Density response from kinetic theory and time-dependent density-functional theory for matter under extreme conditions

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Density Response from Kinetic Theory and Time Dependent Density Functional Theory for Matter Under Extreme Conditions

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Abstract

The density linear response function for an inhomogeneous system of electrons in equilibrium with an array of fixed ions is considered. Two routes to its evaluation for extreme conditions (e.g., warm dense matter) are considered. The first is from a recently developed short-time kinetic equation; the second is from time-dependent density functional theory (tdDFT). The result from the latter approach agrees with that from kinetic theory in the "adiabatic approximation", providing support and `contextual clarity` for each. Both provide a connection to the phenomenological Kubo-Greenwood method for calculating transport properties.

I.   INTRODUCTION

Matter under extreme conditions is of broad current interest, ranging from applications in theoretical astrophysics (e.g., massive exo-planets) to new experimental access to such materials [1]. The state conditions include those for which many traditional methods of plasma physics or condensed matter physics fail or become uncontrolled. However, thermodynamic properties such as pressure, free energy, and structure are treated well by *ab initio* molecular dynamics (AIMD) methods [2], wherein complex electronic states are described by finite temperature density functional theory (DFT). These methods allow inclusion of strong coupling, bound and free states, and quantum effects across a wide range of temperatures and densities. Transport properties and other dynamical features require an extension of these tools [3]. One approach is a recently developed short-time kinetic equation for time correlation functions [4]. It subsumes a practical phenomenology, the Kubo-Greenwood (KG) method [5, 6], used for calculating correlation functions. This approach models the true many-body Hamiltonian by one for non-interacting particles whose excitations are those of the equilibrium Kohn-Sham Hamiltonian. The KG method exploits strong coupling features of equilibrium DFT, extending its advantages to time-dependent properties.

A second approach is time-dependent density functional theory (tdDFT) designed to extend the advantages of equilibrium DFT to dynamical properties [7–9]. Its formulation and application to ground state properties is well-developed, but much less so for the finite temperature extended systems considered here. An extension of van Leeuwen's fundamental theorem for tdDFT [10], to mixed states (ensembles) [11, 20] is proposed and discussed in Appendix A. Its application to linear response [12] about an initial equilibrium state is described in section V. In particular, it is shown that the density response function from tdDFT can be expressed in terms of the KG response function, so its connection to the KG phenomenology is quite direct. Both the kinetic theory and tdDFT provide means to include corrections to the KG method. In the "adiabatic approximation" tdDFT gives corrections that are equivalent to those from kinetic theory, thereby establishing a connection between these two quite different approaches.

Here we address three different groups: 1) those focused upon applications (simulations and experiments) in warm, dense matter, 2) kinetic theory specialists in many-body physics, and 3) time-dependent density functional theorists, mainly from atomic and molec-

ular physics. Typically one group does not follow the literature of the others. The result is loss of insight. We have tried to make the presentation simple, direct, and self-contained for value to all three.

II.   DENSITY RESPONSE AND RELATED PROPERTIES

Linear response for systems at initial equilibrium is treated in most text books on condensed matter physics [13, 14]. A recent updated discussion of linear response can be found in reference [15]. However, for definition of notation and precise specification of linear response as used herein, a brief review follows. Consider a one component system of N identical particles with Hamiltonian $H(t)$

$$H(t) = K + U + V(t). \tag{1}$$

Here K is the kinetic energy, U is a many-body potential energy among the particles (more specifically, below this is chosen to be the Coulomb interactions among electrons and between them and a configuration of fixed ions), and $V(t)$ is an external time dependent potential (perturbation) of the form

$$V(t) = \int d\mathbf{r} v(\mathbf{r}, t) \widehat{n}(\mathbf{r}), \quad \widehat{n}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{q}_i) \tag{2}$$

The number density operator is defined in terms of the particle position operators $\{\mathbf{q}_i\}$ (a caret is included on $\widehat{n}(\mathbf{r})$ in this definition to distinguish the operator from its state-averaged value $n(\mathbf{r})$ introduced below). The form of the external potential $v(\mathbf{r}, t)$ is unspecified at this point. The state of the system is given by its density matrix $\rho(t)$. Its evolution is governed by the Liouville-von Neumann equation, for $t \geq \tau$

$$\partial_t \rho(t) + i [H(t), \rho(t)] = 0, \tag{3}$$

with some given initial condition $\rho(\tau)$.

Choose the initial state $\rho(\tau)$ to be stationary (equilibrium) under the unperturbed Hamiltonian

$$[(K + U), \rho_{eq}] = 0, \quad \rho(\tau) \equiv \rho_{eq} \tag{4}$$

Then the solution to Eq. (3) to linear order in the perturbation is

$$\rho(t) = \rho_{eq} - \int_{\tau}^{t} dt' \int d\mathbf{r} v(\mathbf{r}, t') i [\widehat{n}(\mathbf{r}, t' - t), \rho_{eq}], \tag{5}$$

3

where the time dependence of the local density operator is

$$\widehat{n}(\mathbf{r},t) = e^{i(K+U)t}\widehat{n}(\mathbf{r})e^{-i(K+U)t}. \tag{6}$$

The equilibrium averaged local density to linear order is therefore

$$n(\mathbf{r},t \mid v) = n_{eq}(\mathbf{r}) + \int_\tau^t dt' \int d\mathbf{r}' \chi\left(\mathbf{r},\mathbf{r}';t-t'\right) v(\mathbf{r}',t'). \tag{7}$$

The linear response function $\chi\left(\mathbf{r},\mathbf{r}';t\right)$ is identified as

$$\chi\left(\mathbf{r},\mathbf{r}';t\right) \equiv -i \left\langle [\widehat{n}(\mathbf{r},t),\widehat{n}(\mathbf{r}')] \right\rangle_{eq}, \tag{8}$$

and the bracket with subscript eq denotes the equilibrium average over the initial state,

$$\langle X \rangle_{eq} = Tr\rho_{eq}X. \tag{9}$$

The cyclic invariance of the trace and stationarity of ρ_{eq} have been used to obtain the form Eq. (8).

