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Refined Derivation, Exact Solutions, and Singular Limits of the Poisson–Boltzmann Equation

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The self-consistent equation for the electrostatic potential in a plasma or electrolyte is derived. Allowance is made for the presence of fixed, immovable charges. The plasma particle density is related to the potential using the Principle of Maximum Entropy, giving the well-known Boltzmann distribution in phase space. Conventional derivations assume the energy, whose constancy constrains the entropy maximisation, is linear in the particle density. Here the relation is quadratic. It is shown that the Boltzmann distribution is valid no matter what the relation. Combination of Poisson's equation with the Boltzmann distribution in the spatial subset of phase space leads to the nonlinear Poisson–Boltzmann equation for the potential. Inclusion of a normalisation factor for each charged species, which is often omitted, ensures gauge invariance. Uniqueness of the solution is proved. A detailed investigation of solutions is presented in slab, cylindrical, two dimensional, and spherical geometries. Both single species plasmas and plasmas containing oppositely charged species are investigated. Limiting cases are examined especially closely: low and high temperatures, infinite plasma (with finite net charge and finite average density), and point charges immersed in the plasma in all dimensions. Depending on the circumstance, a point charge is capable of attracting a finite amount of opposite charge out of the plasma arbitrarily close to itself. In particular, in three or more dimensions it attracts an equal and opposite charge (provided only sufficient exists) and is completely neutralised.

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1. Introduction: The Boltzmann Distribution in Full Generality

The Boltzmann distribution for the probability of occupancy of a fixed energy level E_i is given by

$$p_i = Z^{-1} \exp(-\lambda E_i), \tag{1}$$

where the constant of proportionality Z^{-1} is found in terms of λ by normalising, and λ by then substituting back into the equation of energy conservation. The energy increment is deduced by building up the occupancy bit by bit. We have

$$dU = \sum_i E_i \, dp_i \tag{2}$$

which integrates to the required law of energy conservation

$$U = \sum_i E_i p_i \tag{3}$$

on equating the expectation value to the true value. The distribution is derived by maximising the information entropy

$$S = -\sum_i p_i \ln p_i \tag{4}$$

subject to the constraints of (3) and normalisation; λ is the Lagrange multiplier associated with (3). The analysis proceeds even if the value of U is not known, the point being only that energy is conserved.

A technical point: during the build-up process, the probability distribution appears not to be normalised. Indeed, at the start, all the p_i's are apparently zero! In fact, (2) is a shorthand in which p_i represents a (normalised) physical quantity; its probability interpretation comes a posteriori and requires testing. U here is not the total energy but the mean energy of the levels, related to the total energy by a constant factor.

Our variational procedure is an application of an enormously powerful tool, the Principle of Maximum Entropy, interpreted and introduced in full generality by Jaynes [1]; it is this rather than ergodic theory which underpins statistical mechanics. In line with the assumption that occupancy is proportional to the calculated probability of occupancy, Maximum Entropy does not guarantee unconditionally to give the correct answer. Indeed, since the mathematical problem for the occupancies is severely underdetermined it hardly could. Its importance lies in providing a systematic way of tightening up: if the predictions of Maximum Entropy are in conflict with observation, we are being warned that at least one further relevant constraint has been missed. Once further constraints have been identified, the entropy is re-maximised so as to incorporate them. Again the probabilities generated are compared with observation, and so on until agreement is reached. In statistical physics, with systems of $\sim 10^{23}$ particles to average over, we are assured by Shannon's asymptotic equipartition theorem [2] that any lack of agreement is overwhelmingly likely to be due to missing constraints, and not to random fluctuations. Fluctuations noticeable on the macroscale have utterly negligible probabilities of the order of $10^{-(10^{23})}$. Constraints invariably involve "macroscopic" variables such as pressure, or electric or magnetic polarisation. For the Boltzmann distribution, no other macroscopic constraints suggest themselves, and—not surprisingly—the distribution has passed experimental muster for nearly a century.

A picture of the maximum entropy procedure can be gained by imagining a vast number of identical balls placed at the bottom of a ladder whose steps (not necessarily evenly spaced) represent energy levels in the gravitational field. A mechanically perfect robot invested with total energy U is to expend this energy by placing the balls at random on the various steps. Clearly they can be positioned in a huge number of distinct combinations; however, as the number of balls becomes sufficiently large, the proportion due to one combination and its near neighbours approaches one. Combinatorial analysis shows that, after scaling by the total number of balls, this is the distribution of maximum entropy; in the present problem it is the Boltzmann distribution (1). (A "near" neighbour is one in which the ratio of the number of differently positioned balls to the total number is negligible. It is macroscopically indistinguishable from the distribution of maximum entropy.)

Now suppose that the energy levels actually depend dynamically on their occupancies, so that E_i is a function not only of i but also of the p_i's. Merely by pondering the ladder picture one can see that matters now are far more complicated. Yet it emerges below, provided only that energy conservation still holds, that the form of the Boltzmann distribution is preserved: the probability of occupation p_i of the ith level is still exponential in the value E_i of that level. Of course the probabilities themselves are not worked out by this stage; since the E_i's depend on them, the Boltzmann distribution is now a set of transcendental equations for the p_i's.

