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MONTE CARLO CALCULATIONS OF THE RADIAL DISTRIBUTION FUNCTIONS FOR A PROTON–ELECTRON PLASMA

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Summary

A general method is presented for computation of radial distribution functions for plasmas over a wide range of temperatures and densities. The method uses the Monte Carlo technique applied by Wood and Parker, and extends this to long-range forces using results borrowed from crystal lattice theory. The approach is then used to calculate the radial distribution functions for a proton–electron plasma of density 10^{18} electrons/cm^3 at a temperature of 10^4 °K. The results show the usefulness of the method if sufficient computing facilities are available.

I. Introduction

The radial distribution function $g(r)$, defined by $\rho(r) = \rho_0 g(r)$, describes the local microscopic density or structure of a liquid, and has been used extensively in the microscopic approach to liquids to obtain equations involving the macroscopic thermodynamic variables. Because of its important role in the theory there have been several attempts to obtain practical estimates for $g(r)$, and the early work on liquids developed two main methods for finding $g(r)$. The first is the method of integral equations, where the Superposition approximation or other assumptions are made to obtain integral equations from the theory in a form that can be solved numerically. The second is the Monte Carlo technique, a computational approach which can be applied to any substance that may be considered to be composed of individual interacting molecules. Broyles (1962) has recently compared the latest integral equation solutions for liquids with the corresponding Monte Carlo results, which are considered the most accurate.

The extension of the above techniques to plasmas is not as easy as it may seem, owing to the presence of the Coulomb forces, which necessitate a very long-range integration or summation. However, Green (1961) has extended the integral-equation approach to plasmas, and has shown that the Debye–Hückel (D.H.) theory is a first approximation, but that higher corrections are important. Villars (1963) has solved Green's equations and has obtained radial distribution functions for metallic plasmas for a certain range of temperature and number density. Also, Broyles (1961) has extended the integral equations of Perkus and Yevick (1958) and the Convolution Hypernetted Chain approximation to long-range forces, and Carley (1963) has solved these to obtain radial distribution functions for a classical electron gas. At the present time, however, the accuracy of the above solution is in some doubt, and in this paper it is intended to extend the accurate Monte Carlo method and obtain radial distribution functions for a proton–electron plasma of specified number density and temperature.

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II. The Method

A system composed of N individual particles is confined in a volume V at a temperature T. The particles are assumed to obey classical statistics, and further, in the interest of tractability, the particles are assumed to have spherically symmetric potential fields and to interact with the Coulomb potential. Subject to these assumptions the method is not restricted to any range of temperature or density, although it proves more efficient in specific regions.

The problem is reduced to a feasible size by considering only a finite number of particles N, and in this case $N = 32$, a value which proves convenient and gives a reasonable accuracy (see Alder and Wainright 1960). In the initial configuration the particles are placed randomly in a unit cube of volume $V = L^3 = 1$ cubic cell unit (a convenient measure of length), but as the computer can only deal with a finite number of digits k, the coordinates x_{i1}, x_{i2}, x_{i3} of the ith particle are represented by $x_{i\alpha}$ which has a number of digits not greater than k. Another configuration $C(k_r)$ is determined from $C(j_r)$ as follows. The coordinates of one of the particles are changed by a small random amount $\boldsymbol{\delta}\mathbf{x}$ such that $|\boldsymbol{\delta}\mathbf{x}| < \delta_0$. In general the molecule which suffers this displacement may be chosen randomly, or in a systematic fashion as in this calculation. The configuration which is next in the series $C(j_{r+1})$, is either $C(j_r)$ or $C(k_r)$, and, to decide which, the potential energies EP of $C(j_r)$ and ET of $C(k_r)$ are calculated, and a random number RAND is chosen on the interval $0 \leqslant \mathrm{RAND} \leqslant 1$.

If $0 \leqslant \mathrm{RAND} \leqslant (1+\mathrm{e}^{\beta(ET-EP)})^{-1}$, the configuration $C(j_r)$ is taken.

If $(1+\mathrm{e}^{\beta(ET-EP)})^{-1} < \mathrm{RAND} \leqslant 1$, the configuration $C(k_r)$ is taken.

Such a choice (as will be shown later) ensures that the relative frequency of a configuration $C(j)$ with potential energy $V(j)$ in the sequence of configurations is asymptotically $\exp(-\beta V(j))$. As the 32 particles are considered, a store is kept of the pairing energy and distance between any two particles, since this enables quick calculation of the energy and an estimate of the radial distribution function for like particles from

$$g_{\mathrm{L}}(r) = \Delta N_{\mathrm{L}}/2\pi r^2 \Delta r N^2 n, \tag{1}$$

where $N = 32$, and n is the number of large iterations completed in a calculation, a "large iteration" being defined when all 32 particles in the cell have been moved or attempted to move.

ΔN_{L} is the number of like particles recorded at the distance r to $r+\Delta r$ from the given particle; for the unlike case $g_{\mathrm{U}}(r)$, the number of unlike particles ΔN_{U} in that range would be the appropriate value.

