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Kubo–Greenwood approach to conductivity in dense plasmas with average atom models

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ABSTRACT

A new formulation of the Kubo–Greenwood conductivity for average atom models is given. The new formulation improves upon previous treatments by explicitly including the ionic-structure factor. Calculations based on this new expression lead to much improved agreement with *ab initio* results for DC conductivity of warm dense hydrogen and beryllium, and for thermal conductivity of hydrogen. We also give and test a slightly modified Ziman–Evans formula for the resistivity that includes a non-free electron density of states, thus removing an ambiguity in the original Ziman–Evans formula. Again, results based on this expression are in good agreement with *ab initio* simulations for warm dense beryllium and hydrogen. However, for both these expressions, calculations of the electrical conductivity of warm dense aluminum lead to poor agreement at low temperatures compared to *ab initio* simulations.

1. Introduction

An important aspect of modeling warm and hot dense matter is the calculation of electron thermal and electrical conductivities. The former is of particular relevance in the field of inertial confinement fusion [1,2] where it is the main phenomenon that determines the ablation of the cold deuterium/tritium fuel. Currently, we have no reliable model that can predict accurate thermal and electrical conductivities across all temperature and density regimes of interest. In particular, as we move out of the degenerate electron regime, the reliable method of Kohn–Sham density functional theory molecular dynamics (KS-DFT-MD) coupled with the Kubo–Greenwood formalism [3–6] quickly becomes computationally prohibitive. In the degenerate, or nearly degenerate regimes, this method is thought to be accurate and agrees with experiments for materials under normal conditions [7].

Average atom models provide a computationally efficient alternative at the cost of physical accuracy. The central idea is that one tries to calculate the properties of one atom in the plasma that is supposed to represent the average of all atoms in the plasma. Average atom models have been used successfully for many years for equation of state calculations [8–13]. They have also been used for electrical conductivity calculations, primarily by coupling to the Ziman–Evans (ZE) formula [14–20]. Recently, a systematic comparison of calculations of electrical conductivity using this method against Kubo–Greenwood KS-DFT-MD calculations [14] showed generally very good agreement between the methods provided that a judicious choice was made when coupling the average atom model to the ZE formula. However, the ZE formula, unlike the KG method, is not easily generalized to thermal conductivity or optical conductivity. The latter is useful as it can be used to calculate other optical properties, including opacity and reflectivity [21].

A formulation of the Kubo–Greenwood method for average atom models has been developed by Johnson and co-workers [22–24]. However, a subsequent systematic analysis of the method compared to KS-DFT-MD showed some serious inaccuracies [25]. Unlike the ZE formulation, Johnson's KG formulation does not make an explicit account of the ion–ion structure factor $S(k)$. In this work, we give an alternative derivation of the KG formulation for average atom models that explicitly accounts for $S(k)$. The new formulation recovers Johnson's result when $S(k) = 1$. We also give the equations for thermal and optical conductivity.

To evaluate this new formulation, we make comparisons to KS-DFT-MD calculations for hydrogen [1] and beryllium [5]. We also compare to other models [7,15] and experiments for aluminum [26,27]. We use the recently developed pseudoatom molecular dynamics (PAMD) [28,29] to generate the necessary inputs for the KG equation.

In addition to this, we present a slightly modified Ziman–Evans formula that takes into account a non-free electron density of states (DOS). The original ZE formula assumes a free electron DOS and this leads to an ambiguity in the choice of chemical potential and density of scattering electrons. This point was discussed in detail in Reference 14. The present reformulation recovers the original form of the ZE equation when the DOS goes to the free electron form and removes the ambiguity when the DOS is not free electron like. We

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compare calculations based on this new ZE formulation to the new KG formulation and to the KS-DFT-MD results.