The incremental energy for infinitesimal changes in the occupancies is given, as always, by (2). Write this, with the dependence on occupancy of the levels explicitly displayed, as

$$dU = \sum_i E_i(\mathbf{p})\, dp_i. \tag{5}$$

It is required that the RHS be a perfect differential in order that a state function U exists. The configuration could otherwise be built up in one way and dismantled in another, with resultant gain (or, less spectacularly, loss) of energy. Thus E_i must be expressible as

$$E_i = \partial U/\partial p_i, \tag{6}$$

whence

$$\partial E_i/\partial p_j = \partial E_j/\partial p_i. \tag{7}$$

Clearly (7) is a necessary condition that (5) be a perfect differential; it is trivially satisfied when the E_i's are independent of $\mathbf{p}$. The theory of exterior derivatives assures us that (7) is also a sufficient condition.

The next stage is to seek the distribution of maximum entropy by maximising (4). On assigning Lagrange multipliers $(\ln Z - 1)$ to the linear normalisation constraint (this apparently arbitrary form is chosen for later convenience), and λ to the energy constraint

$$U(\mathbf{p}) = \text{constant}, \tag{8}$$

we demand that

$$\delta\Big[S - (\ln Z - 1)\sum_j p_j - \lambda U\Big] = 0 \tag{9}$$

for arbitrary variations δp_i. The coefficients of δp_i, when (9) is written out in full, are required to vanish. This condition is

$$-\ln p_i - \ln Z - \lambda\, \partial U/\partial p_i = 0 \tag{10}$$

or

$$p_i = Z^{-1} \exp[-\lambda\, \partial U(\mathbf{p})/\partial p_i]. \tag{11}$$

But, from condition (6) that U exists (a more basic condition can scarcely be imagined!), this is just

$$p_i = Z^{-1} \exp[-\lambda E_i(\mathbf{p})], \tag{12}$$

which is course the Boltzmann distribution. An obvious additional requirement is that there be no further constraints.

As foretold, (12) remains to be solved for the p_i's. This can be done directly or by substituting $Z^{-1}\exp(-\lambda E_i)$ into the dynamical relation giving E_i in terms of $\mathbf{p}$, solving the resulting self-consistent equation for E_i, and substituting back. In general Eqs. (12) are coupled; they decouple only when each energy level depends exclusively on its own occupancy, so that $\partial E_i/\partial p_j$ contains a factor δ_{ij}. Condition (7) is then always satisfied.

When the constraints are nonlinear in the probabilities, the canonical formalism fails: Z is no longer trivially expressible in terms of λ, for example. Worse, entropy is not necessarily convex in the space of the p_i's, destroying the guarantee on uniqueness of the solution and globality of the entropy maximum. Equation (12) may possess no real solution or more than one, each corresponding to a local entropy maximum. These aspects must be examined afresh for each nonlinear problem studied.

In this paper we report on one such example: the equilibrium of classical charged particles placed in an external electric field. The particles themselves generate a further field, and they move about in the combined field. The energy levels correspond to the electrostatic potential, the dynamical $E_i(\mathbf{p})$ relation is Poisson's equation, and the problem is continuous rather than discrete: the index i becomes the position variable $\mathbf{r}$. Extra degrees of freedom arise in velocity space from thermal motion. The self-consistent equation for the potential which results is now a differential equation, called the Poisson–Boltzmann equation. Since the Boltzmann distribution has been blindly assumed to hold in the past without consideration of the dynamical dependence of E_i upon $\mathbf{p}$, this equation has in fact been studied before. This paper concerns the Poisson–Boltzmann equation as much as it does the validity of the Boltzmann distribution, and the preceding derivation of the distribution is applied to a plasma in Section 2, so as to highlight some points peculiar to the electrodynamic case. The equation itself is examined in Section 3; an equivalent energy-based variational principle is found, existence is examined, and uniqueness is proved. Solution of the equations is effected in Section 4. A perturbation expansion in inverse powers of temperature is set up, and the low-temperature limit is examined. The equation is then studied for both single species plasmas and plasmas consisting of two species of equal and opposite charge, in a variety of geometries: one and two dimensional, and with radial symmetry in two and three dimensions. Explicit solutions are found, and the boundary conditions incorporated, in one dimension and for the single species cylindrically symmetrical case; explicit solutions are available but are far more difficult to match to the boundary conditions in two dimensions for a single species, while for two species in two dimensions, soliton techniques apply. A series solution of the single species, three dimensional radial equation corresponding to specific boundary conditions is presented, and a new study of the equation is made based upon it. The two species radial equation possesses the Painlevé property in two dimensions, but not in higher dimensions. Shrinking of the inner boundary on to a line or point charge is considered, and it is found that a line charge is capable of attracting a finite amount of opposite charge out of the plasma arbitrarily close to itself, although insufficient to neutralise it. In three (or more) dimensions, by contrast, neutralisation *is* complete. Thus the Poisson–Boltzmann equation—which is, it is stressed, itself an approximation—predicts that point charges are electrically invisible. Conclusions are presented in Section 5.

2. Self-Consistent Derivation of the Boltzmann Distribution

For transparency and ease of comparison with the above, only a single charged species is considered in this section. Extension to several species is made in Appendix A.