The theory underlying the above procedure is based on two papers, one by Metropolis *et al.* (1953) who first proposed the Monte Carlo approach to compute distribution functions, and the second by Wood and Parker (1957) who put forward a complete and rigorous theory. A petit canonical ensemble is constructed from a canonical ensemble (i.e. reducing the continuum of configurations to a countable set of configurations) by considering only a finite number of digits in specifying the coordinates of a particle. This effectively divides the unit cell into a very fine mesh, such that the positions of the molecules are specified by a single number associated

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with each mesh cell. This division is inherent in numerical calculation, and it is physically reasonable that a sufficiently fine subdivision will give results indistinguishable from the continuum of configurations. To calculate the equilibrium value of any quantity of interest F, then

$$\bar{F} = \frac{\Sigma_j F_j \exp(-E_j/kT)}{\Sigma_j \exp(-E_j/kT)},$$

where j runs over all coordinate and velocity configurations. Also as velocity-independent forces have been assumed, and if F is not a function of velocity, this can be written

$$\bar{F} = \frac{\Sigma_j F_j \exp(-V(j)/kT)}{\Sigma_j \exp(-V(j)/kT)},$$

where j now runs over all coordinate configurations. Now even in the case where N is reasonably small it is impracticable to carry out the multidimensional sum by usual numerical methods, and so the Monte Carlo method is used. The Monte Carlo method of evaluating many-dimensional integrals consists of integrating over a random sampling of points instead of a regular array of points. In this case, if the Monte Carlo technique were applied in a straightforward manner, a random configuration would be chosen, and then weighted by $\exp(-\beta V(j))$. However, a more practicable method is to choose configurations with a probability $\exp(-\beta V(j))$ and weight them evenly. Thus as Wood and Parker (1957) state "the object is to generate a Markov chain in which asymptotically each state k recurs with a frequency proportional to the Boltzmann factor $\exp(-\beta V(j))$ for that state". Then the average of F_j will converge to the petit canonical ensemble average as the chain length increases. All that is now needed is to show that the relative frequency of $C(j)$ in the sequence of configurations generated above is asymptotically $\exp(-\beta V(j))$. Suppose the probability that j_r should have a value j is $p_r(j)$, and let $C(k)$ be a configuration obtained from $C(j)$ in the manner described above (i.e. $C(k)$ belongs to a set of configurations accessible from $C(j)$ by changing the coordinates of one particle by amounts less than δ_0). If $E(j)$ denotes this set of configurations (ensemble), then $k \epsilon E(j)$. Let Q be the number of distinct configurations in each of the ensembles $E(j)$ and $E(k)$. Now the probability of moving from state j_{r+1} back to state j is $p_{r+1}(j)$, and we have

$$Qp_{r+1}(j) = p_r(j) \sum_{k \epsilon E(j)} [1-\alpha(j,k)] + \sum_{j \epsilon E(k)} p_r(k)\alpha(k,j), \tag{2}$$

where

$$\alpha(j,k) = \{1+\exp[\beta V(k)-\beta V(j)]\}^{-1}, \tag{3}$$

that is, $\alpha(j,k)$ is the probability that $C(j)$ will be changed to $C(k)$ by displacing a molecule in $C(j)$, and $\sum_{k \epsilon E(j)}$ is the summation over all values of k such that $k \epsilon E(j)$. Now the relative frequency of configuration $C(j)$ is asymptotically proportional to $p(j)$. But

$$p(j) = \lim_{S \to \infty} S^{-1} \sum_{r=1}^{S} p_r(j).$$

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Hence from (2)

$$Qp(j) = p(j)\left[Q - \sum_{k \epsilon E(j)} \alpha(j,k)\right] + \sum_{j \epsilon E(k)} p(k)\alpha(k,j),$$

that is,

$$p(j) \sum_{k \epsilon E(j)} \alpha(j,k) = \sum_{j \epsilon E(k)} p(k)\alpha(k,j). \tag{4}$$

This means that the probabilities must satisfy the condition of microscopic reversibility, and gives a set of simultaneous equations to determine the $p(j)$, which, if we replace $\alpha(j,k)$ with (3), has the solution $p(j) = A\exp(-\beta V(j))$, where A is independent of j, and this is the property of the sequence $C(j_1)$, $C(j_2)$, . . . that we wished to prove.

There are other ways of assigning the probabilities $\alpha(j,k)$ so that equation (4) still has a solution $p(j)\alpha\exp(-\beta V(j))$. However, it has been found in simple tests that the choice of $\alpha(j,k)$ given in (3) secures the most rapid convergence of the series. This choice is of considerable practical importance, since in the calculation the average F is found via $\bar{F} = S^{-1} \sum_{r=T+1}^{S} F(j_r)$, with suitably chosen values of T and S, and if a bad choice is made for $\alpha(j,k)$ then these values of T and S will be unnecessarily large. Effectively $\alpha(j,k)$ is a normalized Boltzmann distribution for particles allowed to move between two potential energy states $V(j)$ and $V(k)$. It is the calculation of the potential energy that causes most of the difficulty with plasmas. For a start it is necessary to introduce the "periodic boundary condition" to eliminate surface effects and deal with the long-range forces. The basic cell of 32 particles is considered to be surrounded by exactly similar cells, in each of which the molecular configuration in the basic cell is identically repeated. Hence the appearance is similar to a crystal lattice, with repetition of the basic cell. Alder and Wainright (1960) have shown that for fluids this repetition leads to only small errors for $N \geqslant 30$, but that it causes significant errors for low N or for very dense systems.