To be more specific, consider the example of a system of N_e electrons in equilibrium with a distribution of N_i fixed ions at the initial time τ. The Hamiltonian $H\left(\tau\right) = H_{N_e}$ is then

$$H_{N_e} = K + U = K + \frac{1}{2}\sum_{i \neq j=1}^{N_e} \frac{e^2}{|\mathbf{q}_i - \mathbf{q}_j|} + \sum_{i=1}^{N_e} V\left(\mathbf{q}_i,\{\mathbf{R}\}\right), \tag{10}$$

and the interaction potential for each electron with the ions is

$$V\left(\mathbf{q}_i,\{\mathbf{R}\}\right) \equiv -\sum_{j=1}^{N_i} \frac{Z_j e^2}{|\mathbf{q}_i - \mathbf{R}_j|}. \tag{11}$$

Also, for the stationary equilibrium state, choose the grand canonical ensemble

$$\rho_{eq,N_e} = e^{\beta\Omega}e^{-\beta(H_{N_e}(\tau)-\mu N_e)}\mathcal{S}_{N_e}, \tag{12}$$

where μ is the chemical potential, $\mathcal{S}_{N_e}$ is the N_e particle anti-symmetrization operator, and Ω is the normalization constant

$$e^{-\beta\Omega} = \sum_{N_e>0} Tr^{(N_e)}e^{-\beta(H_{N_e}(\tau)-\mu N_e)}\mathcal{S}_{N_e}. \tag{13}$$

Averages in the grand ensemble are defined by

$$\langle X \rangle_{eq} = \sum_{N_e>0} Tr^{(N_e)}\rho_{eq,N_e}X_{N_e}. \tag{14}$$

4

A. Relationship to dielectric function and conductivity

Define the Fourier-transformed response function

$$\widetilde{\chi}(\mathbf{k}, \mathbf{k}'; t) = \int d\mathbf{r} d\mathbf{r}' e^{-i(\mathbf{k}\cdot\mathbf{r}+\mathbf{k}'\cdot\mathbf{r}')} \chi(\mathbf{r}, \mathbf{r}'; t)$$

$$= -i \left\langle [\widetilde{n}(\mathbf{k}, t), \widetilde{n}(\mathbf{k}')] \right\rangle_{eq} \tag{15}$$

where $\widetilde{n}(\mathbf{k})$ is the Fourier transform of the number operator $\widehat{n}(\mathbf{r})$. A related property is the dielectric function $\epsilon(\mathbf{k}, \mathbf{k}'; t)$ defined by

$$\widetilde{V}(\mathbf{k}) \widetilde{\chi}(\mathbf{k}, \mathbf{k}'; t) = \delta_{\mathbf{k}, -\mathbf{k}'} - \epsilon^{-1}(\mathbf{k}, \mathbf{k}'; t). \tag{16}$$

Here $\widetilde{V}(\mathbf{k})$ is the Fourier transform of the electron-electron Coulomb potential. If $\epsilon(\mathbf{k}, \mathbf{k}', t)$ is expanded to leading order in $\widetilde{V}(\mathbf{k})$ the random phase approximation is obtained

$$\epsilon(\mathbf{k}, \mathbf{k}', t) \rightarrow \epsilon_{RPA}(\mathbf{k}, \mathbf{k}'; t) = \delta_{\mathbf{k}, -\mathbf{k}'} + \widetilde{V}(\mathbf{k}) \widetilde{\chi}^{(0)}(\mathbf{k}, \mathbf{k}'; t), \tag{17}$$

where $\widetilde{\chi}^{(0)}(\mathbf{k}, \mathbf{k}'; t)$ is the response function for non-interacting electrons in the presence of the external ions.

Other properties of interest are related to $\widetilde{\chi}(\mathbf{k}, \mathbf{k}'; t)$, or equivalently to $\epsilon(\mathbf{k}, \mathbf{k}'; t)$, by the microscopic number density conservation law

$$\partial_t \widetilde{n}(\mathbf{k}, t) + i\mathbf{k} \cdot \widetilde{\mathbf{j}}(\mathbf{k}, t) = 0, \quad \widetilde{\mathbf{j}}(\mathbf{k}) = \sum_{i=1}^{N} \frac{1}{2} \left(e^{-i\mathbf{k}\cdot\mathbf{q}_i} \mathbf{v}_i + \mathbf{v}_i e^{-i\mathbf{k}\cdot\mathbf{q}_i} \right), \tag{18}$$

where $\widetilde{\mathbf{j}}(\mathbf{k})$ is the Fourier transformed number flux operator and $\mathbf{v}_i = \mathbf{p}_i/m$ is the velocity operator for particle i. The time derivative of $\widetilde{\chi}(\mathbf{k}, \mathbf{k}'; t)$ gives

$$\partial_t \widetilde{\chi}(\mathbf{k}, \mathbf{k}'; t) = ik_\ell \left\langle i \left[\widetilde{j}_\ell(\mathbf{k}, t), \widetilde{n}(\mathbf{k}') \right] \right\rangle_{eq}. \tag{19}$$

Use the cyclic property of the trace

$$\left\langle \left[\widetilde{j}_\ell(\mathbf{k}, t), \widetilde{n}(\mathbf{k}') \right] \right\rangle_{eq} = Tr \left[\widetilde{n}(\mathbf{k}'), \rho_e \right] \widetilde{j}_\ell(\mathbf{k}, t), \tag{20}$$

and the operator identity

$$i \left[\widetilde{n}(\mathbf{k}'), e^{-\beta H(\tau)} \right] = - \int_0^\beta d\lambda e^{(\beta-\lambda)H(\tau))} i \left[\widetilde{n}(\mathbf{k}'), H(\tau) \right] e^{-\lambda H(\tau))}$$

$$= - \int_0^\beta d\lambda e^{(\beta-\lambda)H(\tau))} i\mathbf{k}' \cdot \widetilde{\mathbf{j}}(\mathbf{k}') e^{-\lambda H(\tau))} \tag{21}$$

5

to get

$$\partial_t \widetilde{\chi}(\mathbf{k}, \mathbf{k}'; t) = i k_m i k_\ell \int_0^\beta d\lambda \left\langle \widetilde{j}_m(\mathbf{k}', -t + i\lambda) \widetilde{j}_\ell(\mathbf{k}) \right\rangle_{eq}. \tag{22}$$

Finally, the Fourier transform in time

$$\widetilde{\widetilde{\chi}}(\mathbf{k}, \mathbf{k}'; \omega) \equiv \int_{-\infty}^\infty dt e^{i\omega t} \widetilde{\chi}(\mathbf{k}, \mathbf{k}'; t) \tag{23}$$

gives

$$\widetilde{\widetilde{\chi}}(\mathbf{k}, \mathbf{k}'; \omega) = i \frac{k_m k_\ell}{\omega} \int_{-\infty}^\infty dt e^{i\omega t} \int_0^\beta d\lambda \left\langle \widetilde{j}_m(\mathbf{k}', -t + i\lambda) \widetilde{j}_\ell(\mathbf{k}) \right\rangle_{eq}$$
$$= 2i \frac{k_m k_\ell}{\omega e^2} \sigma_{m\ell}(\mathbf{k}, \mathbf{k}'; \omega) \tag{24}$$

where the electrical conductivity tensor is

$$\sigma_{m\ell}(\mathbf{k}, \mathbf{k}'; \omega) = \frac{1}{2} e^2 \int_{-\infty}^\infty dt e^{i\omega t} \int_0^\beta d\lambda \left\langle \widetilde{j}_m(\mathbf{k}', -t + i\lambda) \widetilde{j}_\ell(\mathbf{k}) \right\rangle_{eq}. \tag{25}$$

