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EDITORS' CHOICE

Contributions to Plasma Physics

On the Kubo-Greenwood model for electron conductivity

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Currently, the most common approach to calculate transport properties for materials under extreme conditions is based on the phenomenological Kubo-Greenwood method. The results of an inquiry into the justification and context of that model are summarized here. Specifically, the basis for its connection to equilibrium density functional theory (DFT) and the assumption of static ions are discussed briefly.

KEYWORDS
DFT, extreme conditions, kinetic theory, Kubo-Greenwood

1 | INTRODUCTION AND MOTIVATION

Recent interest in matter under extreme conditions provides motivation for new theoretical methods to describe the thermodynamic and transport properties of such systems. The relevant conditions include those of high-pressure materials, warm dense matter, and high-temperature plasmas.[1] The generic example is a system of electrons and ions at equilibrium. Thermodynamic properties such as pressure and free energy are typically described via ab initio molecular dynamics (AIMD) simulation for the classical ions, with the effective forces because of the electrons calculated from finite temperature density functional theory (DFT).[2] Significant progress has been made within DFT for this purpose. In contrast, the exploitation of equilibrium DFT results, particularly Kohn–Sham quantities, for the calculation of electronic transport properties is far from obvious. Nevertheless, plausible but uncontrolled approximations are used in practice to calculate transport properties by promoting the Kohn–Sham Hamiltonian from a tool for constructing the equilibrium density to a generator for the electron dynamics. This bold leap of faith accomplishes the objective of a calculation incorporating the equilibrium tools of AIMD and DFT into the calculation of transport properties.[3,4] The approach is known as the Kubo-Greenwood model. The objective here is to report the results of an inquiry into the justification and context of this approach. Two issues are addressed: the origin of the Kohn–Sham dynamics and the assumption of a frozen ion configuration. Details of these results and their derivation will be presented elsewhere. Although the discussion is focused on electron conductivity, the analysis also applies to other transport coefficients, for example, thermal conductivity and viscosity.

2 | GREEN-KUBO CONDUCTIVITY AND KUBO-GREENWOOD APPROXIMATION

The starting point for the analysis is the formally exact Green-Kubo expression for the frequency-dependent electron conductivity in terms of the current autocorrelation function

$$Re\ \ \sigma(\omega) = \frac{1}{\omega}(1 - e^{-\beta\omega})Re \int_0^\infty dt e^{i\omega t}\psi(t),\ \ \psi(t) = \frac{1}{3V}\langle \widehat{\mathbf{J}}(t) \cdot \widehat{\mathbf{J}} \rangle \tag{1}$$

where $\widehat{\mathbf{J}}$ is the electron current operator, V is the volume, β is the inverse temperature, and the brackets denote an equilibrium grand canonical average. A two-component system comprised of electrons and ions at equilibrium is assumed. Units such as $\hbar = 1$ are used. The ions are considered to be classical, while the electrons are fully quantum mechanical. Equilibrium averages are considered jointly over the states of the electrons and ions. In the following, the electron average is performed first, followed

by the ion average. Thus,

$$\psi(t) = \langle \psi_e(t) \rangle_i = \sum_{N_i} \frac{1}{h^{3N_i} N_i!} \int \{d\mathbf{R}\}\{d\mathbf{P}\} \rho_i(\{\mathbf{R},\mathbf{P}\}) \psi_e(t) \tag{2}$$

where $\{\mathbf{R},\mathbf{P}\}$ denotes the N_i position and momentum vectors for the ions. In addition, $\rho_i(\{\mathbf{R},\mathbf{P}\})$ is the equilibrium ion density matrix defined in terms of the ion Hamiltonian, including the adiabatic (Born-Oppenheimer) potential energy surface due to the electrons. As the classical ion average can be implemented by AIMD (ergodic hypothesis), the difficult many-body problem therefore occurs for the electron average $\psi_e(t)$

$$\psi_e(t) = \psi_e(t \mid \{\mathbf{R}(t)\}) = \frac{1}{3V} \sum_{N_e} Tr^{(N_e)} \widehat{\rho}_e(\{\mathbf{R}(t)\}) \tilde{\mathbf{J}}(t \mid \{\mathbf{R}(t)\}) \cdot \widehat{\mathbf{J}}. \tag{3}$$

