is related to the current-current correlation function

$$\partial_t\chi(\mathbf{r},\mathbf{r}',t) = -\beta\langle\nabla\cdot\widehat{\mathbf{j}}(\mathbf{r},t)\nabla'\cdot\widehat{\mathbf{j}}(\mathbf{r}')\rangle, \tag{28}$$

which determines the electrical conductivity.

The general solution to the kinetic equation is given in Appendix C. When applied to $C(\mathbf{r},\mathbf{r}',t)$ and $\chi(\mathbf{r},\mathbf{r}',t)$ integral equations for each are obtained,

$$C(\mathbf{r},\mathbf{r}',t) = C_0(\mathbf{r},\mathbf{r}',t) + \int_0^t d\tau\int d\mathbf{r}''\chi_{\rm KG}(\mathbf{r},\mathbf{r}'',t-\tau) \times\int d\mathbf{r}'''\mathcal{V}_{ee}(\mathbf{r}'',\mathbf{r}''')C(\mathbf{r}''',\mathbf{r}',\tau) \tag{29}$$

and

$$\chi(\mathbf{r},\mathbf{r}',t) = \chi_{\rm KG}(\mathbf{r},\mathbf{r}',t) + \int_0^t d\tau\int d\mathbf{r}''\chi_{\rm KG}(\mathbf{r},\mathbf{r}'',t-\tau) \times\int d\mathbf{r}'''\mathcal{V}_{ee}(\mathbf{r}'',\mathbf{r}''')\chi(\mathbf{r}''',\mathbf{r}',\tau). \tag{30}$$

In each of these the noninteracting Kubo-Greenwood response function occurs,

$$\chi_{\rm KG}(\mathbf{r},\mathbf{r}',t-\tau) = -\beta\int d\mathbf{v}\phi(v)n(\mathbf{r})e^{-\mathcal{L}_{\rm KG}(t-\tau)}\mathbf{v}\cdot\nabla_{\mathbf{r}}\delta(\mathbf{r}-\mathbf{r}'). \tag{31}$$

Here $\mathcal{L}_{\rm KG}$ is the generator for the Kubo-Greenwood dynamics

$$\mathcal{L}_{\rm KG} \equiv \mathbf{v}\cdot\nabla_{\mathbf{r}} - m^{-1}\nabla_{\mathbf{r}}\mathcal{V}_{ie}(\mathbf{r})\cdot\nabla_{\mathbf{v}}. \tag{32}$$

The correlation function $C_0(\mathbf{r},\mathbf{r}',t)$ has the same dynamics but also the true initial conditions

$$C_0(\mathbf{r},\mathbf{r}',t) = \int d\mathbf{v}\phi(v)n(\mathbf{r})e^{-\mathcal{L}_{\rm KG}t}\{\delta(\mathbf{r}-\mathbf{r}') + n(\mathbf{r}')[g(\mathbf{r},\mathbf{r}')-1]\}. \tag{33}$$

The solutions to (29) and (30) are obtained by first taking their Laplace transforms,

$$\begin{aligned}\widetilde{C}(\mathbf{r},\mathbf{r}',z) &= \int_0^\infty d\tau e^{-zt}C(\mathbf{r},\mathbf{r}',t),\\ \widetilde{\chi}(\mathbf{r},\mathbf{r}',z) &= \int_0^\infty d\tau e^{-zt}\chi(\mathbf{r},\mathbf{r}',t).\end{aligned} \tag{34}$$

Then the solutions are

$$\widetilde{C}(\mathbf{r},\mathbf{r}',z) = \int d\mathbf{r}''\overline{\epsilon}^{-1}(\mathbf{r},\mathbf{r}'',z)\widetilde{C}_0(\mathbf{r}'',\mathbf{r}',z) \tag{35}$$

and

$$\widetilde{\chi}(\mathbf{r},\mathbf{r}',z) = \int d\mathbf{r}''\overline{\epsilon}^{-1}(\mathbf{r},\mathbf{r}'',z)\widetilde{\chi}_{\rm KG}(\mathbf{r}'',\mathbf{r}',z), \tag{36}$$

where $\overline{\epsilon}^{-1}(\mathbf{r},\mathbf{r}'',z)$ is the inverse function for

$$\overline{\epsilon}(\mathbf{r},\mathbf{r}',z) = \delta(\mathbf{r}-\mathbf{r}') - \int d\mathbf{r}''\widetilde{\chi}_{\rm KG}(\mathbf{r},\mathbf{r}'',z)\mathcal{V}_{ee}(\mathbf{r}'',\mathbf{r}'). \tag{37}$$

A. Dielectric function and local field corrections

The function $\overline{\epsilon}(\mathbf{r},\mathbf{r}',z)$ is closely related to the dielectric function defined by

$$\int d\mathbf{r}''V(\mathbf{r}-\mathbf{r}'')\widetilde{\chi}(\mathbf{r}'',\mathbf{r}',z) = \int d\mathbf{r}''\epsilon^{-1}(\mathbf{r},\mathbf{r}'',z)[\epsilon(\mathbf{r}'',\mathbf{r}',z) - \delta(\mathbf{r}''-\mathbf{r}')]. \tag{38}$$

