Correlation between the Kinetic and Potential Energy of an Ionized Gas

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The thermodynamic functions of a system of free electrons and ions are calculated by the methods of classical statistical mechanics under the condition that bound-particle states with negative internal energy, e.g., atoms, are explicitly excluded from the partition function. This exclusion is found to have the following consequences: (1) The radial distribution function of electrons about ions has the form $g^{+-}(r) = 2\pi(\pi kT)^{-3/2} \times \int_0^\infty \exp(-\epsilon/kT)[\epsilon+w(r)]^{1/2}d\epsilon$, where ϵ is the internal energy of an ion-electron pair and $w(r)$ is a potential of average force. (2) $w(r)$ is obtained as an iterative solution of the nonlinearized Poisson equation and used for calculating the system's potential energy U. No divergence arises and U is found different from the Debye-Hückel energy U_D by amounts between 5 and 10% of U_D. (3) The average kinetic energy at position $\mathbf{r}$ is found to depend on $w(\mathbf{r})$. The total kinetic system energy per particle is found to differ from $3kT/2$ by about 50% of U_D.

1. INTRODUCTION

IT is generally believed that the free energy of a system of point charges, such as a fully ionized hydrogen plasma, is infinite according to the formalism of classical statistical mechanics. The origin of the alleged infinity is the Boltzmann factor in the formula for the radial distribution function of electrons about ions,

$$g^{+-}(r) = \exp[-W^{+-}(r)/kT],\qquad (1)$$

where $W^{+-}(r)$ is the potential of the average force acting on an electron in distance r from a positive ion. While the rigorous calculation of $W^{+-}(r)$ is extremely difficult it is a well-defined quantity, and it is generally accepted that $W^{+-}(r)$ is a shielded Coulomb potential which introduces an essential singularity into the Boltzmann factor at $r=0$. Thus, the average potential energy of an ion with charge Ze in the field of the surrounding electrons,

$$\langle u^{+-}\rangle_{\mathrm{av}} = 4\pi Ze^2n \int_0^\infty [r^2g^{+-}(r)/r]dr,$$

$$(n=\text{electron density})\qquad (2)$$

is infinite at all temperatures. In the past this difficulty has been removed by formal devices which are physically not admissible, e.g., linearization of the Boltzmann factor, treatment of the positive ions as a continuum,[1] and introduction of a repulsive core into the expression for $W^{+-}(r)$.[2-5] The latter device is not realistic in a system of free electrons and ions since electrons can penetrate the inner shells of the ions (if there are any) and approach the nucleus to arbitrary close distances. This possibility is confirmed by quantum mechanics since the radial wave function of the s states of free electrons moving in a shielded Coulomb potential is finite at $r=0$.[6] To our knowledge, a systematic analysis of this problem does not exist in the published literature, but it appears to be the opinion of many authors that only quantum mechanics can remove the infinite Coulomb energy. It is one purpose of this paper to

[1] Y. Abe, Progr. Theoret. Phys. (Kyoto) **22**, 213 (1959).
[2] S. F. Edwards, Phil. Mag. **3**, 119 (1958); **4**, 1171 (1959).
[3] I. R. Iukhnovskii, Zh. Eksperim. i Teor. Fiz. **34**, 379 (1958) [English transl.: Soviet Phys.—JETP **7**, 263 (1958)].
[4] T. Morita, Progr. Theoret. Phys. (Kyoto) **22**, 757 (1959).
[5] The problem of the Coulomb divergence arises also in the kinetic theory of plasmas and is often resolved by introducing a hard core.
[6] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Addison-Wesley Publishing Company, Reading, Massachusetts, 1958), p. 110.

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show that classical physics can do the job equally well provided that certain obvious limitations of classical mechanics, to be stated in the following paragraph, are carefully taken into account.

In order to fix the conditions for the validity of a classical theory we consider a system consisting of free electrons, one species of positive ions, e.g., protons, and one species of neutral atoms. The free energy F of the system is a sum of contributions from the three different particle species and it is obvious that the contribution to F from the bound electrons requires quantum mechanics for a correct computation. Only the free electrons and ions are problematic and will be the sole concern of this paper. The exclusion of the bound-particle states is, of course, assumed in all papers on classical plasma statistics, but it is usually not explicitly stated and its consequences are ignored. However, these consequences are quite startling and important and form the main subject of our work. A theoretical determination of the degree of ionization, which requires the partition function of the negative-energy states is, of course, not attempted.

The implications of the exclusion of bound-particle states are most easily demonstrated for systems which are unmarred by the many particle aspects of plasma statistics. For this reason we study first an artificial system consisting of one electron and one proton fixed in the center of a spherical box of radius R and wall temperature T. The partition function can be written in the form

$$Q=Q(\epsilon<0)+Q(\epsilon>0)=\sum_{\epsilon_n<0} g_n \exp(-\epsilon_n/kT)$$

$$+h^{-3}\int_V\int_{\epsilon>0}\exp[-(p^2/2m-e^2/r)/kT]d\mathbf{p}d\mathbf{r}, \quad (3)$$

which indicates that bound states ($\epsilon_n<0$) and free states ($\epsilon>0$) will be treated separately and that classical statistical mechanics will be used for the free states. In order to satisfy explicitly the condition $\epsilon>0$ we introduce ϵ instead of $\mathbf{p}$ as independent variable by means of the relations

$$\epsilon=(p^2/2m)-(e^2/r), \quad d\mathbf{p}=2\pi(2m)^{3/2}(\epsilon+e^2/r)^{1/2}d\epsilon, \quad (4)$$

and obtain

$$Q(\epsilon>0)=2\pi(2m/h^2)^{3/2}\int_0^\infty d\epsilon$$

$$\times\exp[-\epsilon/kT]\int_V(\epsilon+e^2/r)^{1/2}d\mathbf{r}. \quad (5)$$

Obviously, the quantity multiplied into the Boltzmann factor,

$$g(\epsilon)=2\pi(2m/h^2)^{3/2}\int_V(\epsilon+e^2/r)^{1/2}d\mathbf{r}, \quad (6)$$

is the classical density of states for a one-particle system, in agreement with the general classical formula for

