Neighboring atoms in average-atom calculations of hot dense plasmas

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We present here a method for including the effects of neighboring atoms within the framework of the self-consistent average-atom method. The multiple-scattering theory developed for the study of liquid metals and amorphous materials is used to describe the effect of the adjacent scatterers in the dense plasma problem. The case of copper with its prominent *d* resonance at the natural density and at a temperature of 5 eV is treated. The resonance under the influence of the scatterers, which simulate the plasma environment, is observed to broaden significantly while the area under the broadened resonance is seen to decrease with respect to the single-scattering resonance, increasing the number of free electrons and thus the calculated pressure.

I. INTRODUCTION

The properties of matter at high temperature and density are well described by the self-consistent field (SCF) average-atom model.[1,2] This model provides a general framework for treating hot partially ionized plasma of intermediate and high atomic numbers. In particular it is used for obtaining the electron thermal contribution in equation-of-state calculations.[3] The atomic nucleus is assumed in this model to be embedded in a spherical cavity, the radius of which is determined by the Wigner-Seitz sphere. The cavity, which is electrically neutral, is surrounded by a uniform smeared distribution of positive ions extending to infinity and neutralized by the free electrons. An important limitation of the average-atom model lies in its ability to accurately reproduce the electronic density of states (DOS). One major reason for this is that no account is made of the effect of the ions surrounding the atomic cavity.

Dharma-wardana and Perrot[4] in subsequent work introduced a continuous positive-ion distribution by means of the hypernetted-chain (HNC) equation; additional work of a similar nature was also reported by Ofer *et al.*[5] By assuming the continuous ionic charge distribution, however, one disregards the effects of the relatively deep and localized ionic potentials and their fluctuations.

The purpose of this paper is to investigate the effects of nearest neighbors situated at discrete positions relative to the spherical cavity representing the average atom. In particular, our interest lies in the influence of the neighboring ions on the pressure calculated on the basis of the average-atom model and on the density of states. The latter quantity is instrumental in calculating hot dense-plasma transport coefficients.[6]

Recently Younger *et al.*[7] employed a finite-temperature X-α Hartree-Fock-Slater molecular structure code in order to calculate the electronic structure of a nine-atom He plasma over a wide range of density and temperature. In the present paper we chose to use the multiple-scattering formalism employed originally for liquid metals and amorphous materials for calculating the density of states of the average atom surrounded by identical spherical scatterers. The basic idea of using theoretical techniques devised for the study of disordered systems in dense plasmas was first proposed by More.[8]

Specifically we use the multiple-scattering formalism developed by Lloyd[9,10] and first used by Klima, McGill, and Ziman[11,12] for the study of amorphous covalent semiconductors and later by Keller[13] for liquid transition metals. It is noteworthy that the DOS obtained using this formalism for liquid Cu accurately reproduces the experimental data.[14] In adopting this theory to dense plasmas, we make the one-to-one correspondence of free electrons to valence electrons and bound electrons to core electrons. Multiple-scattering theory has previously been used by Perrot and Dharma-wardana[15] for calculating the resistivity of hot dense H plasma.

A preliminary account of the basic idea of the present paper was presented previously.[16] In that publication only the influence of a single neighbor was taken into account. In the present work a cluster of seven neighbors which simulate the plasma environment is treated. These calculations led here to the major result on the destructive interference due to multiple scattering and thus the decrease in the number of electrons under the broadened resonance curve.

II. THEORETICAL MODEL

The derivation of the density-of-states formula in the Lloyd formalism is given by Lloyd[9,10] as well as in a somewhat different manner by other authors. The basic requisites for using the formalism are identical spherical nonoverlapping potentials. The potential need not be of the muffin-tin form,[17] although the potentials derived here are essentially of the muffin-tin form. Denoting by $N_0(E)$ the total number of electron states up to energy E for a uniform unperturbed electron gas, we obtain according to the Lloyd formalism for $N(E)$ the total integrated density of states:

$$N(E)=N_0(E)+\left[-\frac{2}{\pi\Omega}\right]\mathrm{Im}\ln\mathrm{Det}|\delta_{LL'}\delta_{ll'}+G^{+}_{LL'}(l-l')k_L(E)|\ ,$$
$$k_L(E)=-\frac{\tan\eta_l(E)}{\kappa}\ . \tag{1}$$