The structure of this paper is as follows. In section II we derive the Kubo–Greenwood expression for average atom models with explicit account of the ion–ion structure factor. We also give the expression for the thermal conductivity. In section III, we show how the Ziman–Evans formula for the inverse resistivity is modified to account for a non-free electron density of states. In section IV, we discuss the connection of these formulas to the pseudoatom molecular dynamics (PAMD) average atom model. In section V, we use the PAMD model with the new KG and ZE expressions to calculate the DC electrical conductivity of warm dense hydrogen, beryllium and aluminum, and compare to available simulations, models and experiments. For hydrogen we also compare thermal conductivity calculations to KS-DFT-MD simulation results. Lastly, in section VI, we draw our conclusions. Throughout we use Hartree atomic units in which $\hbar = m_e = e = 1$.

2. Kubo–Greenwood approximation

The Kubo–Greenwood expression for the conductivity is [4]

$$\sigma(\omega) = \frac{-2\pi}{V}\int d\epsilon \frac{f(\epsilon_m) - f(\epsilon_n)}{\omega}\int d^3k_m \int d^3k_n \times \left\langle |J_{mn}|^2 \right\rangle \delta(\epsilon_m - \epsilon - \omega)\delta(\epsilon_n - \epsilon) \tag{1}$$

with

$$J_{mn} \equiv \int_V d^3r \psi^*_{\boldsymbol{k}_m}(\boldsymbol{r})\hat{\boldsymbol{v}}_z \psi_{\boldsymbol{k}_n}(\boldsymbol{r}) \tag{2}$$

where $\epsilon_{n(m)} = k^2_{n(m)}/2$ is the energy of the initial (final) electron state and $\psi_{\boldsymbol{k}_{n(m)}}(\boldsymbol{r})$ is the corresponding wave function, $f(\epsilon)$ is the Fermi–Dirac occupation factor and $\hat{\boldsymbol{v}}_z$ is the velocity operator in the $\hat{\boldsymbol{z}}$ direction. Following Evans [30], we now assume that the potential felt by a electron is of muffin-tin form. In this widely used approximation the total scattering potential is the sum of non-overlapping potentials, centered on each nuclear site. Each muffin-tin potential is contained in a sphere of volume V_{MT}. Again, following Evans [30], we further assume that the wave function inside each sphere is given by

$$\psi_{\boldsymbol{k}_n}(\boldsymbol{r}) = \bar{\psi}_{\boldsymbol{k}_n}(\boldsymbol{r}) e^{i\boldsymbol{k}_n \cdot \boldsymbol{R}_\alpha} \tag{3}$$

where

$$\bar{\psi}_{\boldsymbol{k}_n}(\boldsymbol{r}) = \sum_l \sum_m i^l e^{i\delta_l(k_n)} Y_{lm}\left(\hat{\boldsymbol{k}}_n\right) Y^*_{lm}\left(\hat{\boldsymbol{r}}_n\right) \frac{y_l(r,k_n)}{r\sqrt{k}} \tag{4}$$

Here $\boldsymbol{R}_\alpha$ is the position vector of nucleus α. Further assuming that each muffin tin potential is identical and using the definition of the ion–ion structure factor:

$$S(k) = \frac{1}{N}\langle \rho_{\boldsymbol{k}} \rho_{-\boldsymbol{k}} \rangle \tag{5}$$

where

$$\rho_{\boldsymbol{k}} = \sum_{\alpha=1}^{N} e^{i\boldsymbol{k}\cdot\boldsymbol{R}_\alpha} \tag{6}$$

the Kubo–Greenwood conductivity expression is reduced to

$$\sigma(\omega) = -2\pi n_I^0 \int d\epsilon \frac{f(\epsilon_m) - f(\epsilon_m)}{\omega}\int d\hat{\boldsymbol{k}}_m \int d\hat{\boldsymbol{k}}_n \times \left|\sqrt{k_n k_m}\,\bar{J}_{mn}\right|^2 S(|\boldsymbol{k}_n - \boldsymbol{k}_m|) \tag{7}$$

where $\epsilon_m = \epsilon + \omega$, $\epsilon_n = \epsilon$, $n_I^0 = N/V$

$$\bar{J}_{mn} \equiv \int_{V_{MT}} d^3r \bar{\psi}^*_{\boldsymbol{k}_m}(\boldsymbol{r})\hat{\boldsymbol{v}}_z \bar{\psi}_{\boldsymbol{k}_n}(\boldsymbol{r}) \tag{8}$$