N-particle systems.[7] The radial distribution function associated with the free states of the electron is

$$g(r)=[1/Q(\epsilon>0)h^3]\int_{\epsilon>0}\exp[-(p^2/2m-e^2/r)/kT]d\mathbf{p}$$

$$=2\pi(2m/h^2)^{3/2}/Q(\epsilon>0)$$

$$\times\int_0^\infty\exp[-\epsilon/kT](\epsilon+e^2/r)^{1/2}d\epsilon. \quad (7)$$

The average potential energy of the free electron,

$$\bar{u}=-2\pi(2m/h^2)^{3/2}/Q(\epsilon>0)$$

$$\times\int_0^\infty d\epsilon\exp[-\epsilon/kT]\int_V(e^2/r)(\epsilon+e^2/r)^{1/2}d\mathbf{r}, \quad (8)$$

is finite, and its average kinetic energy $\bar{K}(r)$ is a space function of the form

$$\bar{K}(r)=\int_0^\infty\exp[-\epsilon/kT](\epsilon+e^2/r)^{3/2}d\epsilon\Big/$$

$$\times\int_0^\infty\exp[-\epsilon/kT](\epsilon+e^2/r)^{1/2}d\epsilon; \quad (9)$$

the volume integral $\bar{K}$ of $\bar{K}(r)$ is different from $3kT/2$.

These unexpected results have nothing to do with the Coulomb force and are a consequence of the condition $\epsilon>0$. This condition prevents a separation of the partition function into a product of a space integral and a momentum integral and is responsible for a statistical correlation between potential and kinetic energy.[8] For the hyperbolic orbits of the free electron the correlation is such that the radial velocity increases with decreasing r. This reduces the lifetime of the free electron in regions of large negative potential and, thus, prevents the divergence of the potential energy. It is also responsible for the breakdown of the equipartition theorem for the free-electron states. If the ϵ integrations in the Eqs. (7) to (9) are extended to the lower limit $-e^2/r$, Eq. (1) for $g(r)$ is recovered, $\bar{u}$ is found infinite, and $\bar{K}(r)=\bar{K}=3kT/2$ for all r.

From this point of view the essential feature of quantum mechanics is the existence of a ground-state energy $E_{\min}>-\infty$. If the particles have a repulsive core a lower limit $E_{\min}$ exists even in classical physics and the Boltzmann factor in the formula for the radial distribution function remains finite. Quantum effects are then negligible at sufficiently high temperatures and a separate treatment of bound and free particle states is not necessary. However, such a separate treatment is

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[7] A. Münster, *Statistische Thermodynamik* (Springer–Verlag, Berlin, 1956), p. 122.

[8] Potential and kinetic energy are always fully correlated along an orbit of specified energy ϵ. The correlation is completely removed by averaging over all energies, and it is only partially removed by averaging over a limited energy domain.

required if one wants to calculate the degree of dissociation or ionization. In this case the negative-energy states must be explicitly excluded from the partition function $Q(\epsilon>0)$ of the free particles in spite of the existence of a repulsive core. Only if $|Q(\epsilon>0)|\gg|Q(\epsilon<0)|$ the explicit exclusion may be omitted in a first approximation.

Some of the ideas developed in the preceding paragraphs have been mentioned by Fowler,[9] Eddington,[10] and Hill.[11] But they have never been applied to a plasma in a systematic and quantitative fashion. In fact, they have been completely ignored in the more recent papers on the statistical mechanics of plasmas which are mostly concerned with the mathematical subtleties of the many-body problem. These subtleties are definitely not the subject of our paper. Of course, we cannot ignore the many particle aspects of our problem but we plan to treat them in the simplest possible manner and on a level of mathematical rigor which is comparable to that of the original Debye-Hückel theory. Accordingly, we assume that the radial distribution function $g^{+-}(r)$ for the free-particle states in a plasma is given by Eq. (7) if the Coulomb potential e^2/r is replaced by a potential of average force $w(r)$ to be determined as a solution of the Poisson equation. We shall adopt this procedure in Sec. III, and in this fashion we shall be able to estimate the magnitude of the correlation effects; they will be found quite large compared to other corrections of the Debye-Hückel theory. A more rigorous evaluation of $w(r)$ which is extremely difficult because of the condition that bound-particle states must be excluded, will not be attempted in this paper. We shall, however, try to illuminate the physical nature of the potential $w(r)$ by the analysis in Sec. II and Appendix A.

II. THE RADIAL DISTRIBUTION FUNCTION OF FREE POINT CHARGES

We consider a system of N free electrons and N free, positive ions, introduce relative coordinates,

$$\mathbf{R}=(m^+\mathbf{r}^++m^-\mathbf{r}^-)/M, \quad \mathbf{r}=\mathbf{r}^+-\mathbf{r}^-,$$
$$\mathbf{P}=\mathbf{p}^++\mathbf{p}^-, \quad \mathbf{p}=(m^-\mathbf{p}^+-m^+\mathbf{p}^-)/M, \quad (10)$$
$$M=m^++m^-, \quad \mu=m^+m^-/M,$$

for one specified ion-electron pair and write the canonical density in the form

$$g\{\mathbf{r}_i^+, \mathbf{r}_i^-, \mathbf{p}_i^+, \mathbf{p}_i^-\}=[(N!)^2h^{6N}Q_{2N}(\epsilon_i>0)]^{-1}$$
$$\times \exp[-\epsilon/kT-E'/kT], \quad (11)$$
where
$$\epsilon=p^2/2\mu+u^{+-}\{\mathbf{r}; \mathbf{r}_i^+, \mathbf{r}_i^-\} \quad (12)$$

is the internal energy of the specified ion-electron pair,

[9] R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, New York, 1955), p. 64 ff., p. 576.
[10] A. S. Eddington, *The Internal Constitution of the Stars* (Dover Publications, Inc., New York, 1959), p. 262 ff.
[11] T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), p. 152 ff.