The calculation of the potential energy of a configuration utilizes crystal theory, and employs a technique similar to the calculation of the "Madelung energy" for a crystal, a good derivation of which is given by Born and Huang (1954). Let the position of the kth particle in the cell be designated by

$$\mathbf{x}(k) = \mathbf{a}_1 x_1(k) + \mathbf{a}_2 x_2(k) + \mathbf{a}_3 x_3(k),$$

where x_1, x_2, and x_3 are the components of $\mathbf{x}(k)$ along the coordinate vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$. Let the cells be specified by cell indices l_1, l_2, l_3, and define a cell vector

$$\mathbf{x}(l) = l^1\mathbf{a}_1 + l^2\mathbf{a}_2 + l^3\mathbf{a}_3.$$

Hence the position vector of an arbitrary particle is represented by $\mathbf{x}(l)+\mathbf{x}(k)$, written $\mathbf{x}\begin{pmatrix} l \\ k \end{pmatrix}$. It is also useful to define a reciprocal lattice by $\mathbf{b}^\alpha \,.\, \boldsymbol{\alpha}_\beta = \delta_{\alpha\beta}$, and from these reciprocal lattice vectors $\mathbf{b}^\alpha$, a reciprocal cell vector $\mathbf{y}(h)$ can be defined by

$$\mathbf{y}(h) = h_1\mathbf{b}^1 + h_2\mathbf{b}^2 + h_3\mathbf{b}^3.$$

Then $\mathbf{x}(l) \,.\, \mathbf{y}(h) =$ integer, and $\exp(2\pi i\mathbf{y}(h) \,.\, \mathbf{x})$ is periodic in $\mathbf{x}$. With the above

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notation, and assuming that the ions interact as point charges with a Coulomb potential, the electrostatic energy for an arbitrary zero cell may be written as

$$E = \frac{1}{2}\sum_{k}\sum_{l'k'}{}' \xi_k \xi_{k'} \Big/ \left|\mathbf{x}\begin{pmatrix} l' \\ k' \end{pmatrix} - \mathbf{x}\begin{pmatrix} 0 \\ k \end{pmatrix}\right|, \tag{5}$$

where ξ_k is the charge on a particle k, $\xi_{k'}$ is the charge on a particle k', k is an index running from 1 to N on particles in cell $l = 0$, k' is an index running from 1 to N on particles in cell l', and l' is an index running from $-\infty$ to ∞. The Σ' means that when $l' = 0$, k' cannot equal k, as this would include self-interaction energy in the sum. The factor $\frac{1}{2}$ appears in the formulae since the summation includes every interaction twice. Also notice that since a plasma is electrically neutral, then

$$\sum_{k} \xi_k = 0. \tag{6}$$

It is impractical to evaluate (5) by direct summation since the slow decrease of the Coulomb interaction means that the sum should be over an infinity of cells. However, the energy can be expressed as a convergent series in the following manner. Rewrite (5) as

$$E = \frac{1}{2}\sum_{k} \xi_k \lim_{\mathbf{x}\to\mathbf{x}(k)} \left\{ \sum_{l'k'} \frac{\xi_{k'}}{\left|\mathbf{x}\begin{pmatrix} l' \\ k' \end{pmatrix} - \mathbf{x}\right|} - \frac{\xi_k}{|\mathbf{x}(k)-\mathbf{x}|} \right\}, \tag{7}$$

then use Ewald's identity, namely

$$\left|\mathbf{x}\begin{pmatrix} l' \\ k' \end{pmatrix} - \mathbf{x}\right|^{-1} = \frac{2}{\sqrt{\pi}} \int_0^\infty \exp\left\{-\left|\mathbf{x}\begin{pmatrix} l' \\ k' \end{pmatrix} - \mathbf{x}\right|^2 \rho^2\right\} \mathrm{d}\rho,$$

to express the interparticle distance as an integral. Further the integral can be split into two quickly convergent parts by use of the Theta transformation, namely

$$\frac{2}{\sqrt{\pi}} \sum_{l} \exp\{-|\mathbf{x}(l)+\mathbf{x}(k')-\mathbf{x}|^2\rho^2\} \equiv \frac{2\pi}{v} \sum_{h} \frac{1}{\rho^3} \exp\{-\pi^2\rho^{-2}|\mathbf{y}(h)|^2 + 2\pi \mathrm{i}\mathbf{y}(h) \,.\, (\mathbf{x}-\mathbf{x}(k'))\},$$

where v is the cell volume, and since we are dealing with a face-centred cubic lattice the reciprocal cell vectors are equal to the cell vectors. However, it is convenient to talk in terms of the reciprocal lattice vectors as this helps with dimension checks. Now, putting the appropriate series in (7) after dividing the range of integration, so that for small values of ρ the right-hand side of the Theta function identity is used, and for large values of ρ the left-hand side is used, we obtain

$$E = \frac{1}{2}\sum_{k} \xi_k \lim_{\mathbf{x}\to\mathbf{x}(k)} \sum_{l'k'} \xi_{k'} \left[\frac{2\pi}{v} \int_0^R \frac{1}{\rho^3} \exp\{-\pi^2\rho^{-2}|\mathbf{y}(h)|^2 + 2\pi \mathrm{i}\mathbf{y}(h) \,.\, (\mathbf{x}-\mathbf{x}(k'))\} \,\mathrm{d}\rho \right.$$
$$\left. + \int_R^\infty \frac{2}{\sqrt{\pi}} \exp\left\{-\left|\mathbf{x}\begin{pmatrix} l' \\ k' \end{pmatrix} - \mathbf{x}\right|^2 \rho^2\right\} \mathrm{d}\rho - \frac{\xi_k}{\mathbf{x}(k)-\mathbf{x}} \right].$$

