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Quantum Statistical Theory of Plasmas and Liquid Metals*

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A Debye-Hückel-type theory is described for an assembly of completely ionized atoms, the nuclei being treated classically and the electrons by the Thomas-Fermi method. The thermodynamic functions are derived by considering the Debye charging process, and the virial theorem is shown to hold. Numerical results are given for hydrogen and iron near normal solid densities, and are probably accurate only at high temperatures ($kT>5$ ev for hydrogen and $kT>100$ ev for iron). At these temperatures, the results do not differ greatly from those of the ordinary Thomas-Fermi theory of the atom except for the additional contributions of the nuclei.

1. INTRODUCTION

THE temperature-dependent Thomas-Fermi (TF)[1] and Thomas-Fermi-Dirac (TFD)[2] theories of the atom have been recently discussed in detail, and used to calculate equations of state of the elements at high temperatures and pressures. These theories involve a number of approximations, among which are the following. (1) The properties of bulk material are approximated by those of an isolated, spherically symmetric atom whose nucleus is at rest. There are thus no contributions due to nuclear motion nor to interactions between neighboring atoms. (2) The electrons are assumed to be quasi-free, and their distribution about the nucleus is calculated statistically, so that the shell structure of the atom is in no way reproduced. The electron density at the nucleus turns out to be infinite, resulting in absolute binding energies which are considerably too great in magnitude. (3) The electrons are treated in the one-electron approximation, so that there are no correlations in the motions of the electrons due to their mutual electrostatic repulsion, though in the TFD theory some correlation among electrons of parallel spin results from effects of the Pauli exclusion principle.

The Debye-Hückel, Thomas-Fermi (DHTF) theory developed recently by Plock and Kirkwood[3] removes to some extent several of the above approximations. Matter is treated in bulk with associated nuclear effects and interactions between atoms, and electrostatic correlations among the electrons are present. Exchange effects are not included. These can be incorporated in a manner similar to that of the TFD theory [the principal change in the equations given below is to replace $\frac{1}{2}\theta^{3/2}I_{1/2}(\eta)$ by the function $G_2(\theta\eta,\theta)$ defined in reference 2]; however, this would introduce fairly serious numerical complications and would probably not greatly change the calculated results since at low densities, the correlation effects include most or all of the exchange energy.[4]

2. THEORY

We consider an infinite assembly of atoms (of one element) at uniform temperature and density, such that all particles (both nuclei and electrons) are free to move about under the influence of their mutual electrostatic forces. In order to be able to evaluate the thermodynamic functions for this system by considering the Debye charging process, we suppose each particle to carry an arbitrary fraction λ of its true physical charge, the charge on each particle thus being λZe and $-\lambda e$ for nuclei and electrons, respectively. The average densities of nuclei and electrons will be denoted by n_{+0} and n_{-0}; for an electrically neutral system

$$Zn_{+0}=n_{-0}. \tag{1}$$

a. Particle Distributions about a Nucleus

Singling out one particular nucleus, let the average electrostatic potential (resulting from *all* particles, including the nucleus in question) and the average charge density about this nucleus be respectively $\psi_+(r)$ and

$$\rho_+(r)=\lambda Zen_{++}(r)-\lambda en_{-+}(r), \tag{2}$$

where n_{++} and n_{-+} are the average densities of nuclei and electrons at a distance r from the given nucleus. The potential and charge density are related through the Poisson equation

$$\Delta\psi_+=-4\pi\rho_+=-4\pi\lambda e(Zn_{++}-n_{-+}), \tag{3}$$

the boundary conditions being

$$\lim_{r\to 0} r\psi_+(r)=\lambda Ze,$$

$$\lim_{r\to\infty}\psi_+(r)=0. \tag{4}$$

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[1] R. Latter, Phys. Rev. 99, 1854 (1955).

[2] R. D. Cowan and J. Ashkin, Phys. Rev. 105, 144 (1957).

[3] R. J. Plock, Thesis, Yale University, 1956; R. J. Plock and J. G. Kirkwood (to be published).

[4] R. D. Cowan and J. G. Kirkwood, Phys. Rev. (to be published).