$u^{+-}\{\mathbf{r}, \mathbf{r}_i^+, \mathbf{r}_i^-\}$ is the potential energy of the electron in the field of all the other particles, i.e., the sum of *all* pair interactions involving the specified electron, and

$$E'=E-\epsilon=\frac{P^2}{2M}+\sum_i'\frac{P_i^{+2}}{2m^+}+\frac{P_i^{-2}}{2m_i^-}+U'\{\mathbf{r}_i^+, \mathbf{r}_i^-\} \quad (13)$$

is the remaining system energy. The primes indicate that explicit contributions of the fixed electron to E' are excluded. $Q_{2N}(\epsilon_i>0)$ is the partition function of the total system of $2N$ free particles. The radial distribution function of electrons about ions, or vice versa, is a phase space integral of the form

$$g^{+-}(r)=[(N!)^2h^{6N}Q_{2N}(\epsilon_i>0)]^{-1}$$

$$\times \int_{\epsilon_i>0} d\mathbf{R}d\mathbf{P} \prod_i' dr_i^+dr_i^-dp_i^+dp_i^-$$

$$\times \exp[-E'/kT]\int_{\epsilon>0} \exp[-\epsilon/kT]d\mathbf{p}$$

$$=C\left\langle \int_{\epsilon>0} \exp[-\epsilon/kT]d\mathbf{p} \right\rangle_{av}, \quad (14)$$

where the labels $\epsilon_i>0$ and $\epsilon>0$ exclude phase-space regions corresponding to bound-particle states. The symbol $\langle \ \rangle_{av}$ represents averaging against the weighting function $\exp[-E'/kT]$ over all coordinates and momenta with the exception of $\mathbf{p}$ and $\mathbf{r}$, as indicated by the prime on $\prod'$. C is a normalization constant. It is essential to note that the weighting function is, by definition, independent of $\mathbf{r}$. Thus, the whole $\mathbf{r}$ dependence is contained, according to Eq. (12), in the contribution $u^{+-}\{\mathbf{r}; \mathbf{r}_i^+, \mathbf{r}_i^-\}$ to ϵ. Utilizing Eq. (12) we introduce ϵ as independent variable and obtain

$$g^{+-}(r)=C'\left\langle \int_0^\infty \exp[-\epsilon/kT] \right.$$
$$\left. \times (\epsilon-u^{+-}\{\mathbf{r}; \mathbf{r}_i^+, \mathbf{r}_i^-\})^{1/2}d\epsilon \right\rangle_{av}. \quad (15)$$

Equation (15) is rigorous but not very practical. A convenient, approximate form which is completely analogous to Eq. (7) can be obtained on the basis of the following consideration. We represent $u^{+-}\{\mathbf{r}; \mathbf{r}_i^+, \mathbf{r}_i^-\}$ as the sum of the fixed pair interaction $u(\mathbf{r})$ which is not affected by the averaging, and a fluctuating term $u'\{\mathbf{r}; \mathbf{r}_i^+, \mathbf{r}_i^-\}$ which depends on the positions of all particles and is affected by the averaging process implied in Eq. (15). Since in our case $u(\mathbf{r})$ is a Coulomb potential which strongly increases with decreasing r, $u'\{\mathbf{r}; \mathbf{r}_i^+, \mathbf{r}_i^-\}$ can be neglected and $u^{+-}\{\mathbf{r}; \mathbf{r}_i^+, \mathbf{r}_i^-\}$ can be replaced by $u(\mathbf{r})$ if r is sufficiently small. If r is large, $u^{+-}\{\mathbf{r}; \mathbf{r}_i^+, \mathbf{r}_i^-\}\ll\epsilon$ for almost all ϵ, the square root can be linearized and $u^{+-}\{\mathbf{r}; \mathbf{r}_i^+, \mathbf{r}_i^-\}$ may be replaced by its average

$$\langle u^{+-}\{\mathbf{r}; \mathbf{r}_i^+, \mathbf{r}_i^-\}\rangle_{av}=-w(r). \quad (16)$$

Hence, ignoring the more complicated situation in the intermediate r range, $g^{+-}(r)$ may be approximated in the form

$$g^{+-}(r) \approx 2\pi/(\pi kT)^{3/2} \int_0^\infty \exp[-\epsilon/kT][\epsilon+w(r)]^{1/2}d\epsilon$$
$$\approx \underset{r\to\infty,\,w\to0}{[1+w(r)/kT]}, \quad (17)$$

which is normalized to unity.

The actual computation of $w(r)$ from the definition (16) and from Eq. (14) which demonstrates the nature of the required averaging process is probably impossible. Hence, we shall determine $w(r)$ as solution of the Poisson equation subject to the following boundary conditions:

$$\lim_{r\to0} w(r) = (Ze^2/r) + C, \quad (18a)$$

$$\lim_{w(r)/kT\to0} w(r) = (Ze^2/r)\exp[-r/h], \quad (18b)$$

where h is the Debye shielding length. The condition (18a) is obvious for physical reasons and is always imposed on the admissible solutions of the Poisson-Boltzmann equation. The feasibility of the condition (18b) follows from the linearized form of the radial distribution function (17).

The radial distribution function for two particles of equal charge has the conventional form

$$g^{++}(r) = g^{--}(r) = \exp[-w^{++}(r)/kT], \approx 1-w^{++}(r)/kT,$$
$$r\to\infty, \quad w^{++}(r)\approx w(r)\to0 \quad (19)$$

since the interaction energy is positive. Thus no region of phase space is excluded by the condition $\epsilon>0$. In view of the condition (18b) the approximation $w^{++}(r)\approx w(r)$ should be admissible and will be used throughout this paper.[12] We can now form the radial charge distribution

$$\rho(r) = ne[g^{++}(r) - g^{+-}(r)]$$

$$= en\Bigg[\exp(-x) - \exp(x) - 2(x/\pi)^{1/2}$$
$$+ 2(\pi)^{-1/2}\exp(x)\int_0^{x^{1/2}}\exp(-t^2)dt\Bigg], \quad (20)$$

where $x=w/kT$.

In conclusion we wish to make the following observation. The mean free path of point charges in a plasma is generally much larger than the Debye shielding length. We believe that this feature is essential for the applicability of our theory since otherwise negative-energy states could not be identified with bound-particle states and could not be summarily excluded from the partition function of free particles. This leads to the interesting conjecture that the mean free

path should enter explicitly the formulas of classical equilibrium statistical mechanics if it is shorter than the range of the intermolecular forces. Related considerations which illuminate the physical nature of our problem are presented in Appendix A.