The notation $\psi_e(t \mid \{\mathbf{R}(t)\})$ and $\tilde{\mathbf{J}}(t \mid \{\mathbf{R}(t)\})$ denotes a *functional* dependence on the history of the ion configuration $\{\mathbf{R}(\tau)\}$ for all times $\tau \le t$. That history is generated separately by means of an AIMD simulation. In contrast, the density operator for N_e electrons, $\widehat{\rho}_e(\{\mathbf{R}(t)\})$, is a function of the instantaneous ion configuration at time t

$$\widehat{\rho}_e(\{\mathbf{R}(t)\}) = e^{\beta\Omega_e(\{\mathbf{R}(t)\})} e^{-\beta(H_e + U_{ei}(\{\mathbf{R}(t)\}) - \mu_e N_e)}. \tag{4}$$

The electron Hamiltonian $H_e + U_{ei}(\{\mathbf{R}(t)\})$ is for all electrons with their Coulomb interactions for each pair and all electron–ion Coulomb interactions. The corresponding Heisenberg time dependence for the electron current is given by

$$\partial_t \tilde{\mathbf{J}}(t \mid \{\mathbf{R}(t)\}) = i[(H_e + U_{ei}(\{\mathbf{R}(t)\})), \tilde{\mathbf{J}}(t \mid \{\mathbf{R}(t)\})]. \tag{5}$$

The evaluation of $\psi_e(t \mid \{\mathbf{R}(t)\})$ entails confronting the full-quantum, many-body problem for the electrons in a given moving ion configuration. For the complex states of interest here, no adequate first principles theory is currently available.

A practical, plausible but phenomenological mitigation of this formidable Green-Kubo expression results from replacing the electron many-body Hamiltonian by a mean field Hamiltonian comprised of a sum of independent Kohn–Sham single-particle Hamiltonians,

$$H_e + U_{ei}(\{\mathbf{R}(t)\}) \to \sum_{j=1}^{N_e} h_{KS}(j, \{\mathbf{R}\}), \tag{6}$$

$$h_{KS}(j, \{\mathbf{R}\}) = \frac{p_j^2}{2m_e} + v_{KS}(\mathbf{r}_j, \{\mathbf{R}\} \mid n_e). \tag{7}$$

Here, $\mathbf{R} = \mathbf{R}(t=0)$. Thus, in addition to the independent particle approximation, there is the assumption that the ions are frozen for the duration of the electron dynamics. Each particle has an effective interaction with all ions via the Kohn–Sham potential as a functional of the average electron density $n_e(\mathbf{r}, \{\mathbf{R}\})$

$$v_{KS}(\mathbf{r}_j, \{\mathbf{R}\} \mid n_e) = -\sum_{i=1}^{N_i} \frac{Ze^2}{|\mathbf{r}_j - \mathbf{R}_i|} + \int d\mathbf{r} \frac{e^2}{|\mathbf{r}_j - \mathbf{r}|} n_e(\mathbf{r}, \{\mathbf{R}\}) + \frac{\delta F_{xc}[n_e]}{\delta n_e(\mathbf{r}_j, \{\mathbf{R}\})}. \tag{8}$$

The first term is the Coulomb interaction, and the second is the Hartree interaction, while the third is an effect due to the average exchange and correlation among the electrons via the corresponding free energy contribution $F_{xc}[n_e]$. Calculation of the Kohn–Sham potential and the average electron density are the central problems of DFT, requiring determination of the eigenvalues and eigenfunctions of $h_{KS}(i, \{\mathbf{R}\})$ as well. As noted above, this is a well-developed formalism. With the assumed independent particle Hamiltonian, it is now straightforward to calculate $\psi_e(t, \{\mathbf{R}\})$ in terms of these eigenvalues and eigenfunctions. The final average over the frozen ion configurations then is implemented by the ergodic hypothesis and AIMD

$$\psi(t) = \lim_{T\to\infty} \frac{1}{T} \int_0^T d\tau \psi_e(t, \{\mathbf{R}(\tau)\}). \tag{9}$$

In practice, the time average is approximated as an algebraic average of a small number of "snapshots" of different ion configurations.