III. KUBO-GREENWOOD METHOD

The response function (and related equilibrium time correlation functions) is determined from the Hamiltonian, Eq. (10), which appears both in the equilibrium distribution function and the dynamics of $\widehat{n}(\mathbf{r}, t)$ in Eq. (6). Its evaluation for the conditions of interest here involves all the difficulties of the many-body problem for which standard methods of condensed matter physics or plasma physics are questionable or intractable. Instead, a phenomenological mean-field model incorporating strong coupling information from equilibrium DFT commonly is assumed. The actual Hamiltonian is replaced by

$$H_{N_e} \to H_{KS} \equiv \sum_{i=1}^{N_e} h_{KS}(i), \quad h_{KS}(i) = \frac{p_i^2}{2m} + v_{KS}(\mathbf{q}_i, \{\mathbf{R}\}). \tag{26}$$

This is a sum of independent Hamiltonians in each of which the effective single particle potential is the Kohn-Sham potential of equilibrium DFT. It is determined from the equilibrium free energy functional according to

$$v_{KS}(\mathbf{q}_i, \{\mathbf{R}\}) = V(\mathbf{q}_1, \{\mathbf{R}\}) + \frac{\delta F^{(1)}}{\delta n(\mathbf{q}_1, \{\mathbf{R}\})}, \tag{27}$$

where $F^{(1)}$ is the excess free energy, beyond the corresponding non-interacting contribution. It is a functional of the initial equilibrium density $n(\mathbf{q}_1, \{\mathbf{R}\})$. It can be calculated

6

with good confidence for matter under extreme conditions from recently developed finite temperature equilibrium DFT methods [16]. The approximation Eq. (26) is known as the Kubo-Greenwood method. Since it invokes a system of non-interacting particles, the response function can be calculated exactly, for a given $F^{(1)}$ and configuration of the ions $\{\mathbf{R}\}$, in terms of the eigenfunctions and eigenvalues of h_{KS} [6].

The origin and basis for the Kubo-Greenwood method is not clear beyond the hope that the reasonably accurate description of interactions for thermodynamic properties from equilibrium DFT approximations might extend to the dynamics as well. A major objective of the present work is to provide a more convincing rationalization for the replacement shown in (26).

IV. SHORT TIME KINETIC THEORY

The density response function can be written in the equivalent form

$$
\begin{aligned}
\chi\left(\mathbf{r}, \mathbf{r}'; t\right) &= i \left\langle \widehat{n}(\mathbf{r}')\widehat{n}(\mathbf{r}, t)\right\rangle_{eq} - i \left\langle \widehat{n}(\mathbf{r}, t)\widehat{n}(\mathbf{r}')\right\rangle_{eq} \\
&= i \left(C\left(\mathbf{r}, \mathbf{r}'; t\right) - C\left(\mathbf{r}, \mathbf{r}'; t + i\beta\right)\right).
\end{aligned}
\tag{28}
$$

Here $C\left(\mathbf{r}, \mathbf{r}', t\right)$ is the time correlation function

$$
C\left(\mathbf{r}, \mathbf{r}'; t\right) = \left\langle \widehat{n}(\mathbf{r}')\widehat{n}(\mathbf{r}, t)\right\rangle_{eq}.
\tag{29}
$$

To obtain the second line of (28) the cyclic invariance of the trace has been used. Following the formal kinetic theory of reference [17], the correlation function can be written as an average over the single electron subspace

$$
C\left(\mathbf{r}, \mathbf{r}'; t\right) = Tr_1 \delta\left(\mathbf{r} - \mathbf{q_1}\right) \psi\left(1, \mathbf{r}'; t\right),
\tag{30}
$$

Here Tr_1 denotes a trace in the single particle Hilbert space, and the single particle operator $\psi\left(1, \mathbf{r}; t\right)$ is averaging over all other degrees of freedom (analogous to a one-particle reduced density matrix but representing the correlation function). It obeys the formally exact kinetic, equation

$$
\left(\partial_t + B\left(1\right)\right) \psi\left(1, \mathbf{r}'; t\right) = \int_0^t dt' M\left(1;\ t'\right) \psi\left(1, \mathbf{r}'; t - t'\right),
\tag{31}
$$

where B and M are super operators that map the single particle Hilbert space operators onto other single particle operators. For the present, the detailed formal definitions for $B\left(1\right)$

7

and $M(1;t)$ are not needed, beyond the facts that $B(1)$ is time independent and $M(1;t)$ is non-singular at $t = 0$. This means that the exact short time form for the kinetic theory is

$$(\partial_t + B(1))\psi(1,\mathbf{r}';t) = 0, \qquad t \to 0. \tag{32}$$

Use of this form for $t > 0$ constitutes the Markov approximation, whereby the generator of the time dependence does not depend on time. Such an approximation does not `involve` any explicit limitation on coupling strength or other small parameter conditions. Hence it is a good candidate for materials under extreme conditions.

The correlation function $C(\mathbf{r},\mathbf{r}';t)$ calculated using this short time kinetic theory is obtained by integrating (32)

$$C(\mathbf{r},\mathbf{r}';t) = Tr_1\delta(\mathbf{r} - \mathbf{q}_1)e^{-Bt}\psi(1,\mathbf{r}',0), \tag{33}$$

and the corresponding response function from (28) is

$$\chi(\mathbf{r},\mathbf{r}';t) = iTr_1\delta(\mathbf{r} - \mathbf{q}_1)e^{-Bt}\left(1 - e^{-i\beta B}\right)\psi(1,\mathbf{r}';0). \tag{34}$$

This can be simplified using the exact initial value for $\chi(\mathbf{r},\mathbf{r}';t)$ calculated directly from its definition Eq. (15)

$$\chi(\mathbf{r},\mathbf{r}';0) = iTr_1\delta(\mathbf{r} - \mathbf{q}_1)\left[f^{(1)}(1), \delta(\mathbf{r}' - \mathbf{q}_1)\right]. \tag{35}$$

where $f^{(1)}(1)$ is the single-electron equilibrium distribution operator

$$f^{(1)}(1) = \sum_{N_e \geq 2} N_e Tr_{2..N_e}\rho_{eN_e}, \tag{36}$$

and ρ_{eN_e} is the grand canonical equilibrium state of (12) and the trace $Tr_{2..N_e}$ is taken over all degrees of freedom except index 1. This determines $\psi(1,\mathbf{r};0)$ in terms of B

$$\left(1 - e^{-i\beta B}\right)\psi(1,\mathbf{r}';0) = \left[f^{(1)}(1), \delta(\mathbf{r}' - \mathbf{q}_1)\right] \tag{37}$$

to give the final short-time kinetic theory result for the response function

$$\chi(\mathbf{r},\mathbf{r}';t) = Tr_1\delta(\mathbf{r} - \mathbf{q}_1)\phi(1,\mathbf{r}';t), \tag{38}$$

$$(\partial_t + B(1))\phi(1,\mathbf{r}';t) = 0, \qquad \phi(1,\mathbf{r}';0) = i\left[f^{(1)}(1), \delta(\mathbf{r}' - \mathbf{q}_1)\right]. \tag{39}$$