III. THE MODIFIED POISSON-BOLTZMANN EQUATION

As indicated in the introduction we assume that $w(r)$ satisfies approximately the Poisson equation

$$\nabla^2 w(r) = -4\pi e[\rho(r) + eZ\delta(\mathbf{r})], \quad (21)$$

where $eZ\delta(\mathbf{r})$ is the charge distribution associated with the ion at the center of the charge cloud. In order to obtain corrections to the conventional Debye-Hückel theory we must solve Eq. (21) without linearization. We do this by iteration, and by subdividing the r range into four regions, 1–4, separated by the values r_i. The r_i are defined as follows (for details see Appendix B):

$$r_0 = 0,$$
$$w^{(0)}(r_1)/kT = 2,$$
$$w^{(0)}(r_2)/kT = 1, \quad (22)$$
$$w^{(0)}(r_3)/kT = \tfrac{1}{2},$$
$$r_4 = \infty.$$

The zeroth-order solution $w^{(0)}(r)$ for monovalent ions is guessed on the basis of the Eqs. (18) as

$$w^{(0)}(r) \approx e^2/r \quad \text{if} \quad r<r_2,$$
$$w^{(0)}(r) \approx (e^2/r)\exp(-\kappa r) \quad \text{if} \quad r>r_2(\kappa=1/h). \quad (23)$$

Using the following two expansions for the error functions,[13]

$$\text{erf}(\sqrt{x}) = 2(x/\pi)^{1/2}(1 - x/3 + x^2/10\cdots) \quad \text{if} \quad x\ll1,$$
$$\text{erf}(\sqrt{x}) = 1 - \exp(-x)(\pi x)^{-1/2}[1 - (2x)^{-1} \quad (24)$$
$$+ 3(2x)^{-2} - 15(2x)^{-3}\cdots] \quad \text{if} \quad x\gg1,$$

and suitable expansions of exponentials, etc., we find:
(1) $r < r_1$.

$$\rho_1(r) = -ne[g^{+-}(r) - g^{++}(r)]$$

$$= -\frac{ne}{\pi^{1/2}}[2x^{1/2} + x^{-1/2} - \tfrac{1}{2}x^{-3/2} + \tfrac{3}{4}x^{-5/2}]$$
$$+ \frac{ne}{(2.718)^2}\left(\frac{2r}{r_1} - 1\right)H\left(r - \frac{r_1}{2}\right), \quad (25)$$

where

$$H(y) = 0, \quad \text{if} \quad y<0,$$
$$= 1, \quad \text{if} \quad y>0.$$

The second term which involves the step function $H(y)$ implies the approximation that $g^{++}(r)$ is zero if

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[12] Actually $W^{++}(r)$ is quite different from $w(r)$ if r is small. But $g^{++}(r)$ is then so small that its actual value does not matter. Thus the difference is irrelevant.

[13] E. Jahnke and F. Emde, *Tables of Functions* (Dover Publications, Inc., New York, 1945), p. 23 ff.

$r < r_1/2$, and a linear function of r between $r_1/2$ and r. This approximation is perfectly harmless since $g^{++}(r)$ is negligibly small in region 1.

(2) $r_1 < r < r_2$. We expand $\rho(r)$ in a Taylor series about the point r_2 and obtain

$$\rho_2(r) = -ne[-A+B-C+D-x(B-2C+3D) - x^2(C-3D)-x^3D], \quad (26)$$

where

$$A = [-2\sinh x - 2(x/\pi)^{1/2} + \exp(x)\,\mathrm{erf}(x)^{1/2}]_{x=1}$$
$$= -1.19,$$
$$B = [d\rho/dx]_{x=1} = -0.80,$$
$$C = [\tfrac{1}{2}d^2\rho/dx^2]_{x=1} = 0.25, \quad (27)$$
$$D = [\tfrac{1}{6}d^3\rho/dx^3]_{x=1} = -0.086.$$

We note that the conventional form of the radial distribution function in regions 1 and 2 leads to the series $\rho(r) = -2ne(x+x^3/6+\cdots)$. The cubic term which is neglected in the Debye-Hückel theory produces an infinity in the free energy. But in our theory the highest power of x is $\tfrac{1}{2}$ in the critical region 1 and, hence, no infinity exists.

(3) $r_2 < r < r_3$. We use the same expansion as in region 2, but a different zeroth-order solution $w^0(r)$. Thus, $\rho_3(x) = \rho_2(x)$ but $\rho_3(r) \neq \rho_2(r)$.

(4) $r_3 < r$.

$$\rho_4(r) = -2ne[x+x^3/6-(2x^{3/2}/3\pi^{1/2})(1+2x/5)]. \quad (28)$$

The first two terms correspond to the nonlinearized Debye-Hückel theory. The last term which is much larger than the cubic term represents the correlation effects. These effects are quire significant even for large r as can be seen from Fig. 1.

We come now to the evaluation of the electrical field and potential. Since we have guessed the zeroth-order solution (23) the Poisson-Boltzmann equation can be solved by direct integration.
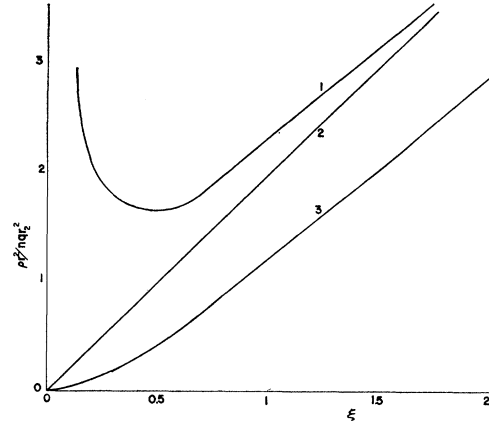

FIG. 1. Radial charge density $\rho(r)$ of a Debye-Hückel cloud corrected for the correlation effects. $\xi = r/r_2 = rkT/e^2$. Curve 1 corresponds to a nonlinearized Debye-Hückel theory in which $\rho(r)$ contains terms of 3rd order in $w(r)$ but is not corrected for correlation effects. Curve 3 takes into account correlation effects. Curve 2 corresponds to the linearized Debye-Hückel theory.

One finds for the average electrical field, in the region j, produced by the charge cloud

$$E_j(r) = \frac{4\pi}{r^2}\left[\sum_{i=1}^{j}\int_{r_{i-1}}^{r_i}\rho_i(r')r'^2dr' + \int_{r_j}^{r}\rho_j(r')r'^2dr'\right], \quad (29)$$

where r_j is the lower bound of the interval in which $E(r)$ is to be evaluated.