Equations (6)–(9) define the Kubo-Greenwood approximation for Equation (3).[3]

3 | ORIGIN AND CONTEXT OF KUBO-GREENWOOD APPROXIMATION

In the Kubo-Greenwood model, the complex Coulomb interactions among the electrons and with the ions is replaced by independent particles. Furthermore, their interactions with the ions occur via the Kohn–Sham potential, which originates in the

Euler equation of DFT for the equilibrium of free energy. What is the justification for, and interpretation of, this unusual approximation? To answer this, return to the original Green-Kubo form and write the time correlation function in a representation appropriate for a kinetic theory evaluation

$$\psi_e(t \mid \{\mathbf{R}\}) = \frac{1}{3V} Tr_1 n_e(\mathbf{r}_1\{\mathbf{R}\})\phi(v_1) e\mathbf{v}_1 \cdot \mathcal{J}\{x_1 t \mid \{\mathbf{R}(t)\}\}, \tag{10}$$

,

$$\mathcal{J}(x_1, t \mid \{\mathbf{R}(t)\}) = \frac{1}{n_e(\mathbf{r}_1, \{\mathbf{R}\})\phi(v_1)} \sum_{N_e} \frac{1}{(N_e - 1)!} Tr_{2,\ldots,N_e} \rho_e(x_1, \ldots, x_{N_e}; \{\mathbf{R}\}) \mathbf{J}(-t). \tag{11}$$

Here, $x_i = \{\mathbf{r}_i, \mathbf{v}_i\}$ denotes the position and velocity vectors for particle i, and $\varphi(v)$ is the Maxwell-Boltzmann distribution. As the current $\mathbf{J}$ is the sum of single-particle operators $e\mathbf{v}_i$, it is possible to carry out the trace formally over all particles except one, leaving the single-particle representation (10). Of course, the difficult many-body problem remains in the evaluation of $\mathcal{J}(x_1, t \mid \{\mathbf{R}(t)\})$. It satisfies an exact "kinetic equation"[5]

$$\partial_t \mathcal{J}(x_1, t \mid \{\mathbf{R}(t)\}) + Tr_2 \mathcal{L}(x_1, x_2, t \mid \{\mathbf{R}(t)\}) \mathcal{J}(x_2, t \mid \{\mathbf{R}(t)\}) = 0, \tag{12}$$

where the generator for the dynamics $\mathcal{L}(x_1, x', t \mid \{\mathbf{R}(t)\})$ is defined in terms of higher-order time correlation functions. This exact representation is useful for addressing the question of origin and context of the Kubo-Greenwood model.

An approximation for $\mathcal{L}(x, x', t \mid \{\mathbf{R}(t)\})$ that does not contravene the conditions of strong Coulomb coupling or other extreme conditions is the Markov limit

$$\mathcal{L}(x, x', t \mid \{\mathbf{R}(t)\}) \to \mathcal{L}(x, x', t = 0, \{\mathbf{R}\}) \tag{13}$$

This means that the generator of the time dependence is the same at all times; as written, this approximation is exact at $t = 0$. At this point, we specialize to the semi-classical limit in which the electrons are treated as classical particles but the ion–electron Coulomb interaction is regularized at short distances (see, e.g., ref. [6]). Remarkably, this generator then can be evaluated without further approximation to give the kinetic equation[7]

$$\begin{aligned} &(\partial_t + \mathbf{v} \cdot \nabla_{\mathbf{r}} - m^{-1} \nabla_{\mathbf{r}} \mathcal{V}_{ie}(\mathbf{r}, \{\mathbf{R}\}) \cdot \nabla_{\mathbf{v}}) \mathcal{J}(x, \{\mathbf{R}\}, t) \\ &= -\mathbf{v} \cdot \nabla_{\mathbf{r}} \beta \int dx' \mathcal{V}_{ee}(\mathbf{r}, \mathbf{r}', \{\mathbf{R}\}) \varphi(v') n(\mathbf{r}', \{\mathbf{R}\}) \mathcal{J}(x', \{\mathbf{R}\}, t). \end{aligned} \tag{14}$$