As an example, the calculation of $B(1)$ in the weak coupling limit is given in reference [17], leading to $B(1)$ for the random phase approximation linear kinetic equation

$$B(1)\phi(1,\mathbf{r}';t) \to i[\left(\frac{p_1^2}{2m} + V(\mathbf{q}_1,\{\mathbf{R}\})\right),\phi(1,\mathbf{r}';t)]$$

$$+ Tr_2 i[V_{ee}(12), f^{(2)}(12)f^{-1}(1)\phi(1,\mathbf{r}';t)]$$

$$+ Tr_2 i[V_{ee}(12), f^{(2)}(12)f^{-1}(2)\phi(2,\mathbf{r}';t)]. \tag{40}$$

Here, $f(1)$ and $f^{(2)}(12)$ are the non-interacting one- and two-particle reduced density operators, including exchange, and $V_{ee}(12) = e^2/\mid \mathbf{q}_1 - \mathbf{q}_2 \mid$. The second term on the right of Eq. (40) represents the Hartree-Fock additions to the single-particle energies, while the third term gives the RPA screening. More generally, to include strong coupling effects, $B(1)$ has been expressed exactly in terms of the one-, two-, and three-particle equilibrium reduced density matrices for the interacting system [17]. However, a more practical representation has been obtained only in the semi-classical limit. That invokes a classical representation for the electrons with short-distance regularization of the Coulomb potentials for electron-electron and electron-ion interactions to account for quantum diffraction and exchange effects. In that case $B(1)$ can be calculated exactly without any limitations on the coupling strength between electrons or electrons and ions [4], and its quantization performed *a posteriori* (see section V of reference [4]). The result again is in the form of the random phase approximation but with the ion-electron and electron-electron potentials renormalized for strong coupling

$$B(1)\phi(1,\mathbf{r}';t) = i[\left(\frac{p_1^2}{2m} + \mathcal{V}(\mathbf{q}_1,\{\mathbf{R}\})\right),\phi(1,\mathbf{r}';t)]$$

$$+ Tr_2 i[\mathcal{V}_{ee}(12), f^{(1)}(1)\phi(2,\mathbf{r}';t)]. \tag{41}$$

with

$$\mathcal{V}(\mathbf{q}_1,\{\mathbf{R}\}) = -\frac{\delta F^{(0)}(\beta \mid n)}{\delta n(\mathbf{q}_1,\{\mathbf{R}\})} \tag{42}$$

$$\mathcal{V}_{ee}(12) = \mathcal{V}_{ee}(\mathbf{q}_1,\mathbf{q}_2) = \frac{\delta^2 F^{(1)}(\beta,\{\mathbf{R}\} \mid n)}{\delta n(\mathbf{q}_1,\{\mathbf{R}\})\,\delta n(\mathbf{q}_2,\{\mathbf{R}\})} \tag{43}$$

Note that these are evaluated at the density of the equilibrium reference state. The free energy for the system $F = F^{(0)} + F^{(1)}$ has been separated into its non-interacting and excess parts. The non-interacting part is related to the Kohn-Sham potential of equilibrium DFT $\delta F^{(0)}(\beta \mid n)/\delta n(\mathbf{r},\{\mathbf{R}\}) \equiv \mu - v_{KS}(\mathbf{r},\{\mathbf{R}\})$ so

$$\mathcal{V}(\mathbf{r},\{\mathbf{R}\}) = v_{KS}(\mathbf{r},\{\mathbf{R}\}) - \mu. \tag{44}$$

9

The chemical potential μ does not contribute to the first term on the right side of Eq. (41), so this becomes the commutator with the Kohn-Sham Hamiltonian of Eq. (26).

The short time kinetic theory Eq. (39) now becomes

$$\partial_t \phi\left(1, \mathbf{r}'; t\right) + i[h_{KS}(1), \phi\left(1, \mathbf{r}'; t\right)] = -Tr_2 i[\mathcal{V}_{ee}(12), f^{(1)}(1)\phi\left(2, \mathbf{r}'; t\right)]. \tag{45}$$

The left side of this equation describes independent particle dynamics generated by the Kohn-Sham Hamiltonian

$$h_{KS}(1) = \frac{p_1^2}{2m} + \mathcal{V}\left(\mathbf{q}_1, \{\mathbf{R}\}\right). \tag{46}$$

This is precisely the generator for the dynamics of the KG method. Indeed, if $\mathcal{V}_{ee}(12)$ is set equal to zero on the right side of Eq. (45) the resulting kinetic theory is equivalent to that method. The more general short-time kinetic theory therefore provides some context for the KG method, and shows that renormalized RPA screening by the electrons is neglected in that method. Further comment on this connection is given in section VI.

The short-time kinetic equation solution as given in Appendix B determines the density response function. The result is given by the linear integral equation

$$\chi(\mathbf{r}, \mathbf{r}', t) = \chi_{KG}\left(\mathbf{r}, \mathbf{r}'; t\right) + \int_0^t dt' \int d\mathbf{r}_1 d\mathbf{r}_2 \chi_{KG}\left(\mathbf{r}, \mathbf{r}_1; t-t'\right) \mathcal{V}_{ee}\left(\mathbf{r}_1, \mathbf{r}_2\right) \chi\left(\mathbf{r}_2, \mathbf{r}'; t'\right). \tag{47}$$

Here χ_{KG} is the response function calculated with the Kohn-Sham Hamiltonian Eq. (26), i.e. that from the KG method.

V.   TIME-DEPENDENT DENSITY FUNCTIONAL THEORY

Time-dependent density functional theory is a well developed tool within dynamic electronic structure methods with a wide range of applications to problems in atomic, molecular, and extended systems in physics, chemistry, and materials science [7, 8]. Typically such applications are pure state dynamics. Formulation and application of tdDFT to the mixed state ensembles at finite temperatures of interest here is more limited [11, 20]. However, an interesting calculation of x-ray Thomson scattering for warm, dense matter conditions has been reported recently [18]. Central to that formulation are the consequences of van Leeuwen's theorem on existence and uniqueness of a time-dependent density representation [7, 8, 10]. For completeness, an extension of van Leeuwen's theorem for general mixed states, including those of thermal equilibrium, is proposed in Appendix

10

A. The argument for this extension assumes physically reasonable behavior (e.g. invertibility, analyticity) to make the point without addressing mathematical difficulties well-known in the pure state case [21].