It has the form

$$\epsilon(\mathbf{r},\mathbf{r}',z) = \delta(\mathbf{r}-\mathbf{r}') + \int d\mathbf{r}'' \int d\mathbf{r}''' V(\mathbf{r}-\mathbf{r}'')\chi_{\rm KG}(\mathbf{r}'',\mathbf{r}''',z) \times D^{-1}(\mathbf{r}''',\mathbf{r}',z) \quad (39)$$

with

$$D(\mathbf{r},\mathbf{r}',z) = \delta(\mathbf{r}-\mathbf{r}') - \int d\mathbf{r}'' \Delta(\mathbf{r},\mathbf{r}'',z)\chi_{\rm KG}(\mathbf{r}'',\mathbf{r}',z). \quad (40)$$

The leading term on the right side of (40) gives the random-phase approximation. The second term contains the "dynamic local field corrections" $\Delta(\mathbf{r},\mathbf{r}'',z)$. In the present case with $\widetilde{\chi}(\mathbf{r},\mathbf{r}',z)$ given by (36) the local field corrections $\Delta(\mathbf{r},\mathbf{r}',z)$ are found to be

$$\Delta(\mathbf{r},\mathbf{r}',z) \to \mathcal{V}_{ee}(\mathbf{r},\mathbf{r}') - V(\mathbf{r}-\mathbf{r}'). \quad (41)$$

These are the static field corrections due to correlations in the definition of $\mathcal{V}_{ee}(\mathbf{r},\mathbf{r}')$ [Eq. (24)],

$$\mathcal{V}_{ee}(\mathbf{r},\mathbf{r}') = -\beta^{-1}c(\mathbf{r},\mathbf{r}'\{\mathbf{R}\}) = \frac{\delta^2 F^{(1)}(\beta,\{\mathbf{R}\} \mid n)}{\delta n(\mathbf{r},\{\mathbf{R}\})\delta n(\mathbf{r}',\{\mathbf{R}\})}. \quad (42)$$

If the Hartree energy is subtracted from $F^{(1)}$, then the remainder is the exchange-correlation free energy F_{xc} and

$$\mathcal{V}_{ee}(\mathbf{r},\mathbf{r}') - V(\mathbf{r}-\mathbf{r}') = \frac{\delta^2 F_{xc}(\beta,\{\mathbf{R}\} \mid n)}{\delta n(\mathbf{r},\{\mathbf{R}\})\delta n(\mathbf{r}',\{\mathbf{R}\})}. \quad (43)$$

Thus the static local field corrections are the second functional derivative of F_{xc}.

B. Electrical conductivity

The frequency-dependent electron conductivity is given by its classical Green-Kubo form [14]

$$\sigma(\omega) = \mathrm{Re}\int_0^\infty dt e^{i\omega t}\psi(t), \quad \psi(t) = \frac{\beta}{3V}\langle\langle \widehat{\mathbf{J}}(t)\cdot\widehat{\mathbf{J}}\rangle\rangle_i. \quad (44)$$

The double brackets $\langle\langle\rangle\rangle_i$ denote an average over the electron degrees of freedom, followed by an average over the ion configurations (see below). The total current $\widehat{\mathbf{J}}$ is the volume integral of the current density $\widehat{\mathbf{j}}(\mathbf{r})$,

$$\widehat{\mathbf{J}} = \widetilde{\mathbf{j}}(\mathbf{k}=\mathbf{0}), \quad \widetilde{\mathbf{j}}(\mathbf{k}) = \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}}\widehat{\mathbf{j}}(\mathbf{r}). \quad (45)$$

The Fourier transform of (28) gives

$$\partial_t\langle\chi(\mathbf{k},\mathbf{k}',t)\rangle_i = \beta k_m k'_n \langle\langle \widetilde{j}_m(\mathbf{k},t)\widetilde{j}_n(\mathbf{k}')\rangle\rangle_i. \quad (46)$$

Once the ion configuration average has been performed, the system is isotropic, so this becomes

$$\partial_t\langle\chi(\mathbf{k},\mathbf{k}',t)\rangle_i = -\frac{1}{3}\beta k^2\langle\langle\widetilde{\mathbf{j}}(\mathbf{k},t)\cdot\widetilde{\mathbf{j}}(-\mathbf{k})\rangle\rangle_i\delta_{-\mathbf{k}\mathbf{k}'}. \quad (47)$$