The first-order approximation $w^1(r)$ is now obtained in the form

$$w^{(1)}(r) = e\int_{r}^{\infty}E(r'')dr'', \quad (30)$$

which satisfies the boundary condition $w(\infty) = 0$. Substituting Eq. (29) into (30)

$$w^{(1)}(r) = -e\left[\int_{r}^{r_{j+1}}E_j(r'')dr'' + \sum_{k=0}^{2-j}\int_{r_{j+1+k}}^{r_{j+2+k}}(r'')dr''\right]$$

$$= -4\pi e\left\{\int_{r}^{r_{j+1}}\frac{dr''}{r''^2}\left[\sum_{i=1}^{j}\int_{r_{i-1}}^{r_i}\rho_i(r')r'^2dr' + \int_{r_j}^{r''}\rho_j(r')r'^2dr'\right]\right.$$

$$\left. + \sum_{k=0}^{2-j}\int_{r_{j+1+k}}^{r_{j+2+k}}\frac{dr''}{r''^2}\left[\sum_{i=1}^{j+1+k}\int_{r_{i-1}}^{r_i}\rho_i(r')r'^2dr' + \int_{r_{j+1+k}}^{r''}\rho_{j+1+k}(r')r'^2dr'\right]\right\}. \quad (31)$$

Equation (31) leads to a very lengthy analytical expression for $w^{(1)}(r)$ which is graphically represented in Fig. 2.[14] We give only the formula for $w_4^{(1)}(r)$ in region 4 which shows that the correlation effect is significant even in large distances from the cloud center, and the formula for $w_c^{(1)}(0)$ which represents the potential energy of the cloud center in the field of the cloud. $W_c^{(1)}(0)$ multiplied with the number of ions is, of course, the total electrostatic

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[14] For details, see W. Deering, Ph.D. thesis, New Mexico State University, 1963 (unpublished).

system energy which may be compared to the result of the Debye-Hückel theory.

$$w_4^{(1)}(r) = \left[\frac{q+q_1+q_2+q_3}{r}\right]_1 + \left[-\frac{qe^{-2\kappa r_2}(1+2\kappa r_2)}{r}+\frac{qe^{-\kappa r}}{r}\right]_2$$

$$-\frac{q\kappa^2 r_2}{6}\left[\frac{-\mathrm{Ei}(-6\kappa r_2)+\mathrm{Ei}(-3\kappa r)}{r/r_2}+3\kappa r_2\,\mathrm{Ei}(-3\kappa r)+\frac{e^{-3\kappa r}}{r/r_2}\right]_3$$

$$-\frac{4q\kappa\sqrt{2}}{9\pi^{1/2}}\left\{\frac{e^{-3/2\kappa r}}{(2r/r_2)^{1/2}}-\frac{e^{-3\kappa r_2}}{r/r_2}-\left(\frac{3\pi\kappa r_2}{4}\right)^{1/2}\left[1-\mathrm{Erf}\left(\frac{3\kappa r}{2}\right)^{1/2}-\frac{\mathrm{erf}(3\kappa r_2)^{1/2}-\mathrm{erf}(3\kappa r/2)^{1/2}}{3\kappa r}\right]\right\}_4$$

$$-\frac{4(10)^{1/2}(\kappa r_2)^{3/2}}{15}\left[1-\mathrm{Erf}\left(\frac{5\kappa r}{2}\right)^{1/2}+\frac{\mathrm{erf}(5\kappa r_2)^{1/2}-\mathrm{erf}(5\kappa r/2)^{1/2}}{5\kappa r}-\left(\frac{10}{25\pi\kappa r}\right)^{1/2}e^{-3\kappa r/2}\right]_5,\quad(32)$$

$$(q=\text{ionic charge})$$

where the terms collected in the numbered brackets have the following meaning:

(1) $q+q_1+q_2+q_3$ is charge inside sphere of radius r_3,
(2) linear term of the Debye-Hückel theory,
(3) cubic term of the Debye-Hückel theory,
(4) dominant correlation correction,
(5) negligible correlation correction.

$$w_c^{(1)}(0) = -e\kappa\{1-0.545(\kappa r_2)^{1/2}+0.321\kappa r_2+0.842(\kappa r_2)^{3/2}$$
$$-3.27(\kappa r_2)^2+\kappa r_2[0.25\mathscr{E}(-2\kappa r_2)$$
$$+(0.042+0.132\kappa r_2)\mathscr{E}(-3\kappa r_2)$$
$$+0.5\kappa r_2\,\mathrm{Ei}(-6\kappa r_2)]\},\quad(33)$$

where

$$-\mathrm{Ei}(-x) = \int_x^\infty (e^{-t}/t)dt,$$

$$\mathscr{E}(-n\kappa r_2) = \mathrm{Ei}(-n\kappa r_2)-\mathrm{Ei}(-2n\kappa r_2).$$
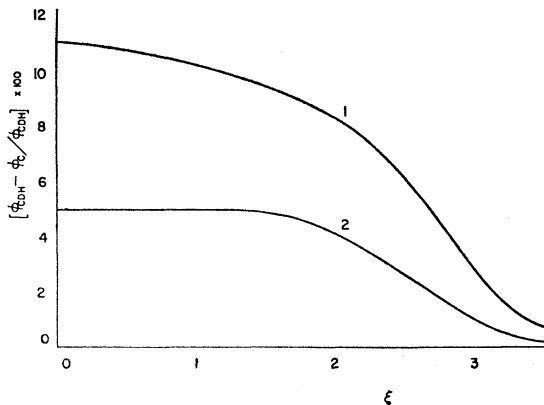

Fig. 2. Percentage difference between the cloud potentials ϕ_{CDH} of the linearized Debye-Hückel theory and ϕ_0 of the corrected theory as a function of $\xi=r/r_2=rkT/e^2$. Curve 2 corresponds to a temperature $T=10^4{}^\circ\mathrm{K}$ and ion density $n\approx10^{15}$ cm^{-3}. Curve 1 corresponds to $T=10^4{}^\circ\mathrm{K}$, $n\approx5\times10^{16}$ cm^{-3}.