Consider again the system of electrons in a charge-neutral background of a given ion configuration at equilibrium. The Hamiltonian is that of (10) and the initial state at time τ is given by (12). Under a time dependent perturbation $V(t) = \int d\mathbf{r} v(\mathbf{r}, t) \widehat{n}(\mathbf{r})$, its average density for $t \geq \tau$ is denoted by $n(\mathbf{r}, t \mid v)$. A consequence of van Leeuwen's theorem is the existence of a unique external perturbation $V_0(t) = \int d\mathbf{r} v_0(\mathbf{r}, t) \widehat{n}(\mathbf{r})$ such that the corresponding system without electron-electron interactions produces the same average time dependent density

$$n_0(\mathbf{r}, t \mid v_0) = n(\mathbf{r}, t \mid v). \tag{48}$$

where $n_0(\mathbf{r}, t \mid v_0)$ is the average density without electron-electron interactions, in the external potential $V_0(t)$. By continuity, it is expected that $v_0 \to 0$ as $v \to 0$ and therefore that this equivalence of densities is preserved to linear order in the two perturbations. Then, repeating the linear response analysis of Section II leads to the equivalence in the initial state

$$n_0(\mathbf{r}, \tau \mid v_0) = n(\mathbf{r}, \tau \mid v), \tag{49}$$

and at later times

$$\int_\tau^t dt' \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}'; t - t') \, \delta v(\mathbf{r}', t') = \int_\tau^t dt' \int d\mathbf{r}' \chi_0(\mathbf{r}, \mathbf{r}'; t - t') \, \delta v_0(\mathbf{r}', t') \tag{50}$$

Here, $\chi_0(\mathbf{r}, \mathbf{r}'; t)$ is the response function for the initial non-interacting system.

Equation (49) is a first condition of van Leeuwen's theorem, that the initial densities should be the same. Furthermore, since the unperturbed states are equilibrium, it follows from equilibrium DFT that the external potential for the non-interacting system at $t = \tau$ is the Kohn-Sham potential as a functional of this initial density

$$v_0(\mathbf{r}, \tau) = v_{KS}(\mathbf{r} \mid n_e). \tag{51}$$

Consequently, $\chi_0(\mathbf{r}, \mathbf{r}'; t)$ is the response function defined by the Kohn-Sham Hamiltonian, both for its equilibrium average and for the generator of its time dependence; this is then the Kubo-Greenwood response function

$$\chi_0(\mathbf{r}, \mathbf{r}'; t) = \chi_{KG}(\mathbf{r}, \mathbf{r}'; t). \tag{52}$$

11

Since this is a non-interacting system, it can be evaluated exactly in terms of the eigenvalues and eigenfunctions of the Kohn-Sham Hamiltonian.

It is a remarkable consequence of van Leeuwen's theorem that the equivalence of the densities allows the more complex interacting system response function to be related to this simpler non-interacting response function. More explicitly, from (50)

$$\chi\left(\mathbf{r}, \mathbf{r}'; t - t'\right) = \int_\tau^t dt'' \int d\mathbf{r}'' \chi_{KG}\left(\mathbf{r}, \mathbf{r}''; t - t''\right) \frac{\delta v_0(\mathbf{r}'', t'')}{\delta v(\mathbf{r}', t')}$$

$$= \chi_{KG}\left(\mathbf{r}, \mathbf{r}'; t - t'\right) + \int_\tau^t dt'' \int d\mathbf{r}'' \chi_{KG}\left(\mathbf{r}, \mathbf{r}''; t - t''\right) \frac{\delta \Delta v_0(\mathbf{r}'', t'' \mid n)}{\delta v(\mathbf{r}', t')} \quad (53)$$

In the second equality the unknown potential $v_0(\mathbf{r}, t)$ has been written as the given potential plus the "excess potential" Δv_0

$$v_0(\mathbf{r}, t) \equiv v(\mathbf{r}, t \mid n) + \Delta v_0(\mathbf{r}, t \mid n), \quad (54)$$

The notation recognizes that the one-to-one relationship of $n_0(\mathbf{r}, t \mid v_0)$ to the potential $v_0(\mathbf{r}, t)$ implies it can be inverted to give

$$\Delta v_0(\mathbf{r}, t) = \Delta v_0(\mathbf{r}, t \mid n_0) = \Delta v_0(\mathbf{r}, t \mid n). \quad (55)$$

(The first equality states the one-to-one relationship of the non-interacting potential to the non-interacting density. The second equality states that the non-interacting and interacting densities are the same, a consequence of the central property of the KS potential.) Then by the chain rule

$$\frac{\delta \Delta v_0(\mathbf{r}, t \mid n)}{\delta v(\mathbf{r}', t')} = \int_\tau^t dt_1 \int d\mathbf{r}_1 \frac{\delta \Delta v_0(\mathbf{r}, t \mid n)}{\delta n(\mathbf{r}_1, t_1)} \frac{\delta n(\mathbf{r}_1, t_1)}{\delta v(\mathbf{r}', t')}$$

$$= \int_\tau^t dt_1 \int d\mathbf{r}_1 \frac{\delta \Delta v_0(\mathbf{r}, t \mid n)}{\delta n(\mathbf{r}_1, t_1)} \chi\left(\mathbf{r}_1, \mathbf{r}'; t_1 - t'\right). \quad (56)$$

The final form for the relationship of χ to χ_{KG} becomes, setting $t' = 0$ in (53) for simplicity of notation,

$$\chi\left(\mathbf{r}, \mathbf{r}'; t\right) = \chi_{KG}\left(\mathbf{r}, \mathbf{r}'; t\right) + \int_\tau^t dt'' \int d\mathbf{r}'' \chi_{KG}\left(\mathbf{r}, \mathbf{r}''; t - t''\right) \int_\tau^t dt_1 \int d\mathbf{r}_1$$

$$\times \frac{\delta \Delta v_0(\mathbf{r}'', t'' \mid n)}{\delta n(\mathbf{r}_1, t_1)} \chi\left(\mathbf{r}_1, \mathbf{r}'; t_1\right). \quad (57)$$

The result Eq. (57) is formally exact and is simply a restatement of the consequence of van Leeuwen's theorem Eq. (48) to first order in the perturbing potentials. Interestingly,

12

the appearance of the KG response function χ_{KG} also is a consequence of this theorem which requires that the initial density of the non-interacting and interacting systems should be the same. For the initial equilibrium state that implies Eq. (51), and hence the Hamiltonian for the non-interacting system is the sum of Kohn-Sham single particle Hamiltonians. This provides an important connection with the KG method and a clarification of its logical context.

