the Poisson equation (22) becomes

$$\phi_-''(x)=\tfrac{3}{2}(4\epsilon)^3\theta^{\frac{3}{2}}x[I_{\frac{1}{2}}(\eta_-)-I_{\frac{1}{2}}(\eta_+)], \tag{28}$$

with boundary conditions

$$\phi_-(0)=-1/Z,$$

$$\lim_{x\to\infty}\phi_-(x)=x(\phi/x)_\infty=x\phi_\infty'. \tag{29}$$

With $I_{\frac{1}{2}}(\eta_+)$ being a known function of x from the solution of (16), (28) can readily be integrated to give ϕ_- and η_- as functions of x, thereby giving the distribution of particles about an electron from (24) and (26).

Similarly to the derivation of (20), the net charge about a given electron is

$$q_-=4\pi r_\lambda^3\int_0^\infty(\lambda Zen_{+-}-\lambda en_{--})x^2dx$$

$$=-\lambda Ze[x\phi_-'-\phi_-]_0^\infty=\lambda e, \tag{30}$$

which is just the negative of the charge on the electron.

c. Thermodynamic Functions

An expression for the Helmholtz free energy $A(v, T)$ of our system will be derived through the artifice of the Debye charging process, and we accordingly write

$$A=A_i+A_e, \tag{31}$$

where A_i is the Helmholtz free energy of the uncharged (ideal) plasma, and A_e is the contribution which arises during the charging process.

The contribution of the nuclei to the ideal Helmholtz energy A_i (per atom) is given by the classical expression

$$A_{i+}=-kT\{1+\ln[(2\pi m_+kT)^{\frac{3}{2}}/h^3n_{+0}]\}, \tag{32}$$

and the contribution of the electrons (per atom) is[8]

$$A_{i-}=ZkT\{\eta_\infty-\tfrac{2}{3}I_{\frac{3}{2}}(\eta_\infty)/I_{\frac{1}{2}}(\eta_\infty)\}. \tag{33}$$

The portion A_e of the Helmholtz energy is the electrical work done in charging up the particles at constant temperature and volume, the particle distributions at each stage in the charging process being the equilibrium distributions for the corresponding value of λ. Thus the contribution of each nucleus to A_e is

$$A_{e+}=\int_0^{Ze}\lim_{r\to0}\left[\psi_+(r,\lambda)-\frac{\lambda Ze}{r}\right]d(\lambda Ze)$$

$$=\frac{Ze^2}{a_0}\left(\frac{4Z^2}{3\pi}\right)^{\frac{2}{3}}\int_0^1\lambda^2\left[\phi_+'(0)-\left(\frac{\phi}{x}\right)_\infty\right]_\lambda d(\lambda^2), \tag{34}$$

and the contribution of Z electrons to A_e is

$$A_{e-}=Z\int_0^{-e}\lim_{r\to0}\left[\psi_-(r,\lambda)+\frac{\lambda e}{r}\right]d(-\lambda e)$$

$$=-\frac{Ze^2}{a_0}\left(\frac{4Z^2}{3\pi}\right)^{\frac{2}{3}}\int_0^1\lambda^2\left[\phi_-'(0)-\left(\frac{\phi}{x}\right)_\infty\right]_\lambda d(\lambda^2), \tag{35}$$

where the quantities $\lambda Ze/r$ and $-\lambda e/r$ have been subtracted from ψ_+ and ψ, respectively, in order to remove the self-energies of the particles, and where $\phi_\pm(x)$ have been expanded in Taylor series about the origin (see Sec. 3), and the boundary conditions (17) and (29) employed. ($a_0=\hbar^2/me^2$ is the first Bohr radius of hydrogen.)

With the Helmholtz free energy calculated in this manner, the pressure and the internal energy per atom can then be obtained from the general relations

$$p=-(\partial A/\partial v)_T,$$

$$S=-(\partial A/\partial T)_v,$$

$$E=A+TS. \tag{36}$$

Alternatively, the pressure *or* the energy can be found from (36) and the other quantity found from the virial theorem,[9] which for Coulombic forces, has the form

$$pv=\tfrac{2}{3}E_k+\tfrac{1}{3}E_p, \tag{37}$$

where E_k and E_p are respectively the kinetic and potential energies of the system. The validity of the virial theorem in the case under consideration can be established as follows:

The energy of the uncharged gas obtained from (32), (33), and (36) is entirely kinetic, and it can be readily shown that $p_iv=\frac{2}{3}E_i$, by using in the case of A_{i-} the relation (9)

$$vT^{\frac{3}{2}}I_{\frac{1}{2}}(\eta_\infty)=\text{constant}, \tag{38}$$

and also the relation[7] $dI_{\frac{3}{2}}/d\eta_\infty=\frac{3}{2}I_{\frac{1}{2}}$. Thus it is necessary to consider only the contribution of A_e to the pressure (p_e) and the energy (E_e). This last quantity includes not only potential energy but also a change in the kinetic energy brought about by the charging process—the potential energy of the fully charged system being the result given by (34) and (35) if the particle distributions are held fixed at their values for $\lambda=1$[10]:

$$E_p=\frac{Ze^2}{a_0}\left(\frac{4Z^2}{3\pi}\right)^{\frac{2}{3}}[\phi_+'(0)-\phi_-'(0)]_{\lambda=1}\int_0^1d(\lambda^2). \tag{39}$$

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[8] See, for example, A. H. Wilson, *Thermodynamics and Statistical Mechanics* (Cambridge University Press, London, 1957), Sec. 6.3.

[9] See, for example, Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), Secs. 3.1b and 6.2b.

[10] This result can also be obtained by a straightforward evaluation of the Coulomb integrals for $\lambda=1$,

$$E_p=\tfrac{1}{2}\int(Ze)\rho_+r^{-1}d\tau+\tfrac{1}{2}Z\int(-e)\rho_-r^{-1}d\tau,$$

where ρ_+ and ρ_- are defined in Eqs. (2) and (21), and the factors $\frac{1}{2}$ must be included to avoid counting pair interactions twice.