Using equation (4) in (7) and after some lengthy algebra (see Appendix) we arrive at the result

$$\sigma(\omega) = \sigma^{(1)}(\omega) + \sigma^{(2)}(\omega) + \sigma^{(3)}(\omega) \tag{9}$$

with

$$\sigma^{(1)}(\omega) = -2\pi n_I^0 \int d\epsilon \frac{f(\epsilon_m) - f(\epsilon_m)}{\omega} \times \sum_{l=0}^{\infty} |I_A(l)|^2 \frac{(l+1)}{2(2l+3)}\left[\left(1 + \frac{l}{2}\right) I_s^{(1)} + \frac{l}{2} I_s^{(2)}\right] \tag{10}$$

$$\sigma^{(2)}(\omega) = 2\pi n_I^0 \int d\epsilon \frac{f(\epsilon_m) - f(\epsilon_m)}{\omega} \times \sum_{l=0}^{\infty} I_A(l) I_B(l+2)\cos(\delta_l(k_n) - \delta_{l+2}(k_n)) \times \frac{(l+1)(l+2)}{2(2l+3)}\left[3I_s^{(2)} - I_s^{(1)}\right] \tag{11}$$

$$\sigma^{(3)}(\omega) = -2\pi n_I^0 \int d\epsilon \frac{f(\epsilon_m) - f(\epsilon_m)}{\omega} \times \sum_{l=0}^{\infty} |I_B(l)|^2 \frac{l}{4(2l-1)}\left[(l-1) I_s^{(1)} + (l+1) I_s^{(2)}\right] \tag{12}$$

where

$$I_s^{(1)} \equiv \int_{-1}^{1} dx S\left(\sqrt{(k_n^2 + k_m^2 - 2k_n k_m x)}\right) \tag{13}$$

$$I_s^{(2)} \equiv \int_{-1}^{1} dx x^2 S\left(\sqrt{(k_n^2 + k_m^2 - 2k_n k_m x)}\right) \tag{14}$$

and I_A and I_B are the same as in Reference 25,

$$I_A(l, k_n, k_m) \equiv \int_0^{R_{MT}} dr y_{l+1}(r, k_m) \times \left(\frac{\partial y_{l_i}(r, k_n)}{\partial r} - (l+1)\frac{y_l(r, k_n)}{r}\right) \tag{15}$$

$$I_B(l, k_n, k_m) \equiv \int_0^{R_{MT}} dr y_{l-1}(r, k_m) \times \left(\frac{\partial y_{l_i}(r, k_n)}{\partial r} + l\frac{y_l(r, k_n)}{r}\right) \tag{16}$$

The sums over the orbital angular momentum quantum number l appearing in equations (10) to (12) formally require an infinity of terms. Fortunately, in practice, the sums converge quickly with a typical maximum l being ~15. A larger number of partial waves is needed as the electrons become less degenerate. This point is further discussed in the context of the Ziman–Evans formula in References 17 and 18.

In the limit $S(k) \to 1\ \forall k$, $\sigma^{(2)}(\omega) = 0$ and the expression for the conductivity is reduced to that of Johnson's result [22,25], provided that the integral over the muffin tin volume $V^{MT} = 4/3\pi R^3_{MT}$ is instead taken over all space. We return to this point in section IV.

As shown in Reference 25, the thermal conductivity κ can be calculated in a straightforward extension. For a plasma of temperature T

$$\kappa = \frac{1}{T}\left(\mathcal{L}_{22} - \frac{\mathcal{L}^2_{12}}{\mathcal{L}_{11}}\right) \tag{17}$$