The excess potential $\Delta v_0(\mathbf{r}, t \mid n)$ remains unknown. While van Leeuwen's theorem provides its existence, the theorem does not provide the explicit functional dependence of $\Delta v_0(\mathbf{r}, t \mid n)$ upon n. However, this dependence is known initially from Eq. (51). A plausible approximation is to assume this functional form persists and that its evolution occurs entirely through the density

$$v_0(\mathbf{r}, t \mid n) \sim v_{KS}(\mathbf{r} \mid n(t)), \tag{58}$$

i.e., the functional form is slowly varying and the dominant change is due to that of its argument. This is referred to as the "adiabatic approximation" of tdDFT [7, 8, 19]. With this approximation

$$\frac{\delta \Delta v_0(\mathbf{r}'', t'' \mid n)}{\delta n(\mathbf{r}_1, t_1)} \rightarrow \frac{\delta \Delta v_{KS}(\mathbf{r}'' \mid n(t''))}{\delta n(\mathbf{r}_1, t_1)} = \frac{\delta^2 F^{(1)}[n(t'')]}{\delta n(\mathbf{r}_1, t_1) \delta n(\mathbf{r}'', t'')}$$

$$= \delta(t_1 - t'') \frac{\delta^2 F^{(1)}[n(t'')]}{\delta n(\mathbf{r}_1, t'') \delta n(\mathbf{r}'', t'')} \tag{59}$$

and the response function Eq. (57) becomes

$$\chi(\mathbf{r}, \mathbf{r}'; t) = \chi_{KG}(\mathbf{r}, \mathbf{r}'; t) + \int_\tau^t dt'' \int d\mathbf{r}'' \chi_{KG}(\mathbf{r}, \mathbf{r}''; t - t'') \int d\mathbf{r}_1$$

$$\times \frac{\delta^2 F^{(1)}[n_e]}{\delta n_e(\mathbf{r}_1) \delta n_e(\mathbf{r}'')} \chi(\mathbf{r}_1, \mathbf{r}'; t''). \tag{60}$$

The density $n(t'')$ is given by Eq. (7) so within this context of linear response it has been replaced on the right side of Eq. (60) by the reference state density $n(\mathbf{r}, t'') \rightarrow n(\mathbf{r}, \tau) = n_e(\mathbf{r})$. Note that the adiabatic approximation does not make any reference to limitations on the electron-electron or electron-ion coupling, hence is an appropriate description for matter under extreme conditions. Remarkably, it is seen that this result from tdDFT is the same as Eq. (47) from the Markov kinetic theory.

13

VI. DISCUSSION

The presentation here is complementary to that of reference [20]. The version of the van Leeuwen theorem in that reference is less comprehensive than that of the Appendix here, in that it refers only to uniqueness (not existence) and only within the context of linear response. On the other hand, the objectives of that reference were to set the stage for improvements of the adiabatic approximation while here the interest is in making connections to other methods within that approximation. Specifically, the objective of the treatment presented here has been to describe the density response function for matter under extreme conditions. This means conditions of strong Coulomb coupling with both free and bound electronic configurations. The detailed form of the interaction potential U in Eq. (1) is not important for the analysis presented here, but an important case is electrons in the presence of a given ionic configuration. Two methods for calculation have been presented, one based in kinetic theory and the other in tdDFT. In both cases the results are expressed in terms of effective interactions that can be obtained from well-developed methods of equilibrium DFT, i.e. functional derivatives of the free energy [16]. Interestingly, approximations to the kinetic theory (short-time Markov limit) and to tdDFT (adiabatic approximation) are found to give equivalent results, Eq. (47) or Eq. (60). Neither of these approximations compromises extreme conditions (although some physical processes are excluded) and hence the result is a good candidate for predictive properties. It has a form similar to that of the RPA. However, the non-interacting response function in RPA is replaced by χ_{KG} which is determined from non-interacting Kohn-Sham single particle Hamiltonians. In this way the electron-ion interaction is described by v_{KS} rather than the bare ion-electron Coulomb potential. Similarly, the RPA screening due to the electron-electron Coulomb potential is replaced by that due to the renormalized potential $\mathcal{V}_{ee}$ of Eq. (43).

The excluded physical processes alluded to above are electron-electron collisional effects. The RPA structure includes mean-field electron-electron screening but not electron-electron scattering. In contrast, for the example above of electrons in the external field of ions, the electron-ion "collisions" are treated in detail by the dynamics of the Kohn-Sham Hamiltonian determining χ_{KS}. In addition to neglecting these electron-electron collisions, the Kubo-Greenwood method is recovered only if the screening effects found here are negligible as well. Thus, an important outcome of the analysis here is to show how the Kubo-Greenwood

14

method appears as an important component of the response function calculation, and also to demonstrate its context - neglect of electron-electron scattering and dynamical screening.

Another interesting outcome is the equivalence of the response function from the short-time kinetic theory and from tdDFT in the adiabatic approximation. In hindsight this is perhaps to be expected since each becomes exact in the short time limit (e.g., compare Eqs. (51) and (58)). This close connection provides some potential to explore approximations in tdDFT beyond the adiabatic approximation. For example the collision operator, M, of the exact kinetic equation, Eq. (31), has been studied in some detail [17] and may provide a route for corresponding improvements of tdDFT applications.

VII. ACKNOWLEDGMENTS

Appendix A: A proposed generalization of van Leeuwen's theorem for mixed states

Based on the extensive studies of van Leeuwen's theorem for pure states, it is reasonable to suppose a corresponding theorem applies for mixed states as well. A complete characterization of the states and necessary conditions is not the objective here. Instead, a constructive argument, at physically plausible levels of rigor, is given to demonstrate van Leeuwen's theorem in the rather general context of ensembles or density matrices as states for the system. We do not revisit the multiple issues of a mathematically complete investigation encountered for pure states over the past two decades. Thus we assume properties such as invertibility, analyticity, etc. are satisfied as required. Readers interested in those issues should consult the recent review for pure states by Ruggenthaler et al. [21]. A more complete justification of the result presented here is under consideration for a future publication.

Consider two systems characterized by the Hamiltonians $H(t)$ and $H_1(t)$

$$H(t) = K + U + V(t), \quad H_1(t) = K + U_1 + V_1(t). \quad (A1)$$

Here, K denotes the kinetic energy, U and U_1 are general many-body potentials, and V and

15

V_1 are sums of single particle potentials

$$V(t) = \int d\mathbf{r} v(\mathbf{r}, t)\widehat{n}(\mathbf{r}), \qquad V_1(t) = \int d\mathbf{r} v_1(\mathbf{r}, t)\widehat{n}(\mathbf{r}). \tag{A2}$$

The number density operator $\widehat{n}(\mathbf{r})$ is given by (2). The expectation value of some observable corresponding to an operator X is

$$\langle X \rangle = Tr\rho X, \qquad Tr\rho = 1. \tag{A3}$$

The trace is taken over an arbitrary complete set of states defining the Hilbert space considered. The state of the system is represented by the positive, semi-definite Hermitian operator ρ normalized to unity. If it is a projection operator onto a single vector in the Hilbert space it is referred to as a pure state. Otherwise, it is a mixed state. The corresponding quantities for the second system are the same but distinguished by a subscript 1.