The term $l' = 0$ may be neglected in the first term above (indicated by a prime on the summation in the second term when rewritten below) because of (6). Then changing

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the order of integration and summation, the integration can be carried out; further, the second term can be written in terms of a standard integral called the Error function, defined by

$$E(x) = \frac{2}{\sqrt{\pi}} \int_0^x \mathrm{e}^{-t^2}\,\mathrm{d}t,$$

since then

$$\frac{R}{Rt}(1-E(Rt)) = \frac{2}{\sqrt{\pi}} \int_R^\infty \mathrm{e}^{-|t|^2\rho^2}\,\mathrm{d}\rho.$$

Completing this and rearranging gives

$$E = \frac{1}{2}\sum_k \xi_k \lim_{\mathbf{x}\to\mathbf{x}(k)} \left[R \sum_{l'k'} \xi_{k'} \frac{1}{R\left|\mathbf{x}\begin{pmatrix} l' \\ k' \end{pmatrix} - \mathbf{x}\right|} \left\{1 - E\left(R\left|\mathbf{x}\begin{pmatrix} l' \\ k' \end{pmatrix} - \mathbf{x}\right|\right)\right\} - \frac{\xi_k}{|\mathbf{x}(k)-\mathbf{x}|} \right.$$

$$\left. + \frac{\pi}{v}\sum_{k'} \xi_{k'} \sum_h{}' \frac{\exp\{-\pi^2 R^{-2}|\mathbf{y}(h)|^2\}\exp\{2\pi\mathrm{i}\mathbf{y}(h)\,.\,(\mathbf{x}-\mathbf{x}(k'))\}}{\pi^2|\mathbf{y}(h)|^2} \right].$$

In taking the limit, it can be seen that apart from the second term and the term $\begin{pmatrix} l' \\ k' \end{pmatrix} = \begin{pmatrix} 0 \\ k \end{pmatrix}$ in the first term, all terms are regular functions of $\mathbf{x}$ in the neighbourhood of $\mathbf{x}(k)$, and hence in these terms directly replace $\mathbf{x}$ by $\mathbf{x}(k)$. The prime on the first summation means the term $\begin{pmatrix} l' \\ k' \end{pmatrix} = \begin{pmatrix} 0 \\ k \end{pmatrix}$ is excluded. Thus

$$E = \frac{R}{2}\sum_{lk'k}{}'' \xi_k \xi_{k'} \frac{1}{R\left|\mathbf{x}\begin{pmatrix} l' \\ k' \end{pmatrix} - \mathbf{x}(k)\right|} \left\{1 - E\left(R\left|\mathbf{x}\begin{pmatrix} l' \\ k' \end{pmatrix} - \mathbf{x}(k)\right|\right)\right\}$$

$$+ \frac{\pi}{2v}\sum_{kk'} \xi_k \xi_{k'} \sum_h{}' \frac{\exp\{\pi^2|\mathbf{y}(h)|^2/R^2\}\exp\{2\pi\mathrm{i}\mathbf{y}(h)\,.\,(\mathbf{x}(k)-\mathbf{x}(k'))\}}{\pi^2|\mathbf{y}(h)|^2}$$

$$+ \frac{1}{2}\sum_k \xi_k^2 \lim_{\mathbf{x}\to\mathbf{x}(k)} \left[\frac{R}{R|\mathbf{x}(k)-\mathbf{x}|}\{1-E(R|\mathbf{x}(k)-\mathbf{x}|)\} - \frac{1}{|\mathbf{x}(k)-\mathbf{x}|}\right]. \tag{8}$$

This last term has the form

$$\lim_{\zeta\to 0}\left[\frac{R}{R\zeta}\{1-E(R\zeta)\} - \frac{1}{\zeta}\right] = \frac{-2R}{\sqrt{\pi}}.$$

The Energy Equation

The equation above calculates the potential energy in two parts; (*a*) short-range interactions, which are accounted for in term 1, and (*b*) long-range interactions which are accounted for in term 2. However, the energy associated with term 1 is *not* the

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energy of the short-range interactions, as term 3 also involves some short-range energy, the amount depending on the parameter R. The energy will be in ergs if ξ_k is in e.s.u., and R is in cm^{-1}. In crystal theory R is usually chosen of order 1/(nearest ion–ion distance) for quick convergence of both series, and this was initially the value given to R, but experience has shown that a better indication of the order of R is given by 1/(Debye shielding distance). The exact value chosen for R was determined by accuracy considerations as follows. To terminate the series of the first term, the energy contribution of particles interacting beyond a distance X_c is neglected; and this effectively considers interactions over only a finite number of cells l. The percentage error can be found as a function of RX_c the error increasing as RX_c increases. Also the calculation of $E\left(R\left|\mathbf{x}\binom{l'}{k'}-\mathbf{x}(k)\right|\right)$ is the most time consuming of all the operations, and as the number of these to be calculated depends on X_c, we require X_c to be as small as possible. A rough estimate can also be calculated for the error in the second term if terms beyond $h_1 = -1, 0, 1$ are neglected, and it is found that the error increases with R. It was found from preliminary calculations that the first term was much larger in magnitude than the second term, and fell slightly in magnitude as R increased, whereas the magnitude of the second term increased rapidly with R. To obtain the minimum error then, with a specified speed, the error in term 1 should approximately equal the error in term 2. This implied giving R a value of $2\cdot7$ (cell units)$^{-1}$, and when this value was tried it gave very accurate values for the potential energy of the cell, only disagreeing in the fifth figure. However, results obtained indicated that it would be much better to have less accuracy, and to improve the speed of the calculation, so X_c was reduced to $0\cdot5$ cell units (note this is still greater than the Debye shielding distance for temperatures below 5×10^4 °K) and by again going through the above analysis, a value of $R = 3\cdot5$ was found to give minimum error, which now became as high as ±1 in the third figure, but the increase in speed amply justified the change.