Here l and l' denote different ion sites, while L is an abbreviation for the angular momentum and magnetic quantum numbers l and m. The second term on the right is a generalization of the Friedel term for a single scatterer (see below), while $\eta_l(E)$ is the phase shift of the lth partial wave. κ is the kinetic energy and Ω the volume. $G^{+}_{LL'}$ is given by

$$G^{+}_{LL'}(R)=\begin{cases} i\kappa\sum\limits_{L''}4\pi i^{l''}h^{+}_{l''}(\kappa R)Y_{L''}(R)C^{L}_{LL''}, & |R|>0 \\ i\kappa\delta_{LL'}, & |R|=0\ , \end{cases} \tag{2}$$

where C are the Gaunt numbers,

$$h^{+}_{l''}(kR)=j_{l''}(kR)+in_{l''}(kR)\ ,$$
$$C^{L,L',L''}=\int Y_L(\Omega)[Y_{L'}(\Omega)]^{*}[Y_{L''}(\Omega)]^{*}d\Omega\ .$$

The Lloyd determinant simply reduces to the Friedel term by equating all off-diagonal terms to zero, thereby eliminating the interaction between the scatterers and by assuming that $\eta_{l'}=0$ for $l'\neq l$:

$$N(E)=\left[\frac{-2}{\pi\Omega}\right]\mathrm{Im}\ln(1-i\tan\eta_l)^{(2l+1)N_s}\ ,$$
$$n(E)=\frac{dN(E)}{dE}$$
$$=-\frac{2}{\pi}\left[\frac{N_s}{\Omega}\right](2l+1)\mathrm{Im}\frac{d\ln(1-i\tan\eta_l)}{dE}\ ,$$
$$n(E)=\frac{N_s}{\Omega}\frac{2}{\pi}(2l+1)\frac{d\eta_l}{dE}\ .$$

Basic to this paper is the introduction of the Lloyd multiple-scattering formalism into our average-atom calculational procedure. Following the INFERNO model[1] this procedure consists of the self-consistent solution of the three following relations. The first involves the one-electron effective potential $V(r)$, where $\rho(r)$ denotes the electron density within the spherical cavity of radius R:

$$V(r)=-\frac{Z}{r}+\int_{r'<R}\frac{\rho(r')}{(r-r')}d\mathbf{r}'-\frac{[3\pi^2\rho(r)]^{1/3}}{\pi}\ . \tag{3}$$

The second is the assumption of the Fermi-Dirac thermal equilibrium level population for the free- and bound-electron eigenstates ε_s. The chemical potential μ is determined from the requirement of the neutrality of the spherical cavity

$$f(\varepsilon_s)=1/[1+\exp(\varepsilon_s-\mu)/kT]\ . \tag{4}$$

The third relation involves the determination of the electron density given by the summation over bound and free electrons. Ψ is the normalized wave function of either bound or free electrons, thus

$$\rho(r)=\sum_s f(\varepsilon_s)|\Psi_s(r)|^2\ . \tag{5}$$

The difference between our calculational procedure and that of Liberman is in the method of normalization of the free-electron wave functions. Liberman uses normalized continuum wave functions and matches these to the solution of the wave equation within the sphere. In our procedure we normalize the free-electron wave functions using the relation

$$\int_0^{R_{\mathrm{WS}}}\Psi_l^2dV\,dE=g_l(E)dE\ . \tag{6}$$

Here R_{WS} is the Wigner-Seitz radius, and $g_l(E)$ the DOS for angular momentum l. Let $g^0_l(E)$ denote the free-electron-gas DOS for angular momentum l. For the case of no interaction between scatterers, corresponding to the INFERNO calculation we write

$$g_l(E)=g^0_l(E)+\frac{2}{\pi}(2l+1)\frac{d\eta_l(E)}{dE}\ . \tag{7}$$

The second term on the right-hand side is the Friedel term, which gives the effect of the potential on the DOS. Lloyd and Smith[10] have shown that matching the wave functions within the sphere, as in INFERNO, is equivalent to adding the Friedel term to the free-electron DOS.