The time-dependence of a state $\rho(t)$ is given by the Liouville - von Neumann equation

$$\partial_t \rho(t) = -i[H(t), \rho(t)], \qquad \rho(t = 0) = \rho. \tag{A4}$$

where without loss of generality the initial time is taken to be $t = 0$. Accordingly, the average number densities for the two systems are

$$n(\mathbf{r}, t \mid v) = Tr\rho(t)\widehat{n}(\mathbf{r}) \equiv \langle \widehat{n}(\mathbf{r}); t \rangle, \qquad n_1(\mathbf{r}, t \mid v_1) = Tr\rho_1(t)\widehat{n}(\mathbf{r}) \equiv \langle \widehat{n}(\mathbf{r}); t \rangle_1 \tag{A5}$$

The notation $n(\mathbf{r}, t \mid v)$ indicates that the density is a space-time functional of $v(\mathbf{r}, t)$. Also the subscript on the bracket $\langle \widehat{n}(\mathbf{r}); t \rangle_1$ indicates an average over $\rho_1(t)$ whose dynamics is generated by $H_1(t)$. The objective here is to show that for a given $n(\mathbf{r}, t \mid v)$ there exists a unique $v_1(\mathbf{r}, t)$ such that $n_1(\mathbf{r}, t \mid v_1) = n(\mathbf{r}, t \mid v)$. The demonstration is based on direct construction of $v_1(\mathbf{r}, t)$ from all of its initial time derivatives under the assumption that the density is analytic at $t = 0$ and upon some domain of non-zero radius [7, 8, 10].

Assume there exists a $v_1(\mathbf{r}, t)$ such that the densities are equal

$$n(\mathbf{r}, t \mid v) = n_1(\mathbf{r}, t \mid v_1), \tag{A6}$$

which gives the formal definition of $v_1(\mathbf{r}, t)$. The right side evolves according to the von Neumann equation

$$\partial_t \rho_1(t) = -i[H_1(t), \rho_1(t)], \tag{A7}$$

16

or equivalently

$$\rho_1(t) = \rho_1(0) - \int_0^t dt' i\, [H_1(t'), \rho_1(t')]. \tag{A8}$$

Then Eq. (A6) becomes

$$n(\mathbf{r}, t \mid v) = \langle \widehat{n}(\mathbf{r}); 0 \rangle_1 - i \int_0^t dt' Tr\, [H_1(t'), \rho_1(t')]\, \widehat{n}(\mathbf{r})$$

$$= \langle \widehat{n}(\mathbf{r}); 0 \rangle_1 + \int_0^t dt' Tr\, \langle i\, [H_1(t'), \widehat{n}(\mathbf{r})]; t' \rangle_1, \tag{A9}$$

where the second line follows from the cyclic invariance of the trace. A further iteration of Eq. (A8) gives

$$n(\mathbf{r}, t \mid v) = \langle \widehat{n}(\mathbf{r}); 0 \rangle_1 + \int_0^t dt' i\, \langle [H_1(t'), \widehat{n}(\mathbf{r})]; 0 \rangle_1$$

$$+ (i)^2 \int_0^t dt' \int_0^{t'} dt'' \langle [H_1(t''), [H_1(t'), \widehat{n}(\mathbf{r})]]; t'' \rangle_1 \tag{A10}$$

This is still exact. The right side is a functional of $v_1(\mathbf{r}, t)$ and hence gives its formal definition in terms of the given density $n(\mathbf{r}, t \mid v)$. Suppose the latter is analytic at $t = 0$ so that its derivatives exist at arbitrary order. Then Eq. (10) can be expanded in powers of t and its coefficients of each term identified. A first condition is that the initial state ρ_1 must deliver the same density as ρ

$$n(\mathbf{r}, t \mid v) = \langle \widehat{n}(\mathbf{r}); 0 \rangle_1 = Tr \rho_1 \widehat{n}(\mathbf{r}), \tag{A11}$$

Next, for example, the first two time derivatives are

$$\partial_t n(\mathbf{r}, t \mid v) = i\, \langle [H_1(t), \widehat{n}(\mathbf{r})]; 0 \rangle_1$$

$$+ (i)^2 \int_0^t dt'' \langle [H_1(t''), [H_1(t), \widehat{n}(\mathbf{r})]]; t'' \rangle_1 \tag{A12}$$

$$\partial_t^2 n(\mathbf{r}, t \mid v) = i\, \langle [\partial_t V_1(t), \widehat{n}(\mathbf{r})]; 0 \rangle_1$$

$$+ (i)^2 \langle [H_0(t), [H_1(t), \widehat{n}(\mathbf{r})]]; t \rangle_1. \tag{A13}$$

The first two derivatives at $t = 0$ are now readily identified.

$$\partial_t n(\mathbf{r}, t \mid v)\, |_{t=0} = i\, \langle [H_1(0), \widehat{n}(\mathbf{r})]; 0 \rangle_1. \tag{A14}$$

and

$$\partial_t^2 n(\mathbf{r}, t \mid v)\, |_{t=0} = i\, \langle [\partial_t V_1(t)\, |_{t=0}, \widehat{n}(\mathbf{r})]; 0 \rangle_1$$

$$+ (i)^2 \langle [H_1(0), [H_1(0), \widehat{n}(\mathbf{r})]]; 0 \rangle_1. \tag{A15}$$

17

Eq. (A14) determines the initial value $v_1(\mathbf{r}', 0)$

$$\int d\mathbf{r}' v_1(\mathbf{r}', 0) \chi_1(\mathbf{r}, \mathbf{r}') = \partial_t n(\mathbf{r}, t \mid v) \mid_{t=0} -i \left\langle \left[(K_1 + U_1), \widehat{n}(\mathbf{r}) \right]; 0 \right\rangle_1, \qquad (A16)$$

where $\chi(\mathbf{r}, \mathbf{r}')$ is the static response function

$$\chi_1(\mathbf{r}, \mathbf{r}') = i \left\langle [\widehat{n}(\mathbf{r}'), \widehat{n}(\mathbf{r})] \right\rangle_1. \qquad (A17)$$

The initial state ρ_1 is taken to be independent of $v_1(\mathbf{r}, 0)$ so that Eq. (A16) is a linear equation for $v_1(\mathbf{r}', 0)$. In van Leeuwen's original theorem, this is interpreted as a requirement that the average current densities of the two systems must be the same for the initial state, using the continuity equation. Here it is seen that this can be imposed by the choice of $v_1(\mathbf{r}, 0)$. Next, equation Eq. (A15) determines the first derivative of $v_1(\mathbf{r}', t)$

$$\int d\mathbf{r}' \partial_t v_1(\mathbf{r}', t) \mid_{t=0} \chi_1(\mathbf{r}, \mathbf{r}') = \partial_t^2 n(\mathbf{r}, t \mid v) \mid_{t=0} -i \left\langle [H_1(0), i[H_1(0), \widehat{n}(\mathbf{r})]]; 0 \right\rangle_1 \qquad (A18)$$

All ingredients on the right side of this equation are known from the first two equations, (A11) and (A16).

