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A simple method for determining the ionic structure of warm dense matter

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ABSTRACT

A model for dense homo-nuclear plasmas that couples an average atom model for the calculation of the electronic structure to the quantum Ornstein–Zernike equations describing the ionic structure is summarized and described pedagogically. The model is applied to the calculation of ion–ion pair distribution functions $g_{ii}(r)$ for tungsten in the warm and hot dense matter regimes. These results are compared to orbital-free molecular dynamics simulations and excellent agreement is found. Calculations of $g_{ii}(r)$ with a simple version of the model (which we call the ion-sphere model) are in remarkable agreement with those of the full model. This ion-sphere model provides a simple and efficient method of calculating accurate $g_{ii}(r)$ for warm and hot dense matter for many applications involving low- to high-Z elements with a modest investment of effort.

1. Introduction

Warm and hot dense matter refers to matter at densities similar to or a few times greater than solid density, and temperatures from around one eV to several keV. It occurs in the interiors of giant planets and exoplanets [1], in substellar brown dwarfs, in dense stars such as white dwarfs [2], and in inertial confinement fusion experiments [3]. Warm dense matter states can be created experimentally by shock compression [4–8] and probed with X-ray scattering experiments [9–14].

Accurately describing warm and hot dense matter is a challenging task due to the interplay of important physical effects such as ion correlations, bound states, and pressure ionization, all of which should in principle be included in a single consistent model. Simulation methods are particularly well-suited to this task as they rely on a small set of approximations. The computational cost for this degree of physical realism is substantial, however. The most popular methods are based on the density functional theory (DFT) of the electrons, such as the quantum Langevin molecular dynamics [15], quantum molecular dynamics [16,17], and orbital-free molecular dynamics (OFMD), which, at its most basic level, treats the electrons with the Thomas–Fermi (TF) approximation [18,19]. Non-DFT methods such as path integral Monte Carlo [20,21] and quantum Monte Carlo [22] have the potential of higher accuracy but are even more computationally expensive and have been applied only to low-Z materials or at high temperatures.

Other approaches include average atom (AA) models, which, crudely speaking, attempt to solve for the properties of one 'average' ion in the plasma that represents an average of the multiple ionic states found in a real plasma. The difficulty and non-uniqueness of defining an average ion in a dense plasma has lead to many different varieties of AA models [23–27] with approximations of varying degrees of realism. Usually ion correlations are ignored altogether [23–25]. However, a given AA model typically has no free parameters (i.e. it is predictive and cannot be tuned to some desirable result), treats all electrons on the same footing within DFT, and naturally accounts for pressure ionization. Both quantum and semi-classical treatments of the electrons are possible. Their great advantage is their low computational cost relative to simulations. This economy comes at the expense of physical realism, principally through the assumptions of spherical symmetry and the neglect of ion correlations.

In Refs. [28,29] we presented a model for warm and hot dense matter that improved upon our earlier work [30,31] that combines an AA model and the quantum Ornstein–Zernike (QOZ) equations [32]. The latter are integral equations that describe the structure of a fluid of classical ions and quantum mechanical electrons. There are no adjustable parameters, all electrons (bound and free) are treated on the same footing, and pressure ionization of bound states and ion correlations are included, all consistently. The AA component is DFT-based and, by assuming spherical symmetry, largely retains the computational economy of AA models that do

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not include ion–ion correlations. The AA model and the QOZ equations are coupled and form a complete, self-consistent, closed set of equations from which the electronic and ionic structures can be obtained for any single species plasma in the warm and hot dense regime. The central assumption is that the plasma is constituted of an ensemble of identical, spherically symmetric 'pseudoatoms'. The averaging of the angular dependencies in the ionic or electronic structures precludes the formation of chemical bonds (e.g. molecules) which can become important at temperatures below a few eV in some materials. Nonetheless, this leaves a large range of densities and temperatures where the model can be applied.

The coupling an AA model to integral equations for the ion structure has been studied fairly extensively before. In Ref. [33] a Thomas–Fermi model for the electrons was coupled to the classical OZ equations [34]. The classical ions interact through effective interaction potentials that are determined within the model, but solutions could only be found at high temperatures. The quantum hyper-netted chain (QHNC) model of Chihara [32] couples a DFT treatment of quantum mechanical electrons to the QOZ equations for the ion structure. Chihara's scheme has found limited practical applications beyond simple liquid metals as it does not sufficiently address the difficulties associated with pressure ionization and it is very difficult to find a stable algorithm to solve the QHNC system of equations. Perrot and Dharma-wardana [35,36] also developed a DFT model coupled to the classical OZ equations with an effective potential. Their scheme also has difficulty treating pressure ionization and the electronic structure of the ion does not take in account ion correlations.