The external field is produced by a prescribed charge density $\rho_{\text{ext}}(\mathbf{r})$. This is held fixed in space and cannot move. It sets up a potential

$$\phi_{\text{ext}}(\mathbf{r}) = \frac{1}{\varepsilon_0} \int d\mathbf{r}' \, G(\mathbf{r}, \mathbf{r}') \, \rho_{\text{ext}}(\mathbf{r}'), \tag{13}$$

where G is the Green's function for Poisson's equation,

$$\nabla^2 G(\mathbf{r}, \mathbf{r}') = -\delta(\mathbf{r} - \mathbf{r}'), \tag{14}$$

to be solved with appropriate homogeneous boundary conditions. If, for example, the plasma in which the test charge is immersed is confined in a conducting vessel, $G = 0$ on its surface, while if the plasma is unconfined, or confined by an insulating vessel, $G = 0$ at $r = \infty$ and takes the well-known form $1/4\pi|\mathbf{r} - \mathbf{r}'|$ in three dimensions. A second condition is that the solution should satisfy Gauss' law, the integral form of Poisson's equation over an arbitrary volume. Since this incorporates the boundary conditions it is more stringent. The Green's function is always symmetrical in $\mathbf{r}$ and $\mathbf{r}'$, since the problem is self-adjoint, but in the presence of conductors is not translationally invariant (i.e., not dependent only on $\mathbf{r} - \mathbf{r}'$).

Suppose that the plasma consists of N particles of charge q. We define a probability density $p(\mathbf{r}, \mathbf{v})$ in the phase space of a single particle, such that $p(\mathbf{r}, \mathbf{v})\, d\mathbf{r}\, d\mathbf{v}$ is the probability element, and identify

$$\rho_p(\mathbf{r}) = Nqp_r(\mathbf{r}) = Nq \int d\mathbf{v}\, p(\mathbf{r}, \mathbf{v}). \tag{15}$$

The corresponding plasma-induced potential is

$$\phi_p(\mathbf{r}) = \frac{1}{\varepsilon_0} \int d\mathbf{r}'\, G(\mathbf{r}, \mathbf{r}')\, \rho_p(\mathbf{r}'). \tag{16}$$

Since Poisson's equation is linear, the total potential ϕ is just the sum of this and the potential of the test charge distribution, and the total electric field $\mathbf{E} = -\nabla\phi$.

The total electrostatic energy is

$$U = \frac{1}{2} \varepsilon_0 \int d\mathbf{r}\, |\nabla\phi|^2 \tag{17}$$

$$= -\frac{1}{2} \varepsilon_0 \int d\mathbf{r}\, \phi\, \nabla^2\phi + \frac{1}{2} \varepsilon_0 \int d\mathbf{S} \cdot (\nabla\phi)\phi. \tag{18}$$

The integral in (17) must run over all space in which the field is nonzero, while that in the first term of (18) need only extend over the plasma since the integrand is zero beyond it. If we adhere to the convention that $\phi = 0$ at infinity, or on a conducting confinement surface, the second term in (18) vanishes; it is merely a correction to the first term to ensure continued gauge invariance. The first term becomes, on employing Poisson's equation,

$$U = \frac{1}{2} \int d\mathbf{r}\, \phi(\mathbf{r})\, \rho(\mathbf{r}). \tag{19}$$

Write $\phi = \phi_{\text{ext}} + \phi_p$, $\rho = \rho_{\text{ext}} + \rho_p$ and subtract off the constant self-energy term of the prescribed charge, $\phi_{\text{ext}}\rho_{\text{ext}}$, to find the electrostatic energy U' associated with the presence of the plasma:

$$U' = \int d\mathbf{r} \left[\frac{1}{2} (\phi_{\text{ext}} \rho_p + \phi_p \rho_{\text{ext}}) + \frac{1}{2} \phi_p \rho_p \right]. \tag{20}$$

But the $\phi_{\text{ext}}\rho_p$ and $\phi_p\rho_{\text{ext}}$ terms both integrate to the same value, since

$$\int d\mathbf{r}\, \phi_p(\mathbf{r})\, \rho_{\text{ext}}(\mathbf{r}) = \frac{1}{\varepsilon_0} \int d\mathbf{r} \int d\mathbf{r}'\, G(\mathbf{r}, \mathbf{r}')\, \rho_{\text{ext}}(\mathbf{r})\, \rho_p(\mathbf{r}') \tag{21}$$

is symmetrical in ρ_{ext} and ρ_p by symmetry of the Green's function. Thus

$$U' = \int d\mathbf{r} \left[\phi_{\text{ext}}(\mathbf{r})\, \rho_p(\mathbf{r}) + \frac{1}{2} \phi_p(\mathbf{r})\, \rho_p(\mathbf{r}) \right] \tag{22}$$

$$= \int d\mathbf{r}\, \phi_{\text{ext}}(\mathbf{r})\, \rho_p(\mathbf{r}) + \frac{1}{2\varepsilon_0} \int d\mathbf{r} \int d\mathbf{r}'\, G(\mathbf{r}, \mathbf{r}')\, \rho_p(\mathbf{r})\, \rho_p(\mathbf{r}'). \tag{23}$$

The first term in (23) is the (linear) interaction term expected if the charges move only in response to the external field; it is the continuum analogue of (3). The second term is the plasma field self-energy.

The sum of the electrostatic energy (23) and the total kinetic energy is constant, if radiation losses are negligible. The mere existence of a conserved energy expressible in the probability density ensures that the functional-differential analogue of the reciprocity condition (7) is satisfied and that the Poisson–Boltzmann distribution emerges. Equation (7) reduces to the condition that G be symmetrical.