The free-electron-gas term $g^0_l(E)$ is given here by

$$g^0_l=g^0(E)(2l+1)\int j_l^2(kr)dV\Big/\left[\sum_l(2l+1)\int j_l^2(kr)dV\right]. \tag{8}$$

The integration is over the Wigner-Seitz sphere and $g^0(E)$ is given by[2]

$$g^0(E)=\frac{1}{2\pi^2}\left[\frac{2m}{\hbar^2}\right]^{3/2}V\sqrt{E}\ .$$

The normalization method of the free-electron wave functions as given in Eqs. (6) and (7), can be immediately adapted for the insertion of the DOS obtained by the Lloyd multiple-scattering method into the average-atom computational procedure. This is accomplished by simply replacing the Friedel term $(2/\pi)(2l+1)d\eta/dE$ by $d[-(2/\pi)\mathrm{Im}\ln\mathrm{Det}A]/dE$, the Lloyd term in Eq. (7). This could, however, add a considerable amount of computational time if inserted within the self-consistent procedure. Thus, at this stage of our calculation, the Lloyd determinant was introduced after convergence was achieved by means of the conventional average-atom method.

The pressure P was calculated according to Pettifor:[18]

$$4\pi R_{\rm WS}^2 P = \sum_l \int_0^\infty dE n_l(E)\phi_l^2(R_{\rm WS},E)[E - V(R_{\rm WS})R_{\rm WS}^2 + (D_l + l + 1) + \cdots] ,$$
$$D_l = \frac{R_{\rm WS}}{\phi_l}\frac{d\phi_l}{dr} , \tag{9}$$

where ϕ_l denotes the normalized radial solution of the Schrödinger equation for angular momentum l, $n_l(E)$ denotes the density of states of angular momentum l, and D_l is the logarithmic derivative. The derivation of the pressure formula is based on the virial theorem recast as a surface integral over the Wigner-Seitz sphere.[18]

$V(R_{\rm WS})$ denotes the potential at the edge of the cavity in relation to the continuum. The pressure calculations which we shall give below deal with the thermal component of the electronic pressure and should not be very sensitive to the accurate choice of $V(R_{\rm WS})$.

III. CALCULATIONS AND RESULTS

Copper with its prominent d resonance was studied using the calculational procedure outlined above. The cluster used here consisted of eight atoms, the central atom and seven scatterers. The SCF average-atom (AA) calculation with no scatterers was first carried out at a temperature of 5 eV and at the natural density. The phase shifts of the d resonance thus obtained were used in order to calculate the DOS in the cluster using the method of Lloyd [Eqs. (1) and (2)]. In the present calculation only the d-d interaction terms were included; it was observed in calculations with a smaller number of scatterers that the addition of the hybridization terms was negligible.

Before giving results of pressure calculations, we present and discuss the DOS for different configurations of scatterers in the eight-particle copper cluster treated here. In Fig. 1(a) the DOS is plotted for the scatterers placed along the diagonals of a cube, at the center of which is the central atom, where each scatterer is at a distance of 2 Wigner-Seitz radii from the central ion. This configuration best simulates the cold fcc copper structure within the framework of the eight-particle cluster. The d resonance is observed to broaden significantly, while the total number of particles under the resonance decreases by 20%. In Fig. 1(b) we plot a typical scatterer configuration used to describe the plasma environment (see below). Here the value of the number of resonance particles decreases by 27%. Due to the lower plasma coupling parameter, the scatterers are positioned closer to the central ion than in the cold Cu. The coordinates of the particle positions are given in the figure. Figure 1(c) demonstrates the effect of moving the scatterers a distance 3 times larger than in Fig. 1(a), along the diagonals of the cube. At this configuration the cluster calculation practically coincides with the single potential resonance. Finally, Fig. 1(d) shows that by decreasing the distance again along the diagonals to 0.8 times twice the Wigner-Seitz radius, the number of particles under the resonance drastically decreases to 60% of the number in the pure resonance.

The results presented in Fig. 1 indicate that multiple scattering broadens the resonance peak significantly, but, more importantly, indicate that the total number of particles under the broadened resonance decreases significantly compared to the single potential resonance. This effect increases as the distance between the scatterers becomes smaller. The decrease in the number of resonance particles is attributed to destructive interference. An effect of very similar nature has been known to exist for some time, as first pointed out by Brueckner,[19] in connection with scattering of π mesons by deuterons. Also, a recent calculation,[20] using the method of partial waves,[21] shows how the scattering cross section from two scatterers for an $l=2$ resonance is decreased and broadened as a result of multiple scattering.

The computation of thermodynamic quantities and of transport properties necessitates the incorporation of the plasma environment into the framework of the multiple-scattering model discussed above. This is accomplished here by introducing the radial distribution function $g(r)$ of the scatterers in relation to the central atom, as well as their fluctuations about their assumed equilibrium configuration. Thus the probability of finding a scatterer between r and $r+dr$ is $4\pi r^2 g(r)dr$.