The purpose of this paper is two-fold. Firstly, we present the equations that define the model [28] with the aim of making the model easier to understand and implement. With this in mind, in Section 2.1 we give an overview of its key concepts and overall structure and in Sections 2.2–2.4 we summarize the equations that are solved, without the formal derivations given in Ref. [28]. Secondly, a useful and interesting result is shown: The ion–ion pair distribution function, $g_{\mathrm{II}}(r)$, obtained from a simple version of the model (the ion-sphere model) that is relatively easy to implement and computationally expedient, is very close to that of the full model (the self-consistent model). In Section 3 we compare new results for the $g_{\mathrm{II}}(r)$ of tungsten calculated with the self-consistent model to OFMD simulations, demonstrating excellent agreement over a wide range of temperatures at a high density. This extends our previous comparisons for low- and mid-Z elements (H, Al and Fe) [28,29] to high-Z and further validates the ion–ion pair potential determined within our model and the use of the integral equations of fluid theory. The $g_{\mathrm{II}}(r)$ from the simpler ion-sphere model are then directly compared to those of the self-consistent model for several cases, with excellent agreement found. The ion–ion pair distribution function of a warm dense plasma (and its Fourier transform, the structure factor) is of interest as it plays an important role in the calculation of the equation of state, diffusion coefficients, transport coefficients and X-ray scattering spectra. Finally, the numerical solution of the system of equations presents a number of technical challenges, the solutions to which are given in an appendix along with other numerical details. Unless otherwise noted, we shall use atomic units throughout with $\hbar = m_{\mathrm{e}} = k_{\mathrm{B}} = e = 1$, where the symbols have their usual meaning.

2. Description of the model

In this section, we first discuss the model in general terms before proceeding with a more detailed description of the average atom model, the QOZ equations, and how they are coupled. This allows the introduction of two variants: the relatively simple ion-sphere (IS) model and the fully self-consistent (SC) model.

2.1. Overview

The quantum Ornstein–Zernike (QOZ) equations are integral equations governing the structure of a neutral fluid mixture of quantum mechanical electrons and classical ions [37]. For given pair interaction potentials, temperature and ion number density and charge, their solution gives the ion–electron and ion–ion pair distribution functions. The QOZ equations must be supplemented with three closure relations that are known as the electron–electron, electron–ion and ion–ion closure relations. While well-known approximations exist for the electron–electron and ion–ion closure relations, we have developed a new approximation for the electron–ion closure relation which uses the electron screening density obtained from an AA model [28].

In the AA model, a nucleus is fixed at the origin and the distribution of the surrounding ions is angularly averaged to reduce the problem to spherical symmetry. The electron distribution around the nucleus is obtained with finite-temperature DFT [38]. Electrons can be treated either quantum mechanically by solving the Schrödinger equation, or semi-classically in the Thomas–Fermi approximation [23,39,40]. With inputs of the nuclear charge and mass, the plasma temperature and mass density, the AA model is solved for the interaction potential, the electronic density and in the quantum-mechanical case, the wave functions and eigenvalues of the bound and continuum states.

A key element of our model is the concept of 'pseudoatom', which consists of a nucleus and its associated cloud of electron charge. The pseudoatom is neutral by construction and its electron density profile is calculated as follows. First, the electron density is calculated with the AA model for a system consisting of the central nucleus and the surrounding ion distribution. This is the 'full' system. Next we find the electronic density for the 'external' system, which has the same distribution of ions but no central nucleus. We define the difference between these two electron densities (full minus external) as being the electron density of the central pseudoatom [41–43]. The plasma is then represented as a collection of these pseudoatoms. The electron–ion closure relation for the QOZ equations is obtained by defining a screening density of electrons $n_{\mathrm{e}}^{\mathrm{scr}}(r)$ that is essentially the free electron (positive energy) part of the pseudoatom electron density.

As noted above the electronic structure in the AA model is determined in the presence of a central nucleus and spherically averaged non-central ions. In the ion-sphere (IS) model, the distribution of these ions is taken to be a step function at the ion sphere radius. The AA screening electron density $n_{\mathrm{e}}^{\mathrm{scr}}(r)$ issued from this calculation is used to close the QOZ equations whose solution gives the ion–ion pair distribution function $g_{\mathrm{II}}(r)$. The collection of AA electronic properties and the $g_{\mathrm{II}}(r)$ constitute what we call the IS approximation. Note that this $g_{\mathrm{II}}(r)$ is not a step function, which is inconsistent with the assumed ion distribution in the AA model. Thus the IS approximation which is similar to the model of Ref. [41] and to the jellium vacancy model of Ref. [44] is inherently inconsistent.

In the self-consistent (SC) model, the $g_{\mathrm{II}}(r)$ resulting from the IS calculation is input into the AA calculation to replace the initial step function distribution of ions. The AA equations are solved again for the electronic structure in the presence of this new ion distribution. This results in a new $n_{\mathrm{e}}^{\mathrm{scr}}(r)$ which is in turn used to close and solve the QOZ equations for a new $g_{\mathrm{II}}(r)$. This procedure is repeated until convergence in $g_{\mathrm{II}}(r)$ is achieved, giving a self-consistent solution to the coupled AA and QOZ problems. We refer to this $g_{\mathrm{II}}(r)$ as the SC result. Note that the IS approximation is essentially the first