Numerical results for cases of practical interest are contained in the following equations:

$$w_c^{(1)}(0) = -e\kappa(1-0.053),\quad\text{if}\quad\kappa r_2=10^{-2},$$
$$n=10^{15}\text{ cm}^{-3},\quad T=10^4{}^\circ\mathrm{K};$$

$$w_c^{(1)}(0) = -e\kappa(1-0.11)\quad\text{if}\quad\kappa r_2=5\times10^{-2},$$
$$n=5\times10^{16}\text{ cm}^{-3},\quad T=10^4{}^\circ\mathrm{K};$$

$$\kappa r_2 = (8\pi)^{1/2}(e^3 k^{-3/2})(n^{1/2}/T^{3/2})$$
$$=3.2\times10^{-4}(n^{1/2}/T^{3/2}).\quad(34)$$

Thus the corrections to the Debye-Hückel energy are about 10% of the uncorrected value $-e\kappa$ in plasmas of moderate density and they are essentially due to the correlation effects. The contribution of the cubic terms to the conventional Debye-Hückel theory is quite negligible compared to the correlation effects. The result (33) has been obtained without imposing the condition of weak shielding anywhere in the derivation. Thus, it should be a fair approximation for plasmas of any density and temperature.

IV. CORRECTIONS TO THE KINETIC ENERGY

If in classical statistical mechanics all particle energies are admitted the average kinetic energy of a particle is $3kT/2$, independent of its position in space. If negative particle energies (or some other energy regions) are excluded, a correlation between kinetic and potential energy is generated such that the average kinetic energy associated with the relative motion of a free electron about an ion becomes a space function $\langle K^{+-}(r)\rangle_{\mathrm{av}}$ $=\langle\epsilon+w(r)\rangle_{\mathrm{av}}$. The space average K^{+-} of $\langle K^{+-}(r)\rangle_{\mathrm{av}}$ can be obtained by integrating over a domain which is representative for the relative lifetime of the electron in regions with potential $w(r)/e$. We assume that the representative domain is the nearest-neighbor zone

with radius $r_0 = (3/4\pi n)^{1/3}$ and obtain

$$K^{+-} = \frac{\int_0^{r_0} \int_0^{\infty} e^{-\epsilon/kT} [\epsilon + w(r)]^{3/2} d\epsilon r^2 dr}{\int_0^{r_0} \int_0^{\infty} e^{-\epsilon/kT} [\epsilon + w(r)]^{1/2} d\epsilon r^2 dr}$$

$$= kT \frac{\int_0^{r_0} e^{w/kT} \left[\int_0^{\infty} e^{-y} y^{3/2} dy - \int_0^{w/kT} e^{-y} y^{3/2} dy \right] r^2 dr}{\int_0^{r_0} e^{w/kT} \left[\int_0^{\infty} e^{-y} y^{1/2} dy - \int_0^{w/kT} e^{-y} y^{1/2} dy \right] r^2 dr}$$

$$= \frac{3kT}{2} \frac{\int_0^{r_0} e^{w/kT} \left[1 - \frac{I_{3/2}(w/kT)}{I_{1/2}(\infty)} \right] r^2 dr}{\int_0^{r_0} e^{w/kT} \left[1 - \frac{I_{1/2}(w/kT)}{I_{1/2}(\infty)} \right] r^2 dr}, \quad (35)$$

where[13]

$$I_{3/2}(Y) = \int_0^Y e^{-y} y^{3/2} dy = \left(\tfrac{2}{5}\right)\left(\tfrac{5}{2}\right)! E_{2/5}(Y^{5/2})$$

$$= \frac{2}{5} Y^{5/2} - \frac{2}{7} Y^{7/2} + \frac{2}{2!9} Y^{9/2} - \cdots \quad \text{if} \quad Y < 1,$$

$$= \frac{3\pi^{1/2}}{4} - Y^{3/2} e^{-Y} \left[1 + \frac{3}{2Y} + \frac{3}{4Y^2} + \cdots \right] \quad \text{if} \quad Y > 1,$$

$$(36)$$

$$I_{1/2}(Y) = \int_0^Y e^{-y} y^{1/2} dy = \left(\tfrac{2}{3}\right)\left(\tfrac{3}{2}\right)! E_{2/3}(Y^{3/2})$$

$$= \frac{2}{3} Y^{3/2} - \frac{2}{5} Y^{5/2} + \frac{2Y^{7/2}}{2!7} - \cdots \quad \text{if} \quad Y < 1,$$

$$= \frac{\pi^{1/2}}{2} - Y^{1/2} e^{-Y} \left[1 + \frac{1}{2Y} - \frac{1}{4Y^2} + \cdots \right] \quad \text{if} \quad Y > 1.$$

Thus

$$1 - [I_{3/2}(r)/I_{3/2}(\infty)]$$

$$= 1 - \frac{4}{3\pi^{1/2}} \left(\frac{2}{5} Y^{5/2} - \frac{2}{7} Y^{7/2} + \frac{2}{2!9} Y^{9/2} - \cdots \right), \quad \text{if} \quad Y < 1$$

$$= \frac{4Y^{3/2}}{3\pi^{1/2}} e^{-Y} \left(1 + \frac{3}{2Y} + \frac{3}{4Y^2} + \cdots \right), \quad \text{if} \quad Y > 1,$$

$$(37)$$

$$1 - [I_{1/2}(r)/I_{1/2}(\infty)]$$

$$= 1 - \frac{2}{\pi^{1/2}} \left(\frac{2}{3} Y^{3/2} - \frac{2}{5} Y^{5/2} + \frac{2}{2!7} Y^{7/2} - \cdots \right), \quad \text{if} \quad Y < 1$$

$$= \frac{2}{\pi^{1/2}} Y^{1/2} e^{-Y} \left(1 + \frac{1}{2Y} - \frac{1}{4Y^2} + \cdots \right) \quad \text{if} \quad Y > 1.$$

Note that for pairs of equal sign the lower limit for the y integration is zero and $\langle K^{++}(r) \rangle_{av} = \langle K^{--}(r) \rangle_{av} = 3kT/2$ for all r.