The preliminary calculations also emphasized the importance of three other factors. The choice of δ_0, the maximum displacement a particle may undergo; the choice of AO, the distance of closest approach between two particles; and the distribution choice $\alpha(j,k)$ given by equation (3). Consider the probability $\alpha(j,k)$ for a transition from a high energy state j to a proposed new state k of lower energy, so

$$\delta E = V(j) - V(k)$$

will be positive, and $\alpha(j,k)$ will always be less than $0\cdot5$. As

$$\alpha(j,k) = \{1+\exp(\delta E/kT)\}^{-1},$$

the probability of a particle staying in state j in preference to k will also depend strongly on the temperature as well as on δE. The initial calculations showed that δE depends in turn on the size and direction of the particle movement, and the position of the closest particle. In future two particles which are closer than 100 mesh units will be referred to as "linked", and it is movements of these particles which cause large changes in δE, and hence give a large probability of the particle moving to the lower energy state. However, it was found that at high temperatures (i.e. 10^5 °K) the particles approximately distribute themselves throughout the cell, and

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have an average interparticle distance of approximately 400 mesh units, so δE was usually small, and $\alpha(j,k) \approx 0 \cdot 5$. At lower temperatures ($\approx 10^4$ °K) more links were formed, and even small changes δE had a greater effect. Perhaps a useful interpretation of how the statistics are built in is to consider that each particle has associated with it an effective statistical radius, beyond which the effect of the statistical distribution is negligible, but within which the statistics appreciably influence particle movements. This effective statistical radius becomes larger as the temperature is lowered. Now as indicated above, δ_0 also has an important influence on the rapidity of convergence and Green (1964) has shown that a $\delta_0 \approx L/3N$ has the right order of magnitude for most calculations. However, if δ_0 is too large, the energy/cell will fluctuate considerably with each new iteration, while on the other hand if δ_0 is too small, not enough samples of configuration space will be obtained in a reasonable time. It is perhaps best to let δ_0 be on the large side to start with, but as the system nears equilibrium to decrease δ_0 to a smaller value. A parameter which is important in the interpretation of the results is AO, which limits the closeness of approach of two particles, and hence the potential energy between them. The value given to AO is twice the Bohr radius, for at this radius (by Bohr's orbit theory) a particle has its lowest potential energy possible without any kinetic energy, and the value of the potential energy is the same as the ionization energy for the particle. However, the importance of AO becomes apparent *if* it is said that "pairing" occurs when two particles are closer than AO (i.e. particles are in the ground state), and particles are not considered as paired when they are in excited states. Such states have previously been referred to by saying the particles are "linked". In Saha's work, which is mentioned when the results are discussed, particles are considered to be paired only if they are in the ground state as above, but excited states (except the continuum) are not allowed to exist. This differs from the above case, where a continuum of excited states is allowed to exist, as particles may move out from AO in a random fashion, modified only by the statistics. The difference in the definition of pairs and links between two charged particles must be kept in mind when comparison is made with Saha's theory.

III. Computation

A program was devised to carry out the procedure discussed in the last section. The major part of the program is concerned with the calculation of the potential energy associated with a particle from equation (8); and considerable effort was made to reduce the computational time for one iteration. Preliminary runs were completed with four particles on an I.B.M. 1620 computer to ascertain the accuracy, and optimum values for R, δ_0, and X_c. Using the four-particle results to start from a favourable configuration, the program was transferred to the I.B.M. 7090, and 16 electrons and 16 protons considered in the unit cell. The electrostatic energy of the 16 electrons and 16 protons in a particular configuration is termed the "cell energy" and this is plotted against the number of iterations done. (An iteration is completed when all 32 particles in the cell have each been considered for possible movement.) When the energy was considered to have reached a stable value, the run was terminated, and graphs of the radial distribution functions for like and unlike particles were compiled from the equilibrium configuration, i.e. where the energy graph

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was relatively level. The number density was constant for all runs, the number of protons equalling the number of electrons $= 10^{18}$ electrons/cm^3. Three main runs were completed, the first at a temperature of $1\cdot35\times10^5$ °K ran for 750 iterations, the second at 2×10^4 °K ran for 1050 iterations, and for both cases $R = 2\cdot7$ (cell units)$^{-1}$, $X_c = 1\cdot0$ cell units, and $\delta_0 = 0\cdot015\sqrt{3}$ cell units. The results for the radial distribution functions were in extreme disagreement with the D.H. theory, and the error seemed to be that not enough iterations were completed and that the system was still proceeding to equilibrium. To overcome this difficulty the program was changed, with the loss of some accuracy, and run 3 was computed for $T = 10^4$ °K, $X_c = 0\cdot5$, $\delta_0 = 0\cdot015\sqrt{3}$, and $R = 3\cdot5$, and allowed to run for 6100 iterations. The results of this run only will be presented. This run took five hours of computing time.