Therefore the current autocorrelation function in the expression for the conductivity [Eq. (44)] is

$$\psi(t) = -\frac{1}{V}\lim_{k\to 0} k^{-2}\partial_t\langle\chi(\mathbf{k},-\mathbf{k},t)\rangle_i, \quad (48)$$

where the response function is given by (36). If the electron screening of $\overline{\epsilon}(\mathbf{r},\mathbf{r}',z)$ could be neglected, then the Kubo-Greenwood model would be obtained,

$$\psi(t) \to -\frac{1}{V}\lim_{k\to 0} k^{-2}\partial_t\langle\chi_{\rm KG}(\mathbf{k},-\mathbf{k},t)\rangle_i. \quad (49)$$

In practice, the conductivity is calculated directly from $\langle\widetilde{\mathbf{j}}(\mathbf{0},t)\cdot\widetilde{\mathbf{j}}(\mathbf{0})\rangle$ in the Kubo-Greenwood approximation for each ion configuration, without reference to the density response function. These conductivities for the disordered systems are then averaged over ion configurations sampled from an AIMD simulation.

The above properties, and the solution to the kinetic equation more generally, are given in terms of the KG response function $\chi_{\rm KG}$. For example, the density response function is obtained from (36) and (37),

$$\widetilde{\chi}(\mathbf{r},\mathbf{r}',z) = \widetilde{\chi}_{\rm KG}(\mathbf{r},\mathbf{r}',z) + \int d\mathbf{r}'' \int d\mathbf{r}''' \widetilde{\chi}_{\rm KG}(\mathbf{r},\mathbf{r}'',z) \times \mathcal{V}_{ee}(\mathbf{r}'',\mathbf{r}''')\widetilde{\chi}(\mathbf{r}''',\mathbf{r}',z). \quad (50)$$

There are well-developed computational codes for Kubo-Greenwood properties and the excess free energy needed for $\mathcal{V}_{ee}(\mathbf{r}'',\mathbf{r}')$ (e.g., VASP). Consequently, the additional computational difficulty to implement the additional physics obtained here is solution to the linear integral equation (50).

V. QUANTUM KINETIC EQUATION

The above-detailed reduction of the short-time generator to a practical representation in terms of the renormalized potentials expressed as functional derivatives of the free-energy functional was accomplished within the limits of the semiclassical limit. The use of quantum potentials to represent diffraction and degeneracy is an uncontrolled approximation. Instead the above kinetic theory should be understood as reliable only for conditions where such effects are weak. For example, a description of conditions where multiple bound electron-ion populations occur would be excluded. However, conditions with electron coupling of the order of unity are included and hence some of the "extreme conditions" of interest are relevant.

In the quantum case the electron correlation function (6) becomes

$$\langle A(t)\delta B\rangle = \mathrm{Tr}_1 f(1)a(1)\overline{b}(1,t), \quad (51)$$

where the trace is taken over a single-electron Hilbert space, and the classical equilibrium one-electron distribution function $n(\mathbf{r})\phi(v)$ has been replaced by its corresponding quantum operator $f(1)$, the equilibrium single-electron-density operator. Similarly, $a(1)$ and $\overline{b}(1,t)$ are the operators generalizing the phase-space functions $a(x)$ and $\overline{b}(x,t)$. The analysis of Appendix A follows in an analogous way [11]. However, the simplifications of the higher-order correlations from the equilibrium hierarchy, (B11) and (B12), are more complex. Furthermore, recognition of $\ln n(\mathbf{r})$ as the functional derivative of the noninteracting free-energy functional no longer applies in the quantum case. Hence, to date the corresponding practical simplification of the generator for the dynamics $L(t=0)$ in the quantum case has not been accomplished.

In the meantime an alternative route is to quantize the classical result derived here. The most direct path is to write the kinetic equation in the equivalent form

$$\partial_t\overline{b}(1,t) - \{h_{\rm KS}(1),\overline{b}(1,t)\} = f^{-1}(1)\mathrm{Tr}_2\{\mathcal{V}_{ee}(1,2), f(1)f(2)\overline{b}(2,t)\} \quad (52)$$

and to quantize it by replacing Poisson brackets by their corresponding commutators. This gives the operator equation

$$\partial_t \bar{b}(1,t) + i[h_{\rm KS}(1), \bar{b}(1,t)] = -f^{-1}(1){\rm Tr}_2 i[\mathcal{V}_{ee}(1,2), f(1)f(2)P(12)\bar{b}(2,t)]. \quad (53)$$

The Kohn-Sham Hamiltonian is the operator corresponding to (23) with the Kohn-Sham potential determined in the same way as (19) from the free-energy functional for the quantum system. Similarly, $\mathcal{V}_{ee}(1,2)$ is determined from that functional as given in (15) and (24). Also, a two-particle symmetrization operator $P(12)$ has been included to represent exchange effects.

Equation (53) is the quantum random-phase approximation for a system of electrons among a configuration of the ions, with renormalized potentials. Its classical limit is (13). The random-phase approximation without renormalization (weak coupling limit) has been established directly for the quantum case [11] and is given correctly by (53). More generally, it predicts a density response function in agreement with the corresponding result from time-dependent density-functional theory [15].