We find $p(\mathbf{r}, \mathbf{v})$ by maximising the continuum generalisation of the discrete entropy (4),

$$S = -\int d\mathbf{r} \int d\mathbf{v}\, p(\mathbf{r}, \mathbf{v}) \ln[p(\mathbf{r}, \mathbf{v})/m(\mathbf{r}, \mathbf{v})], \tag{24}$$

where $m(\mathbf{r}, \mathbf{v})$ is the measure on the phase space. Since no part of position space is a priori preferred to any other, $m(\mathbf{r}, \mathbf{v})$ is uniform in $\mathbf{r}$; and since $\mathbf{r}$ and $\mathbf{v}$ are conjugate variables, extension to uniform measure in $(\mathbf{r}, \mathbf{v})$-space is immediate. Normalisation of $p(\mathbf{r}, \mathbf{v})$ ensures that the measure can be taken as unity without loss of generality. The constraint that kinetic plus potential energy is conserved using (15) and (23) is

$$U_{\text{TOT}} = N \int d\mathbf{r} \int d\mathbf{v}\, \frac{1}{2} m v^2 p(\mathbf{r}, \mathbf{v}) + Nq \int d\mathbf{r} \int d\mathbf{v}\, \phi_{\text{ext}}(\mathbf{r})\, p(\mathbf{r}, \mathbf{v})$$
$$+ \frac{N^2 q^2}{2\varepsilon_0} \int d\mathbf{r} \int d\mathbf{v} \int d\mathbf{r}' \int d\mathbf{v}'\, G(\mathbf{r}, \mathbf{r}')\, p(\mathbf{r}, \mathbf{v})\, p(\mathbf{r}', \mathbf{v}'). \tag{25}$$

The condition that the integrand of $\delta[S-(\ln Z-1)\iint d\mathbf{r}'\, d\mathbf{v}'\, p(\mathbf{r}',\mathbf{v}')-\lambda U_{\mathrm{TOT}}/N]$ vanish for arbitrary variations $\delta p(\mathbf{r},\mathbf{v})$ is

$$-\ln p(\mathbf{r},\mathbf{v})-\ln Z-\frac{\lambda m v^2}{2}-\lambda q\phi_{\mathrm{ext}}(\mathbf{r})$$

$$=\frac{\lambda N q^2}{\varepsilon_0}\int d\mathbf{r}'\int d\mathbf{v}'\, G(\mathbf{r},\mathbf{r}')\, p(\mathbf{r}',\mathbf{v}'). \tag{26}$$

The two terms obtained by varying $p(\mathbf{r},\mathbf{v})$ and $p(\mathbf{r}',\mathbf{v}')$ in the final term of (25) are equal through the symmetry of the Green's function, and together cancel the factor $\frac{1}{2}$ outside the integral. We recognise that $p(\mathbf{r},\mathbf{v})$ is separable as

$$p(\mathbf{r},\mathbf{v})=Z_v^{-1}\exp\left(-\tfrac{1}{2}\lambda m v^2\right) p_r(\mathbf{r}), \tag{27}$$

where

$$Z_v=(2\pi/\lambda m)^{D/2} \tag{28}$$

and p_r satisfies the nonlinear integral equation

$$p_r(\mathbf{r})=Z_r^{-1}\exp\left[-\lambda q\phi_{\mathrm{ext}}(\mathbf{r})-\frac{\lambda N q^2}{\varepsilon_0}\int d\mathbf{r}'\, G(\mathbf{r},\mathbf{r}')\, p_r(\mathbf{r}')\right]. \tag{29}$$

But the integral in the exponent is just $(Nq/\varepsilon_0)^{-1}\,\phi_p(\mathbf{r})$, so that, since $\phi=\phi_{\mathrm{ext}}+\phi_p$, (29) is simply

$$p_r(\mathbf{r})=Z_r^{-1}\exp[-\lambda q\phi(\mathbf{r})] \tag{30}$$

for appropriate Z_r. Moreover,

$$p(\mathbf{r},\mathbf{v})=Z_{rv}^{-1}\exp[-\lambda(\tfrac{1}{2}mv^2+q\phi)], \tag{31}$$

where $Z_{rv}=Z_r Z_v$. These are of course Boltzmann distributions.

Substitution of $\rho_p(\mathbf{r})$ into Poisson's equation gives the Poisson–Boltzmann equation, a nonlinear differential equation for the potential which is examined in subsequent sections.

The Lagrange multiplier λ, from (27), is inverse to the temperature T: we define

$$\lambda=(kT)^{-1}, \tag{32}$$

so that

$$p_r(\mathbf{r})=Z_r^{-1}\exp(-q\phi/kT). \tag{33}$$

The system itself partitions the total energy into kinetic and electrostatic components. In practice it is invariably the Lagrange multiplier itself—the temperature—which is specified. This quantity must always be positive in order that the distribution of velocities be normalisable. It is possible to choose an energy corresponding to negative values of the multiplier if the extra degrees of freedom corresponding to velocity space are absent, the energy is sufficiently large, and the energy level index (here, the position variable) is restricted to a finite range. Negative values then correspond to the high-energy situation of the fixed charges attracting like charge and repelling opposite charge.