The random numbers needed for the program were generated by the power residue method $R_{n+1} = (KR_n+c)\bmod p$, where the constants have been chosen for the 7090 computer by Rotenburg (1960), and Coveyou (1960) has modified them to minimize correlation between successive numbers. The Error function was evaluated in a subprogram using Hasting's approximation. While computing, the problem was most conveniently considered in terms of the *cell unit*, which was further divided into *mesh units* to enable much of the arithmetic to be done in fixed point mode. One cell unit = 1000 mesh units, and its value is determined by the density to be considered. Thus 16 electrons in a cube of 1 cubic cell unit must be equivalent to the electron density N, and hence

$$\begin{aligned} 1 \text{ cell unit} &= (16/N)^{\frac{1}{3}} \text{ cm} \\ &= 2\cdot52\times10^{-6} \text{ cm} \qquad \text{for } N = 10^{18} \text{ electrons/cm}^3. \end{aligned}$$

Energy was computed in terms of (cell units length)$^{-1}$, so that

$$\text{energy in ergs} = 23\cdot96746\times10^{-20}(16/N)^{-\frac{1}{3}}\times\text{energy in cell units},$$

and similarly

$$\beta = \frac{1}{kT} = 16\cdot7102\times\frac{10^{-4}}{2\cdot52}\times\frac{N^{\frac{1}{3}}}{T} \text{ cell units of energy.}$$

IV. Results and Discussion

The results of run 3 are presented first with brief notes, then some of the comparable theories are discussed, and finally the conclusions and limitations of the method are presented.

The Energy Graph

The energy graph (Fig. 1) only shows points which are averaged over 20 energy values, and even then the graph is highly erratic; before averaging it was even more so, large fluctuations occurring within a few iterations. Plotted on the right-hand side of the energy graph are various levels. The Monte Carlo level is the average energy of the calculation for iterations 4000–6100 (i.e. those from which the radial distribution graphs were drawn) and this level is meant to give the equilibrium level, which, as can be seen from the graph, is doubtful. The D.H. line gives the cell energy as found

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by the D.H. theory. The horizontal sloping lines are drawn to indicate the number of pairs existing in the unit cell. The lines slope because of the criterion taken for pairing, so that although only one pair may exist, there is an increasing number of links, or particles not far from pairing, as the calculation proceeds and these links lower the energy level at which one pair is present.

The Distribution Functions

The distribution functions (Fig. 2) are obtained from equation (1). To graphically represent the results and obtain a smooth graph, ΔN is summed in steps of $\Delta r = 10$ mesh units. The interval 0–10 mesh units is not considered, as particles within

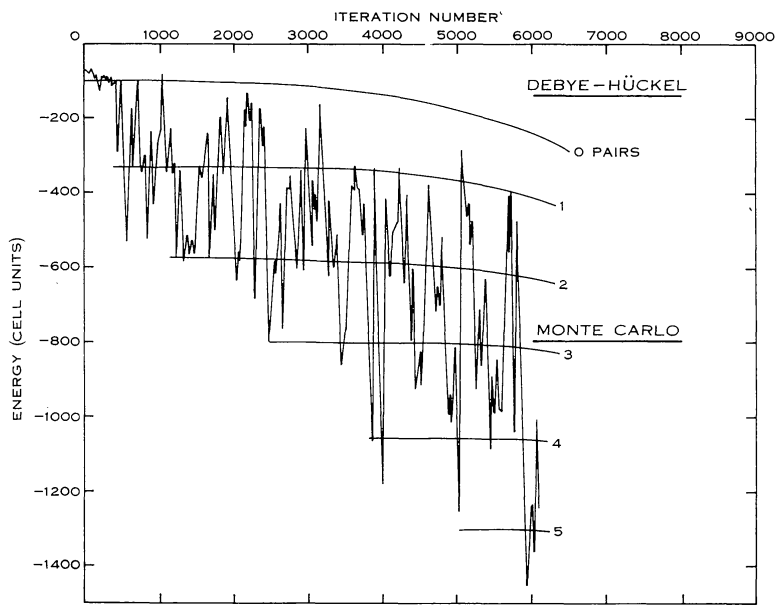

Fig. 1.—Energy graph for a plasma of density 10^{18} electrons/cm^3 at a temperature of 10^4 °K.

4·2 mesh units are paired. The radial distribution function is normalized, so that $g(r) \to 1$ as $r \to \infty$, but since the self-interaction distance is not counted, it follows that only 15 like interparticle distances are recorded in the cell for one particle, so one may expect $\rho_0 = 32 \times 15$ as the 32 particles are moved. However, if this is used to obtain the normalization constant, then it leads to a large error when the energy/cell is calculated from the radial distribution function, as now the number of electrons (N_a) is not equal to the number of protons (N_b), and the cell is not electrically neutral, so that the macroscopic energy components in the formula

$$U_e = \Sigma_a \Sigma_b \tfrac{1}{2} N_a N_b \Sigma_r (g(r) - 1) \phi_{ab} 4\pi r^2 \Delta r \tag{9}$$

do not cancel. This means ρ_0 must be the same for like and unlike particles, and the radial distribution functions are obtained using normalization factors with $\rho_0 = 16 \times 32$

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in both. Figure 2 includes a graph of the D.H. radial distribution function for comparison, and the Debye shielding distance is marked by λ_D, to indicate the distance beyond which the change of the reference particle should be neutralized. Before discussing the graphs and their implications in detail, the other theories will be briefly presented and discussed, so that later comparisons can be made.