VI. DISCUSSION

The objectives here have been twofold. The first is to describe a kinetic theory for electrons in a disordered array of ions that is both practical and free from any assumptions regarding electron-electron or ion-electron coupling. In particular, the purpose is to do so without the need for distinction of free and bound electrons. This was accomplished by an evaluation of the generator for time dependence at $t = 0$, followed by the assumption that this generator is a reasonable approximation at all later times (Markov assumption). The second objective is to make contact between a controlled many-body theory and the phenomenology of the Kubo-Greenwood model. This was accomplished by observing that the short-time generator has a single-particle dynamics that is the same as the Kubo-Greenwood model, including the ion-electron force determined from the Kohn-Sham potential of equilibrium DFT. In addition, the context of that model was exposed, requiring additional effects of electron-electron screening via a renormalized potential also determined from DFT. The correlation functions have the structure of the random-phase approximation for an inhomogeneous system, modified by these potentials from DFT.

Although these conceptual issues of strong coupling, connection to DFT, and clarification of the Kubo-Greenwood model have been addressed, the practical application of the kinetic equation developed here is limited by its semiclassical nature. Some of the most interesting state conditions of warm, dense matter include strong electron degeneracy, outside the domain of the regularized quantum potentials assumed here. For these cases the quantum theory of Sec. V should be a useful practical tool. The detailed origin for this equation and its limitations (e.g., absence of electron-electron collisional effects) will be provided elsewhere.

The semiclassical electrons assumed here nevertheless have an important domain of validity where degeneracy is weak but electron-electron and electron-ion coupling can be strong. They have been used in early MD simulations of hydrogen plasmas [8], where electron coupling strengths of order one were studied at weak to moderate degeneracy. Subsequent simulations have demonstrated that such potentials can describe the transition from fully ionized to atomic states but fail for molecular formation [16]. More recently simulations to test the accuracy of different forms of these effective quantum potentials have been reported [9,10].

The role of the frozen ion configuration is passive in this analysis of the electron dynamics. In practice the systems of interest are ions and electrons in which both species are mobile. It is assumed, however, that the ions are effectively static on the time scale for electron properties. In this case the latter properties are calculated as here for a given configuration, and then an average is performed over configurations. The latter are sampled from an *ab initio* simulation of the ions [2]. A discussion of the effect of ion motion is deferred to a later point [5].

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APPENDIX A: KINETIC THEORY

The dynamics of $\langle A(t)\delta B\rangle$ is conveniently expressed in terms of the fundamental correlation function $G(x,x';t)$

$$\langle A(t)\delta B\rangle = \int dx dx' a(x) G(x,x';t) b(x'), \quad (A1)$$

$$G(x,x';t) = \langle f(x,t)(f(x') - \langle f(x')\rangle)\rangle,$$

$$f(x) = \sum_{\alpha=1}^{N_e} \delta(x - x_\alpha). \quad (A2)$$

This gives the representation (6)

$$\langle A(t)\delta B\rangle = \int dx n(\mathbf{r})\phi(v) a(x)\bar{b}(x,t), \quad (A3)$$

with the identification

$$\bar{b}(x,t) = \frac{1}{n(\mathbf{r})\phi(v)} \int dx' G(x,x';t) b(x'). \quad (A4)$$

The initial value is

$$\bar{b}(x,0) = \bar{b}(x) = \frac{1}{n(\mathbf{r})\phi(v)} \int dx' G(x,x';0) b(x'). \quad (A5)$$

Evaluation of $G(x,x';0)$ is straightforward from the definitions of the one- and two-particle equilibrium distribution functions

$$n(\mathbf{r}_1)\phi(v_1) = \sum_{N_e>1} N_e Tr_{2,..N_e}\rho(\{\mathbf{R}\},\{x\}), \quad (A6)$$

$$n(\mathbf{r}_1)n(\mathbf{r}_2)g(\mathbf{r}_1,\mathbf{r}_2)\phi(v_1)\phi(v_2) = \sum_{N_e>2} N_e(N_e-1){\rm Tr}_{3,..N_e}\rho(\{\mathbf{R}\},\{x\}), \quad (A7)$$

where $\rho(\{\mathbf{R}\},\{x\})$ is the N electron grand-canonical distribution function of (4). The result is

$$G(x,x';0) = n(\mathbf{r})\phi(v)[\delta(x-x') + \phi(v')n(\mathbf{r}')h(\mathbf{r},\mathbf{r}')], \quad (A8)$$

with the hole function defined by $h(\mathbf{r},\mathbf{r}') = g(\mathbf{r},\mathbf{r}') - 1$. This leads to (12)

$$\bar{b}(x) = b(x) + \int dx' n(\mathbf{r}')\phi(v')h(\mathbf{r},\mathbf{r}')b(x'). \tag{A9}$$