A broadly similar derivation has been given by Joyce and Montgomery [3]; the Maximum Entropy Principle is derived ab initio from combinatorial considerations and is applied to a medium containing two oppositely charged species. This analysis restricts itself to two spatial dimensions and ignores velocity space from the start, thus allowing for the possibility of negative Lagrange multiplier—although since it has nothing to do with velocity space, this quantity should not be called temperature. These authors quote a corresponding physical situation: drift of the guiding centres of particle motion perpendicular to the magnetic field direction in a strongly magnetised plasma. Even this is not the first nonlinear application of maximum entropy; van Kampen [4] used a quadratic energy constraint in deriving van der Waals' equation and stated that the method dates back to Ornstein's unpublished thesis of 1908!

The Boltzmann distribution in space can also be obtained by assuming that p_r depends on position solely through ϕ, for gauge invariance then demands that

$$\frac{p_r(\phi(\mathbf{r}_1))}{p_r(\phi(\mathbf{r}_2))} = f(\phi(\mathbf{r}_1) - \phi(\mathbf{r}_2)), \tag{34}$$

a functional equation with unique solution $p \propto \exp(-\kappa\phi)$. We stress the assumption underlying this derivation, for position is introduced into the problem independently through $\rho_{\text{ext}}(r)$ and also any boundary confining the plasma. Subject to this assumption, we are guaranteed that there are no more constraints of physical consequence.

3. The Poisson–Boltzmann Equation: General Considerations

We now write down the Poisson–Boltzmann equation in the form in which it will be examined subsequently. Suppose that the plasma is confined to a volume V_p; define a function $v(\mathbf{r})$ to be one within V_p and zero outside it:

$$v(\mathbf{r}) = \begin{cases} 1, & \mathbf{r} \in V_p \\ 0 & \mathbf{r} \notin V_p. \end{cases} \tag{35}$$

The multi-species Boltzmann distribution is at hand in Appendix A. On substituting the charge density (A9) into Poisson's equation, we find the Poisson–Boltzmann equation for the potential ϕ, valid everywhere,

$$\varepsilon_0 \nabla^2 \phi = -\rho_{\text{ext}}(\mathbf{r}) - v(\mathbf{r}) \sum N_s q_s n_s \exp(-q_s \phi / kT), \tag{36}$$

where the normalisation factor n_s is given by

$$n_s^{-1} = \int_{V_p} d\mathbf{r} \exp(-q_s\phi/kT). \tag{37}$$

Substitution of the solution of (36) into (37) gives transcendental equations for the n_s's, whose solutions are then put back into the solution of the equation. Generalisation to disparate regions of confined plasmas, with differing temperatures and constituents, is immediate: a different $v(\mathbf{r})$ and temperature is defined for each.

Equation (36) is supplemented with the appropriate boundary conditions. These could be incorporated at once by using the Green's integral form; but since we know less about solving nonlinear integral equations than nonlinear differential equations, the present formulation is preferable.

So far, nothing has been said about overlap of plasma and fixed charge volumes; (36) is entirely general. Nevertheless our overwhelming interest concerns situations in which the plasma volume V completely surrounds the fixed charge, for then the immersion of point fixed charges in plasmas is a limiting case.

The Poisson–Boltzmann equation contains no time derivatives. Stability of its solutions must therefore be determined in a more general framework. Clemmow and Dougherty [5] assert that the solutions of more general self-consistent equations are in general unstable. In some circumstances we agree; but we do not expect instability of, say, the "screening" solutions for point charges. Stability is not examined further.

The Poisson–Boltzmann equation can be rewritten with only polynomial nonlinearity by taking $\exp(\pm he\phi/kT)$ as a dependent variable, where h is the highest common factor of the quanta l_s of the charges on the particle species,

$$q_s = l_s e, \tag{38}$$

where e (>0) is the magnitude of the electronic charge. The concentration of each species is then a power of this new variable.

For a two species, overall neutral plasma with equal ionisation ($q_1 = -q_2 = q$, $N_1 = N_2 = N$), the equation simplifies to

$$\varepsilon_0 \nabla^2\phi = -\rho_{\text{ext}}(\mathbf{r}) + 2Nq(n_1 n_2)^{1/2}\, v(\mathbf{r}) \sinh(q\phi/kT + \tfrac{1}{2}\ln(n_2/n_1)). \tag{39}$$

In the limit $V \to \infty$, concentrations remaining finite, it is invariably assumed that $n_1 = n_2 = V^{-1}$ (in the gauge $\phi(\infty) = 0$), and the concentrations N_s/V taken as $N_s n_s$ and written as a single variable C_s. This is incorrect if $\exp(-q_s\phi/kT)$, and hence ϕ, has nonintegrable singularities; see Section 4.12. Equation (39) is easily reduced to the commonly encountered form by making the linear transformation $\phi \to \phi - \frac{1}{2}(kT/q)\ln(n_2/n_1)$ and rescaling.

Existence of solutions has been established by MacGillivray [6] for a cylindrically symmetrical plasma consisting of two species with equal and opposite charge and by Friedman and Tintarev [7] for an otherwise arbitrary three species plasma in two dimensions. Tintarev [8] has also considered the same problem with a point external charge. A general and elementary proof that the number of solutions is not greater than one (uniqueness) is given in a moment. When combined with a proof that their number is nonzero (existence), it leads immediately to the conclusion that there is precisely one solution. Further information on existence of solutions is available in the extensive existence-and-uniqueness studies of the equation $\nabla^2\phi = -F[\phi]$ [9, 10]. We may reasonably expect as profound a simplification in studies of existence for our particular form of $F[\phi]$ as takes place for uniqueness. The reader is warned that dependence of the factor n on ϕ necessarily restricts application of these studies in the Poisson–Boltzmann equation. Certain results derived by these authors depend crucially on positivity of solutions, whereas n can, by gauge invariance, be chosen to make positive any solution of the Poisson–Boltzmann equation which is bounded below.