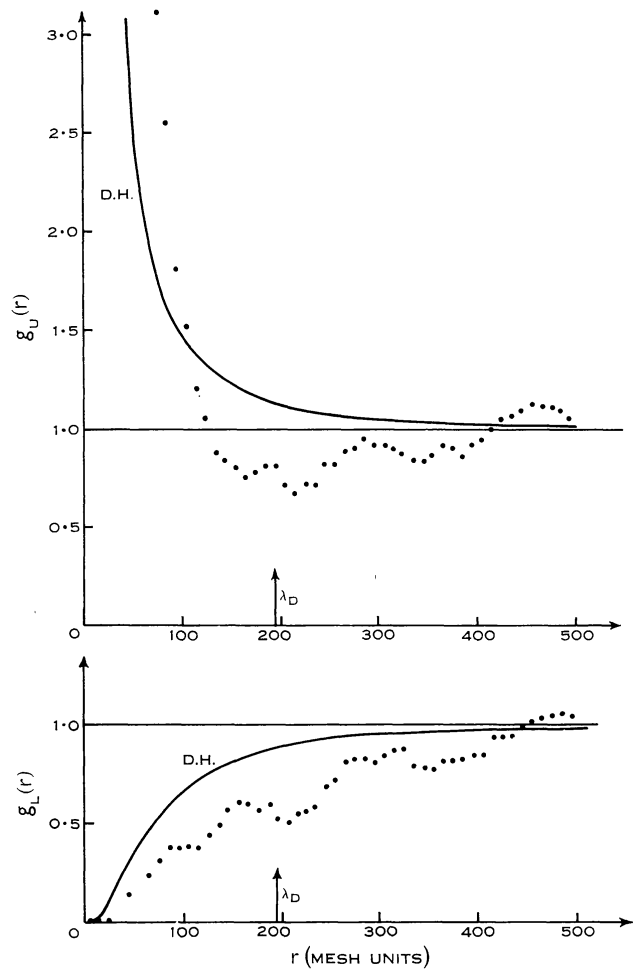

Fig. 2.—Radial distribution functions for a plasma (of density 10^{18} electrons/cm^3 at a temperature of 10^4 °K) calculated from iterations 4000 to 6100.

The Debye–Hückel theory can be applied to plasmas, i.e. fully ionized gases whose resultant macroscopic charge is zero. The theory uses Boltzmann's distribution law and Poisson's equation, and assumes the interionic potential is small compared with the thermal energy, to obtain the following equations for the distribution function

$$g_{ab}(r) = \exp\left\{\frac{e_a e_b}{rkT} \cdot \frac{1}{\exp(r/\lambda_D)}\right\},$$

where $\lambda_D = (kT/8\pi ne^2)^{\frac{1}{2}}$ and is called the Debye shielding distance, e_a, e_b are the charges

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on the particles of type a and type b, T is the absolute temperature, and n = number density of particles of type a = number density of particles of type b.

This distribution function emphasizes an exponential form, and there is a complete lack of oscillation. It also implies that surrounding a given ion there is a sheath of ions of opposite sign, and that outside a distance λ_D the sheath has neutralized the potential field of the ion. If $g_{DH}(r)$ is substituted in equation (9) and a linear approximation used, the energy/unit volume is given by

$$E_{DH} = \frac{ne^2}{\lambda_D}\{\exp(-b_0/\lambda_D) - \exp(-a_0/\lambda_D)\},$$

where b_0 is the range of the distribution function, and a_0 is the distance of closest approach. The D.H. level on the graph of Figure 2 is for $a_0 = 0$ and $b_0 \to \infty$. The D.H. theory then will be inaccurate when the density of the plasma is high, as the interionic potential is large compared with the thermal energy. Gronwall, La Mer, and Sandved (1928) have shown that there will be at least a 10% correction in the D.H. energy level for the density and temperature considered.

Broyles, Sahlin, and Carley (1963) have recently extended to plasmas the most successful of the integral equation methods used to find radial distribution functions for fluids, and Carley (1963) has applied the techniques in detail to a classical electron gas (i.e. electrons considered moving in a neutralizing uniform background of positive charge), and distribution functions for various densities and temperatures are presented in terms of a parameter θ, where $\theta \approx 370T/N$, T being the temperature in °K, and N the number of electrons/cm^3. For $T = 10^4$ °K and $N = 10^{18}$ electrons/cm^3 the like radial distribution functions given by the Percus-Yevick and Broyles-Sahlin methods agree well, but disagree with the D.H. and Convolution Hypernetted Chain approximations. This disagreement is enough to alter energy values considerably, but the form of the distribution function from all methods is very similar, and hence has not been drawn on the graphs, the D.H. form being deemed sufficient. They notice no oscillatory behaviour of g for values of $\theta > 0\cdot5$, but below this value some oscillatory nature is evident; however, at this stage the solution of the integral equations becomes difficult, the convergence being slower and less stable.