A kinetic equation follows from the definition of the inverse for $G(x,x';t)$,

$$\int dx'' G^{-1}(x,x'';t)G(x'',x';t) = \delta(x-x'), \tag{A10}$$

and differentiation of (A4),

$$\begin{aligned}\partial_t \bar{b}(x,t) &= \frac{1}{n(\mathbf{r})\phi(v)}\int dx' \partial_t G(x,x';t)b(x') \\ &= \frac{1}{n(\mathbf{r})\phi(v)}\int dx' dx''(\partial_t G(x,x';t)) \\ &\quad \times\ G^{-1}(x',x'';t)n(\mathbf{r}'')\phi(v'')\bar{b}(x'',t).\end{aligned} \tag{A11}$$

The generator for the dynamics is identified as

$$\partial_t \bar{b}(x,t) + \int dx' L(x,x';t)\bar{b}(x',t) = 0, \tag{A12}$$

$$\begin{aligned}L(x,x';t) \equiv -\frac{1}{n(\mathbf{r})\phi(v)}\int dx''(\partial_t G(x,x'';t)) \\ \times G^{-1}(x'',x';t)n(\mathbf{r}')\phi(v').\end{aligned} \tag{A13}$$

APPENDIX B: EVALUATION OF $L(x,x';0)$

The Markov approximation is based on using $L(x,x';0)$ as the generator for dynamics,

$$\begin{aligned}L(x,x';0) = \frac{1}{n(\mathbf{r})\phi(v)}\int dx''\partial_t G(x,x'';t)\mid_{t=0} \\ \times G^{-1}(x'',x';0)n(\mathbf{r}')\phi(v').\end{aligned} \tag{B1}$$

Consider first $G^{-1}(x'',x';0)$ in the form

$$G^{-1}(x,x';0) = \frac{1}{n(\mathbf{r})\phi(v)}\delta(x-x') - c(\mathbf{r},\mathbf{r}'). \tag{B2}$$

Then this obeys the inverse condition (A10) with (A8) if $c(\mathbf{r},\mathbf{r}')$ obeys the equation

$$c(\mathbf{r},\mathbf{r}') = h(\mathbf{r},\mathbf{r}') - \int d\mathbf{r}'' h(\mathbf{r},\mathbf{r}'')n(\mathbf{r}'')c(\mathbf{r}'',\mathbf{r}'). \tag{B3}$$

This definition for $c(\mathbf{r},\mathbf{r}')$ is the Ornstein-Zernicke equation [13].

Next $\partial_t G(x,x'';t)\mid_{t=0}$ is evaluated from its definition (A2) and Newton's equations

$$\begin{aligned}&[\partial_t + \mathbf{v}\cdot\nabla_{\mathbf{r}} - m^{-1}\nabla_{\mathbf{r}}V_{ie}(\mathbf{r})\cdot\nabla_{\mathbf{v}}]f(x,t) \\ &\quad = \int dx'(\nabla_{\mathbf{r}}V_{ee}(\mathbf{r},\mathbf{r}'))\cdot m^{-1}\nabla_{\mathbf{v}} \\ &\qquad \times [f(x,t)f(x',t) - \delta(x-x')f(x',t)].\end{aligned} \tag{B4}$$

This gives

$$\begin{aligned}&\partial_t G(x,x';t)\mid_{t=0} \\ &\quad = -[\mathbf{v}\cdot\nabla_{\mathbf{r}} - m^{-1}\nabla_{\mathbf{r}}V_{ie}(\mathbf{r})\cdot\nabla_{\mathbf{v}}]G(x,x';0) \\ &\qquad + \int dx''[\nabla_{\mathbf{r}}V_{ee}(\mathbf{r},\mathbf{r}'')]\cdot m^{-1}\nabla_{\mathbf{v}}\langle[f(x)f(x'') \\ &\qquad - \delta(x-x'')f(x'')](f(x') - \langle f(x')\rangle)\rangle.\end{aligned} \tag{B5}$$

The average in the second term on the right-hand side can be evaluated using the expressions

$$\langle f(x)\rangle = \phi(v)n(\mathbf{r}), \tag{B6}$$

$$\begin{aligned}\langle f(x)f(x')\rangle &= \delta(x-x')\phi(v)n(\mathbf{r}) \\ &\quad + \phi(v)\phi(v')n(\mathbf{r})n(\mathbf{r}')g(\mathbf{r},\mathbf{r}'),\end{aligned} \tag{B7}$$

$$\begin{aligned}&\langle[f(x)f(x'') - \delta(x-x'')f(x'')]f(x')\rangle \\ &\quad = [\delta(x-x') + \delta(x''-x')]\phi(v)\phi(v'')n(\mathbf{r})n(\mathbf{r}'')g(\mathbf{r},\mathbf{r}'') \\ &\qquad + \phi(v)\phi(v')\phi(v'')n(\mathbf{r})n(\mathbf{r}')n(\mathbf{r}'')g(\mathbf{r},\mathbf{r}',\mathbf{r}'').\end{aligned} \tag{B8}$$