We now prove uniqueness of any solution known to exist. The entropy maximum is therefore still unique in this nonlinear problem. It is temperature, rather than energy, which is taken as specified. Define the difference between two possible solutions ϕ_1, ϕ_2 as $\psi = \phi_1 - \phi_2$; the aim is to show $\psi \equiv 0$. In Green's first identity

$$\int_{\partial V} d\mathbf{S} \cdot \psi \nabla\psi = \int_V dV(|\nabla\psi|^2 + \psi \nabla^2\psi), \tag{40}$$

at each point on ∂V either ψ or $\nabla\psi \cdot d\mathbf{S}$ vanishes depending on the boundary conditions, so the LHS is zero. Upon substituting from the Poisson–Boltzmann equation for $\nabla^2\psi$ into the RHS, writing n_s explicitly using (37), and putting $\chi^s = q_s\phi/kT$ for simplicity, we have

$$\begin{aligned} &\langle|\nabla(\phi_1-\phi_2)|^2\rangle + kT/\varepsilon_0 \\ &\quad\times\sum_s N_s\left\langle[-\chi_1^s+\chi_2^s]\left[\frac{\exp(-\chi_1^s)}{\langle\exp(-\chi_1^s)\rangle}-\frac{\exp(-\chi_2^s)}{\langle\exp(-\chi_2^s)\rangle}\right]\right\rangle = 0, \end{aligned} \tag{41}$$

where the angled brackets denote that the quantity is integrated over the volume V. On defining $\xi^s = \exp(-\chi^s)$, the summand becomes

$$\begin{aligned} &N_s\langle[\ln(\xi_1^s/\langle\xi_1^s\rangle) - \ln(\xi_2^s/\langle\xi_2^s\rangle) + \ln(\langle\xi_1^s\rangle/\langle\xi_2^s\rangle)] \\ &\quad\times[\xi_1^s/\langle\xi_1^s\rangle - \xi_2^s/\langle\xi_2^s\rangle]\rangle. \end{aligned} \tag{42}$$

The $\ln(\langle\xi_1^s\rangle/\langle\xi_2^s\rangle)$ term does not contribute once the outer $\langle\ \rangle$ bracket is taken; on deleting it the square brackets always take the same sign, so that (42) is nonnegative. Equation (41) can therefore be satisfied only if each of the two integrals is separately zero, implying that $\phi_1 = \phi_2$ almost everywhere.

Uniqueness fails for negative temperatures: Ting *et al.* [11] construct a nontrivial solution to the Dirichlet problem of constant potential on the boundary, additional to the trivial solution $\phi = \text{constant}$. Negative temperature has a physical interpretation when the particles all attract each other, as under gravity. The problem is then relevant to galactic evolution.

The Poisson–Boltzmann equation has been derived from an entropy-maximising variational principle. It can also be derived from an energy-minimising principle $\delta I[\phi]=0$, where

$$I[\phi]=\int dV\left(\frac{1}{2}\varepsilon_0\,|\nabla\phi|^2-\rho_{\text{ext}}\phi\right)-kT\sum_s N_s\ln[n_s[\phi]\,V]. \tag{43}$$

For weak variations of ϕ, the second term is approximately $-\sum_s N_s q_s \phi$, as expected. Under the gauge transformation $\phi\to\phi+C$, we have $I\to I-Q_{\text{plasma}}C$.

What happens if an inexhaustible battery is connected between two points within the plasma? Unless the difference in potential between the two points, calculated from the solution of the Poisson–Boltzmann equation, equals the potential difference of the battery, the plasma will be perturbed. More precisely, it will exhaust itself onto the terminals until the solution for the amount of plasma remaining corresponds to the potential difference of the battery. If that is not possible, the plasma either will exhaust itself of all charges of one polarity in a vain attempt to attain this state or, if the discrepancy is in the opposite sense, will pile positive charges onto the positive terminal and negative ones onto the negative terminal as appropriate.

Finally we comment on the assertions that the Poisson–Boltzmann equation is only self-consistent when linearised [12, 13]. This assertion goes back at least as far as the influential text of Verwey and Overbeek [14]. The dynamical relation between charge density and potential (Poisson's equation) is of course linear; but that observation by no means forces the converse relation, derived by maximum entropy, to be likewise. Lampert [15] makes the same point, while simultaneously drawing attention to Onsager's observation that the neglect of correlations is a separate inconsistency (see Appendix A).

In electrolyte theory, several rival formulations to the Poisson–Boltzmann equation exist [16]. Here, however, we take the equation as our starting point.

4. Solutions of the Poisson–Boltzmann Equation

No general analytical method of solving equations as nonlinear as the Poisson–Boltzmann equation yet exists in higher dimensions, and numerical techniques provide the only means to solution in most cases. Some numerical solutions for neutral plasma are available for spherical symmetry [17–19] and for cylindrical symmetry [20, 21]. The reader is also referred to the further references contained therein. Few numerical solutions address the self-consistency of the normalisation constant n. Runge–Kutta methods are unreliable near zeros of the equation [21]. Problems arise in connection with classification of numerical solutions: the most obvious scheme, of relating the solution to that of the linearised problem and its eigenspectrum, is nonunique [11].