We shall now perform the space integrations in two steps, first from $r=0$ to $r=r_2$ covering the region in which $Y>1$, and then from $r=r_2$ to $r=r_0$. Since $r_0 \ll h$ in most practical cases we can use an unshielded Coulomb potential for $w(r)$ in the whole range of integration. One finds, with

$$\gamma = r_0/r_2 = (3/4\pi n)^{1/3} kT/e^2 = 373 T/n^{1/3}, \quad (38)$$

$$\int_0^{r_0} e^{r_2/r} [1 - I_{3/2}(r_2/r)/I_{3/2}(\infty)] r^2 dr$$

$$= r_2^3 [-0.34 + \gamma^3/3 + \gamma^2/2 + \gamma], \quad (39)$$

$$\int_0^{r_0} e^{r_2/r} [1 - I_{1/2}(r_2/r)/I_{1/2}(\infty)] r^2 dr$$

$$= r_2^3 [+0.67 + \gamma^3/3 + \gamma^2/2 - 8\gamma^{3/2}/9\pi^{1/2}]. \quad (40)$$

We can now calculate the kinetic energy K^{+-}, and in order to bring out clearly the physical meaning of our result we shall consider only cases of sufficiently weak shielding for which $\gamma > 10$. This condition is satisfied for most plasmas of practical interest. If $\gamma > 10$ we may keep only the leading powers of γ and find

$$K^{+-} = \frac{3kT}{2} \frac{1}{1 - 8/3(\pi)^{1/2}\gamma^{3/2}} \approx \frac{3kT}{2} \left[1 + \frac{8}{3(\pi)^{1/2}\gamma^{3/2}} \right]$$

$$= \frac{3kT}{2} + 0.92 \frac{e^2}{h}. \quad (41)$$

We see that the correction to the kinetic energy is positive and almost identical in magnitude with the average negative potential energy of a charged particle in a plasma. Since the exact value of the number 0.92 is an accidental consequence of our approximate treatment, we can summarize our result by the simple statement that the correction to K^{+-} is opposite and equal to the Debye-Hückel energy e^2/h, and $\bar{\epsilon} = 3kT/2$. The same conclusion may be reached by simple physical reasoning as follows: If an electron moves from a field-free region with Maxwellian velocity distribution into a nearest-neighbor zone with nonvanishing potential energy, the total energy ϵ is conserved if we assume that the mean free path is much larger than r_0. If the nearest-neighbor zone is occupied by a positive ion it is fully accessible to electrons of any arbitrary energy. Thus the distribution of the energy associated with the relative motion of an electron about an ion inside the nearest-neighbor zone of the ion is the same as outside in the field-free region, and $\bar{\epsilon} = 3kT/2$. This is quite different for the relative motion of two particles with equal sign. Such particles interact with repulsive forces and hence, the nearest-neighbor zone of the one particle is not fully accessible to the other particle. As an example consider two electrons, one acting as field

particle in the center of its nearest-neighbor zone, the other acting as test particle. Let the average potential energy of the test particle in distance r from the field particle be $w(r)$. Then, only test particles with energy $\epsilon > w(r)$ can approach the field particle to a distance smaller than r. Hence the average energy of the test electrons in distance r from the field electron is larger than $3kT/2$ since the average has been formed with a selected sample of test electrons from which particles with energy smaller than $w(r)$ have been excluded. This agrees with the familiar result of statistical mechanics that for repulsive interaction, for which exclusion of negative energies is not necessary, $\bar{\epsilon}(r) = 3kT/2 + w(r)$.

Utilizing this result we can now calculate the total thermal energy of a fully ionized two-component plasma. The average kinetic energy K^{++} and K^{--} associated with the relative motion of two equal particles is $3kT/2$, and the same is true for the kinetic energy associated with the center-of-mass motion of any pair. Thus the kinetic energy of an ion-electron pair is $3kT + e^2/h$, and the kinetic energy of pairs of equal charge is $3kT$. Since at each instance we have $(N/2)$ electron-ion pairs and $(N/2)$ other pairs the total thermal plasma energy is

$$E = 2N\left[\frac{3kT}{2} - \frac{e^2}{2h} + \frac{e^2}{4h}\right] = 2N\left[\frac{3kT}{2} - \frac{e^2}{4h}\right]. \quad (42)$$

The kinetic-energy correction is an almost constant fraction of the Debye-Hückel energy and persists up to the highest temperatures and lowest ion concentrations. Thus, it is more significant than all the other corrections to the Debye-Hückel energy which vanish in the limit T, $h \rightarrow \infty$, or $n \rightarrow 0$. An experimental test of this result is possible in principle, but should be quite difficult in practice.

For particles with repulsive core and non-Coulombian intermolecular attraction the situation is quite similar. If, for the purpose of calculating the degree of dissociation, bound and free particles are treated separately, the equipartition theorem for the kinetic energy breaks down, and $\bar{\epsilon}(r) = 3kT/2$ if r corresponds to a negative potential interaction energy of a pair.

APPENDIX A: DERIVATION OF THE RADIAL DISTRIBUTION FUNCTION OF FREE ELECTRONS ABOUT AN ION BY ORBITAL STATISTICS

The mean free path of an electron in a plasma is generally much longer than the Debye shielding length, and for this reason the vast majority of electron orbits may be well approximated by straight lines. Nevertheless, the speed of an electron varies strongly when it passes through the region of negative potential energy in the neighborhood of a positive ion. Since the time an electron spends in distance r from an ion is inversely proportional to its radial velocity, a statistics of electron

orbits and the associated radial velocities leads to the radial distribution function.

Essentially one needs the average radial velocity $\langle \dot{r}(r,\epsilon) \rangle_{av}$ of an electron with energy ϵ in distance r from an ion. The average is to be taken over orbits with different collision parameters p and with different particle configurations in the local Debye spheres of radius h about the ion. For each configuration the effective force acting on the electron and, hence, the orbit corresponding to a specified collision parameter is different and, in principle, $\langle \dot{r}(r,\epsilon,p) \rangle_{av}$ has to be obtained from a large number of different orbits. However, if the straight-line approximation is valid, one can first introduce the average force or the potential of average force with magnitude $w(r)$ and calculate $\dot{r}(r,\epsilon,p)$ from one single orbit through an average potential field $w(r)$.[15] We shall adopt this procedure and shall identify $w(r)$ with the average potential defined by Eq. (16). But orbits through the average potential field $w(r)$ will no longer be assumed straight in the following analysis.