In the present report the pressure calculation of a 5-eV Cu plasma at the natural density is described. As a first step, the plasma coupling parameter Γ, equal to $(Z^*e)^2/(kTR_{\rm WS})$, where Z^* is the effective ionic charge, is computed. The SCF AA calculations described above give 18 bound electrons and close to seven resonance electrons. The number of free electrons Z^* equal to the ionic charge is thus assumed to be equal to the total number of electrons less the bound and resonance electrons, yielding $Z^*=4$, and thus $\Gamma=32$.

A basic simplifying assumption made here is that $g(r)$ is given by the corresponding one-component-plasma (OCP) radial distribution function as computed, for example, by Brush *et al.*[22] The probability of finding a scatterer between r and $r+dr$ is $4\pi r^2 g(r)dr$. On this basis we construct the "basic" scatterer configuration, positioning the scatterers relative to the central atom in accordance with the above-mentioned $g(r)$. The neighboring scatterers themselves are distanced from each other by the order of $2R_{\rm WS}$ or larger. The Cartesian coordinates of this configuration in units of $2R_{\rm WS}$ are (0,0,0), (0.75,0,0), (0,0.85,0), (0,0,0.95), (0,0,−1.02), (−1.1,0,0), (0,−1.15,0), and (0.7,0.7,0.7).

Another prominent plasma property is the fluctuations of the ions about their mean assumed equilibrium configuration, derived above. The mean-square displacement $\bar{r}_0$ is estimated following Laughlin[23] by $\frac{1}{2}k\bar{r}_0^2 = 3k_B T$, with Hook's laws constant k given by $k = 3Z^{*2}/R_{\rm WS}$. The scatterers were thus displaced relative to the "basic" configuration defined above.