This is not to say that analytical progress has not been forthcoming. A trivial solution in the absence of any test charges, for overall neutral plasma ($\sum_s N_s q_s = 0$), is $\phi(\mathbf{r}) = \text{constant}$; all concentrations are uniform and the field is zero. At infinite temperature the plasma is also uniform. In less trivial situations one can fruitfully examine the equation in terms of existing classification schemes for differential equations. In some cases a first integral can be found. Exact solutions have been obtained in planar and cylindrical geometries, and in two cartesian variables using soliton techniques. Given any one solution, families of solutions can be generated by exploiting translational and rotational invariance. Since the equation is nonlinear it is instructive to see directly how these families satisfy the equation. This section covers all these analytical aspects. We begin by investigating the high- and low-temperature limits.

4.1. *The High-Temperature Expansion*

Let us attempt an expansion of the potential in inverse powers of temperature. Write

$$\phi(\mathbf{r}) = \sum_{j=0}^{\infty} (kT)^{-j} \phi_j(\mathbf{r}) \tag{44a}$$

and

$$n_s = \sum_{j=0}^{\infty} (kT)^{-j} n_{sj}. \tag{44b}$$

Suppose also that the boundary conditions on the potential are homogeneous; if not, the problem is easily transformed to make them so. We can then use the Green's integral version of the Poisson–Boltzmann equation at all orders of $(kT)^{-1}$. It is

$$\phi(\mathbf{r}) = \phi_{\text{ext}}(\mathbf{r}) + \frac{1}{\varepsilon_0} \sum_s N_s q_s n_s \int_{V_p} d\mathbf{r}'\, G(\mathbf{r}, \mathbf{r}') \exp(-q_s \phi(\mathbf{r}')/kT), \tag{45}$$

where $\phi_{\text{ext}}(\mathbf{r})$ and G are defined by (13) and (14). On substituting (44a) and (44b) into this version and collecting terms, we find

$$\phi_0(\mathbf{r}) = \phi_{\text{ext}}(\mathbf{r}) + \frac{1}{\varepsilon_0} \sum_s N_s q_s n_{s0} \int_{V_p} d\mathbf{r}'\, G(\mathbf{r}, \mathbf{r}'), \tag{46}$$

$$\phi_1(\mathbf{r}) = \frac{1}{\varepsilon_0} \sum_s N_s q_s \int_{V_p} d\mathbf{r}'\, G(\mathbf{r}, \mathbf{r}') \{n_{s1} - q_s n_{s0} \phi_0(\mathbf{r}')\}, \tag{47}$$

$$\phi_2(\mathbf{r}) = \frac{1}{\varepsilon_0} \sum_s N_s q_s \int_{V_p} d\mathbf{r}' \, G(\mathbf{r}, \mathbf{r}')$$

$$\times \left\{ n_{s2} - q_s[n_{s1}\phi_0(\mathbf{r}') + n_{s0}\phi_1(\mathbf{r}')] + \frac{1}{2} q_s^2 n_{s0} \phi_0(\mathbf{r}')^2 \right\}, \tag{48}$$

and so on; and by collecting terms in (37),

$$n_{s0} = \left[\int_{V_p} d\mathbf{r} \right]^{-1} = V_p^{-1}, \tag{49}$$

$$n_{s1} = q_s n_{s0}^2 \int_{V_p} d\mathbf{r} \, \phi_0(\mathbf{r}), \tag{50}$$

$$n_{s2} = \frac{n_{s1}^2}{n_{s0}} + q_s n_{s0}^2 \int_{V_p} d\mathbf{r} \left[\phi_1(\mathbf{r}) - \frac{1}{2} q_s \phi_0(\mathbf{r})^2 \right], \tag{51}$$

and so on. The advantage of using the Green's integral form is now obvious: ϕ_{j+1} is an integral involving only $\phi_j, \phi_{j-1}, ..., \phi_0$, so that recursion gives us ϕ_{j+1} by elementary quadrature. The coefficient n_{j+1} *does* appear in the quadrature for ϕ_{j+1}; however, the scheme shows that it can be determined in advance of ϕ_{j+1}.

The zeroth order, infinite-temperature approximation corresponds to a uniform distribution of the particles throughout the volume V. The expansion fails when the potential has a singularity within V, and higher order quadratures diverge. It converges most rapidly when the potential is weakly varying, and the electric field is consequently small. We are not free, as gauge considerations appear to imply, to subtract an arbitrary constant from the potential everywhere so as to make it "small" and accelerate convergence; such a procedure violates the required homogeneity of the boundary conditions. The physical explanation is subtle: if the potential is weakly varying *everywhere*, the homogeneous boundary condition ($\phi = 0$) implies it is small everywhere, and convergence rapid; but if there is a small region of strong variation, the potential becomes large there. Moreover this region may very well dominate the normalisation factors n_s.