In order to simplify normalization, we assume that $w(r)$ is zero if $r > R$, and we shall treat R as an adjustable parameter which will drop out of the final formulas.

The total energy ϵ of an electron moving through the effective potential field $w(r)$ of an ion with collision parameter p may be written

$$\epsilon = \tfrac{1}{2}\mu\dot{r}^2 + (p^2\epsilon/r^2) - w(r); \quad (A1)$$

hence

$$\dot{r} = \left\{\frac{2}{\mu}\left(\epsilon + w(r) - \frac{p^2\epsilon}{r^2}\right)\right\}^{1/2}, \quad (A2)$$

and the maximum collision parameter consistent with a specified value of ϵ and r, i.e., that value of p which corresponds to $\dot{r} = 0$, is

$$p_m = r\{[\epsilon + w(r)]/\epsilon\}^{1/2}. \quad (A3)$$

We are interested in the probability density $g(r,\epsilon)$ that an electron has energy ϵ and distance r from an ion. We write $g(r,\epsilon)$ as an integral of the form

$$g(r,\epsilon) = \int_0^{p_m} g(r,\epsilon,p)\,dp, \quad (A4)$$

where $g(r,\epsilon,p)$ is the probability density that r,ϵ,p have specified values. Next, we introduce the basic notion that $g(r,\epsilon,p)$ is inversely proportional to $\dot{r}(r,\epsilon,p)$ and find

$$r^2 g(r,\epsilon,p) = R^2 g(R,\epsilon,p)\frac{\dot{r}(R)}{\dot{r}(r)}$$

$$= R^2 g(R,\epsilon,p)\left(\frac{1 - p^2/R^2}{1 + w(r)/\epsilon - p^2/r^2}\right)^{1/2}, \quad (A5)$$

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[15] For small r the straight-line approximation is, of course, not valid. But the effective force is then an almost unshielded Coulomb force for practically all particle configurations and the use of an average force can be justified without invoking the straight-line approximation.
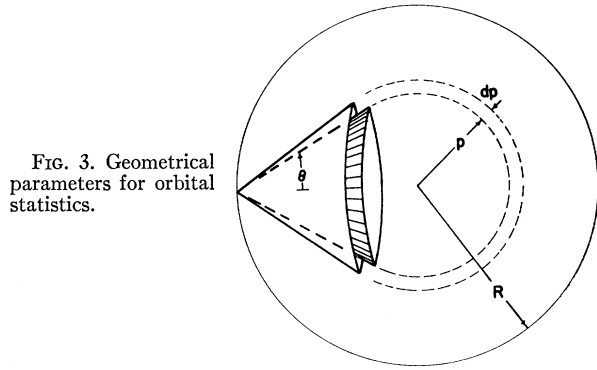
FIG. 3. Geometrical parameters for orbital statistics.

where use has been made of the boundary condition $w(R)=0$. $g(R,\epsilon,p)$ is related to $g(R,\epsilon)$ by the relations (see Fig. 3)

$$g(R,\epsilon,p)dp = g(R,\epsilon)d\omega/2\pi, \qquad (A6)$$

where

$$d\omega = 2\pi \sin\theta d\theta = pdp/R(R^2-p^2)^{1/2} \qquad (A7)$$

is the solid angle subtended at r by a spherical shell of radius p and width dp.

Using (A5), (A6), (A7), and (A3) we can evaluate the integral (A4) as

$$g(R,\epsilon)[1+w(r)/\epsilon]^{1/2}. \qquad (A8)$$

We now assume a Maxwellian energy distribution for the electrons outside the range of $w(r)$, i.e.,

$$\lim_{r>R} g(r,\epsilon) = \frac{2\epsilon^{1/2}e^{-\epsilon/kT}}{\pi^{1/2}(kT)^{3/2}}, \qquad (A9)$$

and obtain

$$g(r) = \frac{2\pi}{(\pi kT)^{3/2}} \int_0^\infty e^{-\epsilon/kT}[\epsilon + |w(r)|]^{1/2}d\epsilon. \qquad (A10)$$

This is identical with Eq. (17).

For repulsive interaction, the lower limit for the ϵ integration is not zero but $w(r)$, and the sign of $w(r)$ in the square root has to be changed. This leads then to the conventional exponential form of the radial distribution function.

APPENDIX B: THE RADIAL CHARGE DISTRIBUTION AS A FUNCTION OF THE EFFECTIVE POTENTIAL W

The full line in Fig. 4 is an exact graphical representation of Eq. (20). The dotted line labeled 2 in Fig. 4 represents Eq. (28). It is a good approximation for $0<x<0.5$ which is equivalent to the r interval between ∞ and r_3. The curve labeled 4 represents Eq. (25). This curve is a fairly good approximation in the range $2<x<\infty$, equivalent to $0<r<r_1$. Since the small r region contributes only negligibly to the potential energy of the
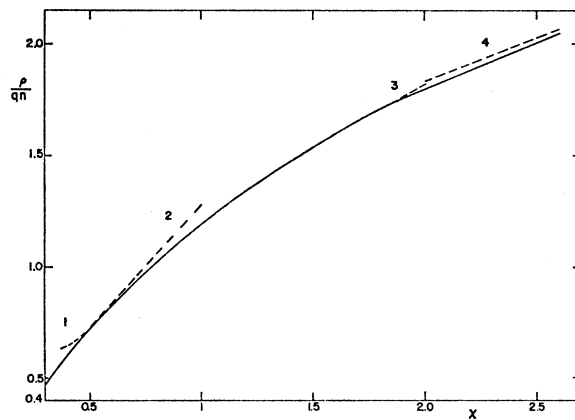

FIG. 4. Graphical representation of the radial charge distribution. The full line represents Eq. (20). The dotted lines labeled 2, 4, and 1, 3 represent the Eqs. (28), (25), and (26).

cloud center (if a divergence is avoided) the small displacement between the dotted line 4 and the full line is irrelevant. It is, however, obvious from Fig. 4 that the approximations (25) and (28) are not admissible in the region $r_1<r<r_3$. For this reason, we have expanded $\rho(r)$ in the Taylor series (26) about $x=1$ $(r=r_2)$. This approximation fits perfectly in the region $0.5<x<2$, but it breaks down outside this region as indicated by the dotted lines labeled 1 and 3.