The pressure and 5 eV at 8.9 g/cm^3 was calculated

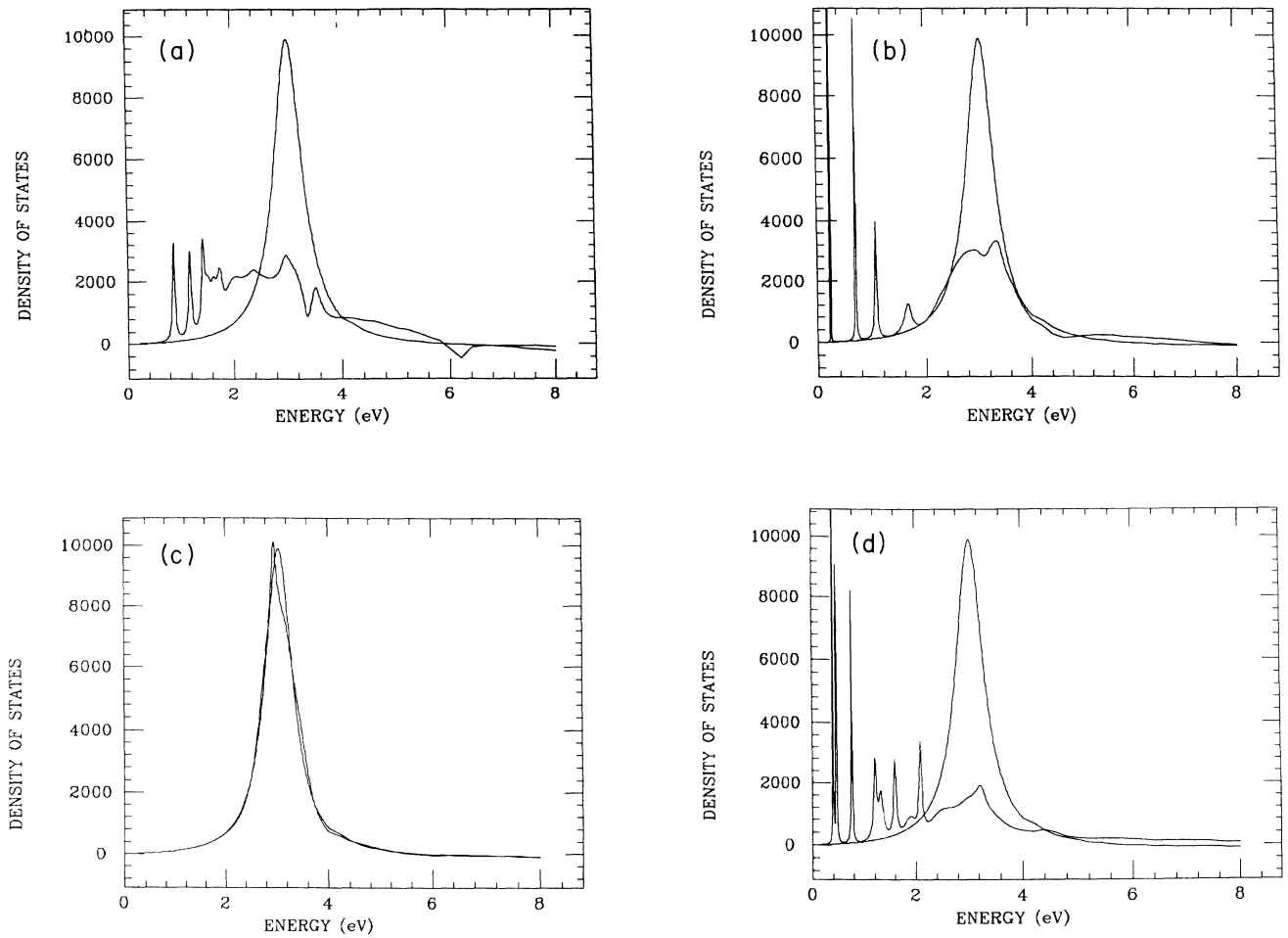

FIG. 1. Density of states as a function of energy of the d resonance of Cu for various configurations of the seven scatterers surrounding the central atom, which is placed at the origin of the Cartesian coordinate system. In (a), (c), and (d) the scatterers are along the diagonals of the cube, the center of which is at (0,0,0). In (a), all scatterers are at $2R_{\mathrm{WS}}$ from the origin; in (c) and (d) all are at distances 6 and $1.6R_{\mathrm{WS}}$ from the origin, respectively. In (b), a typical plasma configuration, the coordinates are (0.75,0,01,−0.18), (0.01,0.97,0.15), (0.16,0.14,1.10), (−0.16,−0.21,−1.04), (−1.25,0.15,0.07), (0.08,−1.19,−0.01), and (0.50,0.77,0.59), where the unit of length is $2R_{\mathrm{WS}}$. The symmetric curve is the density of states of the single scatterer.

averaging over ten different configurations of scatterers. In each of these configurations the positions of the scatterers were randomly shifted about the "basic" configuration. The mean-square displacement averaged over the configurations was equal to $\bar{r}_0$ as determined from Hook's law. In order to obtain the thermal component of the electron pressure, the zero-temperature electron pressure at the same density must be subtracted from the result obtained at 5 eV. The cold configuration was simulated by placing the scatterers along the diagonals of a cubic, each of them at a distance of two Wigner-Seitz radii from the central ion. The temperature was taken at 0.1 eV. The thermal component of the electron pressure thus obtained was 2.1 Mbar.

The standard average-atom calculation with no scatterers gave here 1.37 Mbar (the corresponding INFERNO result is, however, 1.60 Mbar). The inclusion of multiple scattering thus cause an increase of the order of 50% in the calculated thermal component of the electron pressure. In the multiple-scattering case, resonance electrons whose contribution to the pressure is relatively small are shifted to higher-energy free-electron states.

IV. CONCLUSIONS

To conclude, we have incorporated the effect of neighboring scatterers within the framework of the average-atom model using the Lloyd multiple-scattering theory. The positioning of the scatterers about the central atom was based on the plasma radial distribution function and on the ionic fluctuations. An increase of 50% in the calculated thermal electronic pressure was obtained with the inclusion of multiple scattering, as compared to the conventional average-atom calculation for Cu at 5 eV and at the natural density. Larger clusters will be used and effects of hybridization will be included in subsequent work. This procedure can in the future also be incorporated into the INFERNO calculation.

The procedure described in the present paper could be used to calculate dense-plasma resistivity. Here the

ensemble-averaged T matrix of the cluster must be calculated. A recent multiple-scattering calculation of resistivity in liquid metals has been performed using the "path operator" technique for calculating the T matrix.[24] Such a calculation can be averaged over the plasma configurations as determined here for the DOS calculation. The result can then be compared to that obtained from a single-site calculation.[6]

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