Villars (1963) has numerically solved a set of integral equations which were proposed by Green (1961) for metallic plasmas. For 10^{18} electrons/cm^3 at 10^4 °K he obtains unlike radial distribution functions very similar to the D.H. curve, only being slightly displaced, this being significant when calculating some of the thermodynamic variables. During the numerical procedure he finds that it is necessary to use a D.H. tail to the radial distribution function, that $g(r)$ must also be renormalized, and that if this is done then the results converge rapidly for temperatures of 10^7 °K and 10^6 °K, slowly for 10^5 °K, but diverge for 10^4 °K.

*Saha's theory** on the thermal ionization of gases also provides some comparison with the above results. His equation, derived from the viewpoint of chemical equilibria, has proved reasonably useful and has been used extensively since its proposal. For a hydrogen gas of density 10^{18} electrons/cm^3 he predicts that the degree of

* See Saha and Saha (1934).

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ionization (i.e. number density of ions/number density of atoms originally in the gas) is 5% at 10^4 °K and approximately 90% at 2×10^4 °K. Referring to the basic cell of 32 atoms used in the Monte Carlo approach, this means that from Saha's theory one might expect 1 pair of particles at 2×10^4 °K with the other 30 particles existing as ions, whereas at 10^4 °K one would expect only 2 ions and the other 30 atoms to be existing as 15 pairs. However, the Saha equation involves certain approximations; thus it neglects excited states, an ion being either in its lowest bound state or in the continuum, and it also includes thermodynamic assumptions.

From the above theories one may not be surprised if these results differ from the D.H. theory considerably, as the approximations of that theory are large in the range of these results, and also the occurrence of pairing invalidates the D.H. theory to a large extent. It is also not surprising that the results disagree with the results of Broyles, Sahlin, and Carley (1963), and of Carley (1963) as they deal with an electron gas, and not a proton–electron plasma. The results of Villars (1963) are in some doubt because they do not converge for this temperature. However, the large discrepancies of the other runs gave an indication that the disagreement in the case of the higher temperatures was due to the system only approaching equilibrium very slowly, and that at the end of the run the configuration still retained memory of the initial configuration, and this effect certainly contributes to the disagreement for the low temperature case also, as it can be seen that the energy graph has not reached anything like a stable level. However, while searching for causes of discrepancy, several interesting features came to light. The energy peaks are closely related to particle movements. Thus when two unlike particles approach, or two like particles separate, a sudden downward peak appears. The particles move in a random walk fashion and at high temperatures become randomly dispersed throughout the volume, but at the lower temperature chosen, once the particles have collided they remain fairly close together, only rarely escaping the influence of the other particle. These results of the system approaching equilibrium may be useful for obtaining information about irreversible processes, as Green (1964) has shown that the study of one particle throughout several collisions is sufficient to determine the transport coefficients for the system, and the results may be later applied to this aspect.

In spite of the fact that Figure 2 does not show the equilibrium distribution functions, some general features are becoming evident. For unlike particles there is a peak indicating the definite preference for particles to pair, this being followed by a trough at about 200 mesh units suggesting an absence of unlike particles, and then the curve returns to something like an average value. The like distribution function also has a depression at $r = 200$. However, when distribution graphs were drawn of the first few iterations, the unlike distribution function had no pronounced peaks or troughs; except for $r < 50$ the graph fell to zero. On the other hand, the like distribution function had a sharp peak at $r = 50$ (but still below $1\cdot0$), a very deep trough between $r = 100$–200, and then rose steadily to a high peak at 450. Thus, as the run has progressed the unlike distribution function has developed the depression below 50 to a huge peak, and also developed a trough at 200, and a small peak at 450; while the unlike function has reduced the peak at 50, filled in the trough from 100 to 200 to a very large extent, and also reduced considerably the peak at 450. Thus it seems

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that some form of long-range structure is being set up in the plasma, as the oscillatory pattern seems to be strengthening for the unlike case. The structure is not nearly as precise as a metallic crystal, and it may be connected with the theory of Bohm and Pines (1952), who have shown that collective excitations occur for an oscillation wavelength greater than the Debye shielding distance. As λ_D is small for a low temperature plasma of high density, one would expect plasma oscillations particularly in such a case.

The results agree quite closely with Saha's theory, and, although at the end of the run there are at the most 5 pairs present whereas Saha's theory predicts 15, if the run were continued it is possible that more pairs would develop. A brief run at 10^3 °K showed that at this temperature all particles remained paired, as Saha predicts, and another run at 2×10^4 °K found no pairing, while one pair is suggested by Saha. Long runs at 9×10^3 °K and $1\cdot5\times10^4$ °K are needed to fully verify Saha's theory.

In conclusion, the Monte Carlo method of calculating radial distribution functions in a plasma is a feasible approach if significant computing time is available. Compared with other methods it has the advantage of giving the percentage ionization if the plasma is not fully ionized, and this is especially useful for dense plasmas. The results indicate that at least 10 000 iterations must be completed before the system can be considered near to its equilibrium state, and for a badly chosen starting configuration, the run would need to be considerably longer. The results also indicate that the Saha equation for the degree of ionization in a plasma is remarkably accurate, and the ionization occurs quite suddenly at about 10^4 °K. The distribution functions *imply*, and the emphasis in this word must be stressed, that, in the region of this electron density, oscillation appears in the radial distribution functions. However, for more conclusive results a longer run is needed so that the energy of the system can settle into an equilibrium pattern and steady-state radial distribution functions can be obtained.

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