The structure of Eq. (A18) is similar for all higher derivatives as well. Return to Eq. (A12) and differentiate it $m+1$ times at $t=0$, for $m > 0$

$$\partial_t^{m+1} n(\mathbf{r}, t \mid v) \mid_{t=0} = \partial_t^m Tri \left[H_1(t), \rho_1(t) \right] \widehat{n}(\mathbf{r}) \mid_{t=0}$$

$$= \sum_{p=0}^{m} \frac{m!}{p!(m-p)!} Tri \left[\partial_t^{m-p} V_1(t), \partial_t^p \rho_1(t) \right] \widehat{n}(\mathbf{r}) \mid_{t=0}$$

$$= \left\langle [\partial_t^m V_1, \widehat{n}(\mathbf{r})]; 0 \right\rangle_0 \mid_{t=0} + \sum_{p=1}^{m} \frac{m!}{p!(m-p)!} Tri \left[\partial_t^{m-p} H_1(t), \partial_t^p \rho_1(t) \right] \widehat{n}(\mathbf{r}) \mid_{t=0} \qquad (A19)$$

Rearranging gives

$$\int d\mathbf{r}' \partial_t^m v_1(\mathbf{r}', t) \mid_{t=0} \chi_1(\mathbf{r}, \mathbf{r}') = \partial_t^{m+1} n(\mathbf{r}, t \mid v) \mid_{t=0}$$

$$- \sum_{p=1}^{m} \frac{m!}{p!(m-p)!} Tri \left[\partial_t^{m-p} H_1(t), \partial_t^p \rho_1(t) \right] \widehat{n}(\mathbf{r}) \mid_{t=0} \qquad (A20)$$

The highest derivative of the second term on the right side is of order $m-1$ and hence denotes a quantity depending on known derivatives of lower order than m.

The argument above constitutes a demonstration of the *existence* of $v_1(\mathbf{r}, t)$ in the domain of analyticity of the chosen density about $t = 0$, subject to constraints on the initial state

and the invertibility of $\chi_1(\mathbf{r}, \mathbf{r}')$. The argument also can be used to demonstrate *uniqueness*, as follows. Consider two systems that are the same except for their external potentials

$$H(t) = K + U + V(t), \qquad H_1(t) = K + U + V_1(t). \tag{A21}$$

If it is assumed both potentials give the same density, then the construction of their derivatives given above can be applied to each potential. The result is that the equations for $\partial_t^m v(\mathbf{r}, t)\mid_{t=0}$ and for $\partial_t^m v_1(\mathbf{r}, t)\mid_{t=0}$ are the same (up to a constant). Consequently $v(\mathbf{r}, t)$ and $v_1(\mathbf{r}, t)$ are the same (they can differ by a function of time $c(t)$ since the Liouville-von Neumann equation is invariant under such a change). In summary, there is a one-to-one relationship of the density and the single-particle potential for a given system.

Appendix B: Solution to Markov kinetic equation

A formal solution to the kinetic equation, Eq. (45) for $\phi(1, \mathbf{r}'; t)$ is

$$\phi(1, \mathbf{r}'; t) = \phi_{KS}(1, \mathbf{r}'; t) - \int_0^t dt' e^{-iH_{KS}(t-t')} \int d\mathbf{r}_1 d\mathbf{r}_2 \mathcal{V}_{ee}(\mathbf{r}_1, \mathbf{r}_2) I(1, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}', t') e^{iH_{KS}(t-t')}, \tag{B1}$$

where

$$\phi_{KS}(1, \mathbf{r}'; t) = e^{-iH_{KS}t} \phi(1, \mathbf{r}'; 0) e^{iH_{KS}t}, \tag{B2}$$

$$H_{KS} = \sum_{i=1}^{N_e} h_{KS}(i), \qquad h_{KS}(i) = \frac{p_i^2}{2m} + v_{KS}(\mathbf{q}_i, \{\mathbf{R}\}). \tag{B3}$$

Recall that $v_{KS}(\mathbf{q}_i, \{\mathbf{R}\})$ is a functional of the initial equilibrium density and therefore H_{KS} is time independent. Also,

$$
\begin{aligned}
I(1, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}', t') &\equiv Tr_2 i[\delta(\mathbf{r}_1 - \mathbf{q}_1)\,\delta(\mathbf{r}_2 - \mathbf{q}_2)\,, f^{(1)}(1)\phi(2, \mathbf{r}'; t')] \\
&= i[\delta(\mathbf{r}_1 - \mathbf{q}_1)\,, f^{(1)}(1)] Tr_2 \phi(2, \mathbf{r}'; t')\,\delta(\mathbf{r}_2 - \mathbf{q}_2) \\
&= -\phi(1, \mathbf{r}_1; 0)\,\chi(\mathbf{r}_2, \mathbf{r}'; t')\,.
\end{aligned}
\tag{B4}
$$

The definition of $\phi(1, \mathbf{r}; 0)$ in Eq. (39) and of $\chi(\mathbf{r}, \mathbf{r}_2; t')$ in Eq. (38) has been used in the last line.

The response function is given by Eq. (34)

$$\chi(\mathbf{r}, \mathbf{r}'; t) = Tr_1 \delta(\mathbf{r} - \mathbf{q}_1)\,\phi(1, \mathbf{r}'; t)\,. \tag{B5}$$

19

With Eq. (B1) this becomes

$$\chi\left(\mathbf{r}, \mathbf{r}'; t\right) = \chi_{KG}\left(\mathbf{r}, \mathbf{r}'; t\right) + \int_0^t dt' \int d\mathbf{r}_1 d\mathbf{r}_2 \mathcal{V}_{ee}\left(\mathbf{r}_1, \mathbf{r}_2\right) Tr_1 \delta\left(\mathbf{r} - \mathbf{q}_1\right) e^{-iH_{KS}(t-t')} \phi\left(1, \mathbf{r}_1; 0\right) e^{iH_{KS}(t-t')} \chi\left(\mathbf{r}_2, \mathbf{r}'; \right.$$

$$= \chi_{KG}\left(\mathbf{r}, \mathbf{r}'; t\right) + \int_0^t dt' \int d\mathbf{r}_1 d\mathbf{r}_2 \chi_{KG}\left(\mathbf{r}, \mathbf{r}_1; t - t'\right) \mathcal{V}_{ee}\left(\mathbf{r}_1, \mathbf{r}_2\right) \chi\left(\mathbf{r}_2, \mathbf{r}'; t'\right) \qquad (B6)$$

where the Kubo-Greenwood response function is

$$\chi_{KG}\left(\mathbf{r}, \mathbf{r}'; t\right) = Tr_1 \delta\left(\mathbf{r} - \mathbf{q}_1\right) \phi_{KS}\left(1, \mathbf{r}'; t\right). \qquad (B7)$$

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