Here $g(\mathbf{r},\mathbf{r}',\mathbf{r}'')$ is defined from the three-electron reduced distribution function

$$\begin{aligned}&n(\mathbf{r}_1)n(\mathbf{r}_2)n(\mathbf{r}_3)g(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\phi(v_1)\phi(v_2)\phi(v_3) \\ &\quad = \sum_{N_e>3} N_e(N_e-1)(N_e-2)\mathrm{Tr}_{3,..N_e}\rho(\{\mathbf{R}\},\{x\}).\end{aligned} \tag{B9}$$

Then (B5) becomes

$$\begin{aligned}\partial_t G(x,x';t)\mid_{t=0} = &-[\mathbf{v}\cdot\nabla_{\mathbf{r}} - m^{-1}\nabla_{\mathbf{r}}V_{ie}(\mathbf{r})\cdot\nabla_{\mathbf{v}}]G(x,x';0) - \beta\mathbf{v}\cdot[\nabla_{\mathbf{r}}V_{ee}(\mathbf{r},\mathbf{r}')]\phi(v)\phi(v')n(\mathbf{r})n(\mathbf{r}')g(\mathbf{r},\mathbf{r}') \\ &+ n(\mathbf{r})m^{-1}\nabla_{\mathbf{v}}\cdot\delta(x-x')\phi(v)\int d\mathbf{r}''[\nabla_{\mathbf{r}}V_{ee}(\mathbf{r},\mathbf{r}'')]n(\mathbf{r}'')g(\mathbf{r},\mathbf{r}'') \\ &- n(\mathbf{r})n(\mathbf{r}')\phi(v')\phi(v)\beta\mathbf{v}\cdot\int d\mathbf{r}''[\nabla_{\mathbf{r}}V_{ee}(\mathbf{r},\mathbf{r}'')]n(\mathbf{r}'')[g(\mathbf{r},\mathbf{r}',\mathbf{r}'') - g(\mathbf{r},\mathbf{r}'')].\end{aligned} \tag{B10}$$

The two integrals on the right-hand side can be evaluated using the first two equations of the BBGKY hierarchy

$$\int d\mathbf{r}''[\nabla_{\mathbf{r}}V_{ee}(\mathbf{r},\mathbf{r}'')]n(\mathbf{r}'')g(\mathbf{r},\mathbf{r}'') = -\beta^{-1}\nabla_{\mathbf{r}}\ln n(\mathbf{r}) - \nabla_{\mathbf{r}}V_{ie}(\mathbf{r}), \tag{B11}$$

$$\begin{aligned}&\int d\mathbf{r}''[\nabla_{\mathbf{r}}V_{ee}(\mathbf{r},\mathbf{r}'')]n(\mathbf{r}'')[g(\mathbf{r},\mathbf{r}',\mathbf{r}'') - g(\mathbf{r},\mathbf{r}'')] \\ &\quad = -[\nabla_{\mathbf{r}}V_{ee}(\mathbf{r})]g(\mathbf{r},\mathbf{r}') - [\nabla_{\mathbf{r}}V_{ie}(\mathbf{r}) + \beta^{-1}\nabla_{\mathbf{r}}\ln n(\mathbf{r})]h(\mathbf{r},\mathbf{r}') - \beta^{-1}\nabla_{\mathbf{r}}h(\mathbf{r},\mathbf{r}')\end{aligned} \tag{B12}$$

to get

$$\partial_t G(x,x';t)\,|_{t=0} = -[\mathbf{v}\cdot\nabla_{\mathbf{r}} - m^{-1}\nabla_{\mathbf{r}} V_{ie}(\mathbf{r})\cdot\nabla_{\mathbf{v}}]G(x,x';0) - n(\mathbf{r})m^{-1}\nabla_{\mathbf{v}}\cdot\delta(x-x')\phi(v')[\beta^{-1}\nabla_{\mathbf{r}}\ln n(\mathbf{r}) + \nabla_{\mathbf{r}} V_{ie}(\mathbf{r})] + n(\mathbf{r})n(\mathbf{r}')\phi(v')\phi(v)\beta\mathbf{v}\cdot[\nabla_{\mathbf{r}} V_{ie}(\mathbf{r},\mathbf{r}') + \beta^{-1}\nabla_{\mathbf{r}}\ln n(\mathbf{r})]h(\mathbf{r},\mathbf{r}') + n(\mathbf{r})n(\mathbf{r}')\phi(v')\phi(v)\beta\mathbf{v}\cdot\beta^{-1}\nabla_{\mathbf{r}} h(\mathbf{r},\mathbf{r}'). \tag{B13}$$