The left side describes the motion of independent particles interacting with the ions via a "renormalized" potential, which is found to be

$$\mathcal{V}_{ie}(\mathbf{r}, \{\mathbf{R}\}) = v_{KS}(\mathbf{r}, \{\mathbf{R}\} \mid n_e), \tag{15}$$

where $v_{KS}(\mathbf{r}, \{\mathbf{R}\} \mid n_e)$ is the Kohn–Sham potential defined in terms of the classical electron free energy functional. This is precisely the dynamics generated by the Kubo-Greenwood model (in its classical limit)!

If these particles were truly independent, then the right side of Equation (14) would vanish. This is not the case for the kinetic theory here, showing that the Kubo-Greenwood model neglects an interaction among these particles. The right side of Equation (14) describes a dynamical screening due to the renormalized electron–electron interaction

$$\mathcal{V}_{ee}(\mathbf{r}, \mathbf{r}', \{\mathbf{R}\}) = -\beta^{-1} c(\mathbf{r}, \mathbf{r}', \{\mathbf{R}\}), \tag{16}$$

where $c(\mathbf{r}, \mathbf{r}', \{\mathbf{R}\})$ is the electron direct correlation function.[8] In summary, the Kubo-Greenwood model (in its semi-classical limit) is shown to be given by the exact short-time dynamics with neglect of the dynamical screening.

4 | KUBO-GREENWOOD WITH ION DYNAMICS

Return now to the exact Green-Kubo form (3) and introduce the Kubo-Greenwood approximation (6) but without the additional assumption of static ions

$$H_e + U_{ei}(\{\mathbf{R}(t)\}) \to \sum_{i=1}^{N_e} h_{KS}(j, \{\mathbf{R}(t)\}), \tag{17}$$

$$h_{KS}(j, \{\mathbf{R}(t)\}) = \frac{p_j^2}{2m_e} + v_{KS}(\mathbf{r}_j, \{\mathbf{R}(t)\} \mid n_e). \tag{18}$$

As the Hamiltonian is for independent particles, the correlation function (3) can be reduced to a single-particle average

$$\psi_e(t, \mid \{\mathbf{R}(t)\}) = \frac{1}{3V} Tr_1 n(\{1, \mathbf{R}(t)\}) U^\dagger(1, t) \mathbf{j}(1) U(1, t)(1 - n(1, \{\mathbf{R}(t)\})) \cdot \mathbf{j}(1), \tag{19}$$

where $\mathbf{j}(1) = e\mathbf{v}_1$, and $n(1, \{\mathbf{R}_k(t)\})$ is the Fermi occupation number operator

$$n(1, \{\mathbf{R}_k(t)\}) = (e^{\beta(h_{KS}(1,\{\mathbf{R}_k(t)\})-\mu)} + 1)^{-1}. \tag{20}$$

The single-particle time dependence is obtained from

$$U(1,t) = T\exp\left(-i\int_0^t \overline{\varepsilon}(\tau)d\tau\right), \tag{21}$$

where T is a time-ordering operator (earlier times to the right). The quantity $\overline{\varepsilon}(\tau)$ has matrix elements in a representation using the eigenvalues of $h_{KS}(1, \{\mathbf{R}_k(t)\})$

$$\overline{\varepsilon}_{\kappa_1(t),\kappa_2(t)}(\tau) = \sum_{\kappa(\tau)} c(\kappa_1(t), \kappa(\tau))\varepsilon_{\kappa(\tau)}(\{\mathbf{R}(\tau)\})c(\kappa(\tau), \kappa_2(t)). \tag{22}$$

The notation $\kappa(t)$ labels the eigenfunction $h_{KS}(1, \{\mathbf{R}(t)\})$ with eigenvalue $\varepsilon_{\kappa(t)}(\{\mathbf{R}(t)\})$. The coefficients $c(\kappa_1(t), \kappa(\tau))$ are overlap integrals between the eigenfunctions of $h_{KS}(1, \{\mathbf{R}(\tau)\})$ and those of $h_{KS}(1, \{\mathbf{R}(t)\})$.