Finally, eliminate the delta function in the second term of the right-hand side using (A6)

$$\partial_t G(x,x';t)\,|_{t=0} = -[\mathbf{v}\cdot\nabla_{\mathbf{r}} + m^{-1}\beta^{-1}\nabla_{\mathbf{r}}\ln n(\mathbf{r})\cdot\nabla_{\mathbf{v}}]G(x,x';0) + n(\mathbf{r})n(\mathbf{r}')\phi(v')\phi(v)\beta\mathbf{v}\cdot\beta^{-1}\nabla_{\mathbf{r}} h(\mathbf{r},\mathbf{r}'). \tag{B14}$$

Together with (B1), (B2), and (B3), this gives the desired result,

$$L(x,x';0) = [\mathbf{v}\cdot\nabla_{\mathbf{r}} - m^{-1}\beta^{-1}\nabla_{\mathbf{r}}\ln n(\mathbf{r},\{\mathbf{R}\})\cdot\nabla_{\mathbf{v}}]\delta(x-x') - n(\mathbf{r}',\{\mathbf{R}\})\phi(v')\mathbf{v}\cdot\nabla_{\mathbf{r}} c(\mathbf{r},\mathbf{r}',\{\mathbf{R}\}). \tag{B15}$$

APPENDIX C: SOLUTION TO MARKOV KINETIC EQUATION

A formal solution to the kinetic equation (13) for $\overline{b}(x,t)$ is

$$\overline{b}(x,t) = e^{-\mathcal{L}_{\rm KG}t}\overline{b}(x) - \int_0^t d\tau\, e^{-\mathcal{L}_{\rm KG}(t-\tau)}\mathbf{v}\cdot\nabla_{\mathbf{r}} \times \int d\mathbf{r}'\beta\mathcal{V}_{ee}(\mathbf{r},\mathbf{r}')I(\mathbf{r}',\tau), \tag{C1}$$

where the generator for the effective single-particle (Kubo-Greenwood) dynamics is

$$\mathcal{L}_{\rm KG} \equiv \mathbf{v}\cdot\nabla_{\mathbf{r}} - m^{-1}\nabla_{\mathbf{r}}\mathcal{V}_{ie}(\mathbf{r})\cdot\nabla_{\mathbf{v}} \tag{C2}$$

and the source term $I(\mathbf{r},t)$ is

$$I(\mathbf{r},t) \equiv \int d\mathbf{v}\phi(v)n(\mathbf{r})\overline{b}(x,t). \tag{C3}$$

Use of (C1)–(C3) gives an integral equation for $I(\mathbf{r},t)$,

$$I(\mathbf{r},t) = I_0(\mathbf{r},t) + \int_0^t d\tau\int d\mathbf{r}'\chi_{\rm KG}(\mathbf{r},\mathbf{r}',t-\tau) \times \int d\mathbf{r}''\mathcal{V}_{ee}(\mathbf{r}',\mathbf{r}'')I(\mathbf{r}'',\tau), \tag{C4}$$

with

$$I_0(\mathbf{r},t) \equiv \int d\mathbf{v}\phi(v)n(\mathbf{r})e^{-\mathcal{L}_{\rm KG}t}\overline{b}(x) \tag{C5}$$

and

$$\chi_{\rm KG}(\mathbf{r},\mathbf{r}',t-\tau) = -\beta\int d\mathbf{v}\phi(v)n(\mathbf{r})e^{-\mathcal{L}_{\rm KG}(t-\tau)}\mathbf{v}\cdot\nabla_{\mathbf{r}}\delta(\mathbf{r}-\mathbf{r}'). \tag{C6}$$

1. Dynamic structure factor

The dynamic structure factor is determined from the density-density time correlation function

$$C(\mathbf{r},\mathbf{r}',t) = \langle\widehat{n}(\mathbf{r},t)\delta\widehat{n}(\mathbf{r}')\rangle, \tag{C7}$$

which corresponds to $a(x_1) = \delta(\mathbf{r}_1-\mathbf{r})$ and $b(x_1) = \delta(\mathbf{r}_1-\mathbf{r}')$ in (6). Then with (C1) the dynamic structure factor obeys the integral equation

$$C(\mathbf{r},\mathbf{r}',t) = C_0(\mathbf{r},\mathbf{r}',t) + \int_0^t d\tau\int d\mathbf{r}''\chi_{\rm KG}(\mathbf{r},\mathbf{r}'',t-\tau) \times \int d\mathbf{r}'''\mathcal{V}_{ee}(\mathbf{r}'',\mathbf{r}''')C(\mathbf{r}''',\mathbf{r}',\tau), \tag{C8}$$

where

$$C_0(\mathbf{r},\mathbf{r}',t) = n(\mathbf{r})\int d\mathbf{v}\phi(v)e^{-\mathcal{L}_{\rm KG}t}[\delta(\mathbf{r}-\mathbf{r}') + n(\mathbf{r}')h(\mathbf{r},\mathbf{r}')]. \tag{C9}$$