Consider first the case of static ions $\{\mathbf{R}(t)\} \to \{\mathbf{R}\}$. Then, (19) can be evaluated using the eigenfunctions and eigenvalues of $h_{KS}(1, \{\mathbf{R}\})$

$$\psi_e(t, \{\mathbf{R}\}) = \frac{1}{3V}\sum_{\kappa_1,\kappa_2} Tr_1 n_{\kappa_1}(\{\mathbf{R}\})e^{i(\varepsilon_{\kappa_1}(\{\mathbf{R}\})-\varepsilon_{\kappa_2}(\{\mathbf{R}\}))t}\ \mathbf{j}_{\kappa_1\kappa_2}(1 - n_{\kappa_2}(\{\mathbf{R}\}))\cdot\mathbf{j}_{\kappa_2\kappa_1}, \tag{23}$$

$$n_{\kappa_1}(\{\mathbf{R}\}) = (e^{\beta(\varepsilon_{\kappa_1}(\{\mathbf{R}\})-\mu)} + 1)^{-1}. \tag{24}$$

Here, $\varepsilon_\kappa(\{\mathbf{R}\})$ is an eigenvalue of $h_{KS}(1, \{\mathbf{R}\})$. These are the Kubo-Greenwood results.

More generally, with $\{\mathbf{R}(t)\}$, Equation (19) can be evaluated using the eigenfunctions of $h_{KS}(1, \{\mathbf{R}(t)\})$ as a basis set

$$\psi_e(t, \{\mathbf{R}(t)\}) = \frac{1}{3V}\sum_{\kappa_1,\kappa_2} Tr_1 n_{\kappa_1(t)}(\{\mathbf{R}(t)\})U^\dagger_{\kappa_1(t)\kappa_4(t)}(t)\mathbf{j}_{\kappa_4\kappa_3}U_{\kappa_3(t)\kappa_2(t)}(t)$$
$$\times(1 - n_{\kappa_2(t)}(\{\mathbf{R}(t)\}))\cdot\mathbf{j}_{\kappa_2(t)\kappa_1(t)}. \tag{25}$$

The evaluation of $U_{\kappa_3(t)\kappa_2(t)}(t)$ now is somewhat more complex as it entails the overlap integrals $c(\kappa_1(t), \kappa(\tau))$ for all $\tau < t$. In practice, the time evolution of the ions is provided by AIMD on a discrete set of times, the ion time step. Then, $U_{\kappa_3(t)\kappa_2(t)}(t)$ can be written as an ordered product for each time interval. If the time correlation function $\psi_e(t, \{\mathbf{R}(t)\})$ decays sufficiently rapidly, only a few members of this product might be required. For any finite time dependence for the ions, the time integral of Equation (1) will entangle the electron and ion dynamics so that the usual Kubo-Greenwood form will no longer hold.

5 | DISCUSSION

The analysis summarized in Section 3 provides partial support for the Kubo-Greenwood phenomenology (origin of the assumed independent single-particle dynamics based on the equilibrium Kohn–Sham Hamiltonian) and its context (nature of the corrections due to interactions among these "quasi-particles"). The latter corrections can be incorporated through the exact solution to the kinetic equation (14), giving rise to a random-phase approximation form with a Kubo-Greenwood polarization function and electron–electron interactions replaced by Equation (16). Still missing in this kinetic equation are the effects of electron–electron collisions (ion–electron collisions are, in fact, accurately described by Equation (14)). The effects of these collisions can be added via a single relaxation time model collision operator. Their importance has been the subject of recent investigations.[9,10]

The effects of ion motion during the single-particle Kohn–Sham electron dynamics are described in Section 4. The inclusion of these effects, while still within the context of Kohn–Sham calculations, compromises some of the simplicity of the Kubo-Greenwood model. It is expected that the time scales of the electron and ion dynamics differ by roughly the square root of their mass ratio. It remains to determine how rapidly the electron-averaged correlation function $\psi_e(t\,|\,\{\mathbf{R}(t)\})$ decays in order to assess the importance of ion dynamics.

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