The solution to the linear equation (C8) is obtained first by defining the Laplace transform

$$\widetilde{f}(z) = \int_0^\infty d\tau\, e^{-zt}f(t) \tag{C10}$$

to get

$$\widetilde{C}(\mathbf{r},\mathbf{r}',z) = \widetilde{C}_0(\mathbf{r},\mathbf{r}',z) + \int d\mathbf{r}''\widetilde{\chi}_{\rm KG}(\mathbf{r},\mathbf{r}'',z) \times \int d\mathbf{r}'''\mathcal{V}_{ee}(\mathbf{r}'',\mathbf{r}''')\widetilde{C}(\mathbf{r}''',\mathbf{r}',z). \tag{C11}$$

Next define

$$\epsilon(\mathbf{r},\mathbf{r}',z) = \delta(\mathbf{r}-\mathbf{r}') - \int d\mathbf{r}''\chi_{\rm KG}(\mathbf{r},\mathbf{r}'',z)\mathcal{V}_{ee}(\mathbf{r}'',\mathbf{r}'), \tag{C12}$$

so the solution to (C11) is

$$\widetilde{C}(\mathbf{r},\mathbf{r}',z) = \int d\mathbf{r}''\epsilon^{-1}(\mathbf{r},\mathbf{r}'',z)\widetilde{C}_0(\mathbf{r}'',\mathbf{r}',z). \tag{C13}$$

2. Density response function

The density response function is related to the density correlation function by (26)

$$\chi(\mathbf{r},\mathbf{r}',t) = \beta\partial_t C(\mathbf{r},\mathbf{r}',t). \tag{C14}$$

Then differentiating (C8) gives

$$\chi(\mathbf{r},\mathbf{r}',t) = \chi_0(\mathbf{r},\mathbf{r}',t) + \int d\mathbf{r}''\chi_{\rm KG}(\mathbf{r},\mathbf{r}'',0)\int d\mathbf{r}'''\mathcal{V}_{ee}(\mathbf{r}'',\mathbf{r}''')C(\mathbf{r}''',\mathbf{r}',t) - \int_0^t d\tau\int d\mathbf{r}''\beta\partial_\tau\chi_{\rm KG}(\mathbf{r},\mathbf{r}'',t-\tau) \times \int d\mathbf{r}'''\mathcal{V}_{ee}(\mathbf{r}'',\mathbf{r}''')C(\mathbf{r}''',\mathbf{r}',\tau),$$

$$= \chi_0(\mathbf{r},\mathbf{r}',t) + \int d\mathbf{r}''\chi_{\rm KG}(\mathbf{r},\mathbf{r}'',t)\int d\mathbf{r}'''\mathcal{V}_{ee}(\mathbf{r}'',\mathbf{r}''')C(\mathbf{r}''',\mathbf{r}',0) + \int_0^t d\tau\int d\mathbf{r}''\chi_{\rm KG}(\mathbf{r},\mathbf{r}'',t-\tau)$$
$$\times \int d\mathbf{r}'''\mathcal{V}_{ee}(\mathbf{r}'',\mathbf{r}''')\chi(\mathbf{r}''',\mathbf{r}',\tau), \tag{C15}$$

$$\chi(\mathbf{r},\mathbf{r}',t) = \chi_{\rm KG}(\mathbf{r},\mathbf{r}',t) + \int_0^t d\tau\int d\mathbf{r}''\chi_{\rm KG}(\mathbf{r},\mathbf{r}'',t-\tau)\int d\mathbf{r}'''\mathcal{V}_{ee}(\mathbf{r}'',\mathbf{r}''')\chi(\mathbf{r}''',\mathbf{r}',\tau). \tag{C16}$$

The Ornstien-Zernicke equation (B3) has been used to make the identification

$$\chi_{\rm KG}(\mathbf{r},\mathbf{r}',t) = \chi_0(\mathbf{r},\mathbf{r}',t) + \int d\mathbf{r}''\chi_{\rm KG}(\mathbf{r},\mathbf{r}'',t)$$
$$\times \int d\mathbf{r}'''\mathcal{V}_{ee}(\mathbf{r}'',\mathbf{r}''')C(\mathbf{r}''',\mathbf{r}',0). \tag{C17}$$

Taking the Laplace transform of (C16) gives the solution

$$\widetilde{\chi}(\mathbf{r},\mathbf{r}',z) = \int d\mathbf{r}''\overline{\epsilon}^{-1}(\mathbf{r},\mathbf{r}'',z)\widetilde{\chi}_{\rm KG}(\mathbf{r}'',\mathbf{r}',z), \tag{C18}$$

where $\overline{\epsilon}^{-1}(\mathbf{r},\mathbf{r}',z)$ is the inverse function associated with

$$\overline{\epsilon}(\mathbf{r},\mathbf{r}',z) = \delta(\mathbf{r}-\mathbf{r}') - \int d\mathbf{r}''\chi_{\rm KG}(\mathbf{r},\mathbf{r}'',z)\mathcal{V}_{ee}(\mathbf{r}'',\mathbf{r}'). \tag{C19}$$

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