An important and related expansion procedure is to expand the equation, but not its solution, in inverse powers of the temperature. The result is an equation for the potential with polynomial nonlinearity of order equal to the truncation order. The zeroth approximation yields $\phi_0(\mathbf{r})$ once again; retaining terms in $(kT)^{-1}$ gives the well-known, linear, Debye–Hückel equation. Its homogeneous solutions vary asymptotically (and in one dimension, exactly) as exponentials of the position variable. It is inconsistent with the expansion scheme to consider anything other than the small potential limits; even there, the inverse temperature expansion of the asymptotic solution cannot coincide with the scheme of (44a) and (44b), since in the Debye–Hückel equation distance is scaled by the square root of the temperature. The Debye–Hückel solution will give a good idea of the spatial variation and a perturbation scheme based upon it is likely to be better, if messier, than the above. Indeed its domain of validity extends well into the region in which linearisation of the Poisson–Boltzmann equation is inaccurate, because even though $\nabla^2\phi$ differs widely in the exact and linearised versions, ϕ itself need not. To understand this, write the equation as $\nabla^2\phi = -F[\phi]$, where $F[\phi]$ has linear approximation $L[\phi]$. The solution is, symbolically, $\phi = \int GF[\phi]$, where G is the Green's function; and the criterion for accuracy is *not* that $F[\phi] \approx L[\phi]$, but that $\int GF \approx \int GL$. The major contribution to the integral should come from the linear regime, a far less stringent requirement. More intuitively ∇^2 represents curvature, and two functions with widely different curvature can approximate each other tolerably well in some region before diverging [22]. Numerical comparisons, and the criterion for eventual failure of the approximation, have been given by Lampert and Crandall [23].

Traditionally the Debye–Hückel equation has been viewed as a low-field approximation in plasmas for which the leading term $\sum_s N_s q_s n_s$ is zero, a condition invariably asserted to imply overall neutrality, although this is so only if all the n_s are equal (as is true only for no field). The equation is more consistently viewed in the foregoing scheme.

4.2. *The Low-Temperature Regime*

As $kT \to 0$ the kinetic energy decreases and the electrostatic energy becomes dominant. Its minimisation, demanded by variational principles equivalent to Poisson's equation, corresponds to reduction of the electric field within the bulk of the plasma to as small as value as possible. In the low temperature limit it is consistent to decouple Poisson's equation and the Boltzmann distribution. Provided only that there is enough plasma charge to accomplish the task, all test charge distributions immersed in the plasma will be completely neutralised by an appropriate plasma charge "frozen" on to their surfaces. (It is a mathematical theorem that a volume charge distribution is equivalent, outside itself, to a surface charge distribution over its boundary.) Any excess plasma charge then distributes itself over the outer boundary of the plasma (or at infinity, if unbounded) as it would over the surface of a similarly shaped conductor. Since the field within a charged conductor is zero, and the test charges within the plasma are neutralised, there is no electric field whatsoever within the plasma. When the temperature is truly zero the fate of the "unfrozen" portion of the plasma, which is electrically neutral, is mathematically unspecified; but at infinitesimal temperatures it will be distributed uniformly throughout the volume available to it.

The exception to this rule occurs in one dimension. The field due to a charge does not diminish with distance in one dimension, and the two surfaces of the test charge are coated with those charges which put equal and opposite total charges at the plasma boundary, again so as to ensure $\mathbf{E} = \mathbf{0}$ with the plasma.

When the plasma contains more than one charged species with polarity opposite to the fixed charge, the species with particles bearing the greatest charge condenses out first, then the next, and so on until neutralisation is complete. This is proved in section 4.12.

4.3. *Planar Solutions: General Discussion*

For variation in one space dimension z, within the plasma but away from the fixed charge, (36) simplifies to

$$\varepsilon_0 \frac{d^2\phi}{dz^2} = -\sum_s N_s q_s n_s \exp(-q_s\phi/kT), \tag{52}$$

where N_s is now the total number of particles of species s per unit area of the plane normal to the z-axis, and n_s^{-1} is the integral of the exponential along the z-axis. The first integral of (52) is

$$\frac{1}{2}\left(\frac{d\phi}{dz}\right)^2 = -\frac{1}{2}A^2 + \frac{kT}{\varepsilon_0}\sum N_s n_s \exp(-q_s\phi/kT), \tag{53}$$

where A is the integration constant. This can, in principle at least, be integrated directly. Reduction to polynomial nonlinearity facilitates comparison with standard forms.

For planar solutions to be useful in practice, spontaneous symmetry breaking must be energetically unfavourable in planar geometries. We expect this to follow from (43). In any case any solution varying in a single dimension, for a problem with planar boundary conditions, is unique.

We shall examine solutions for both single, and two equal and oppositely charged species in planar geometry. No important new features are likely to arise by considering plasmas with more species in this or any other geometry. Solutions have however been given for $q_2 = -q_1 = -2q_3$ in terms of elliptic functions [24].

4.4. *Single Species Planar Solutions*

Define first

$$\zeta = \exp(-q\phi/kT). \tag{54}$$

This is of course the transformation to polynomial form. The first integral (53) becomes

$$\left(\frac{kT}{q}\right)^2\left(\frac{1}{\zeta}\frac{d\zeta}{dz}\right)^2 = -A^2 + \frac{2NnkT}{\varepsilon_0}\zeta \tag{55}$$

which, on defining the RHS as α^2, reduces to

$$\frac{d\alpha}{dz} = \pm\frac{q}{2kT}(\alpha^2 + A^2) \tag{56}$$

with solution

$$\alpha = \pm A \tan\left[\frac{qA}{2kT}(z - z_0)\right]; \tag{57}$$

whence, undoing the transformations,

$$\phi(z) = -\frac{kT}{q} \ln\left[\frac{\varepsilon_0 A^2}{2NnkT} \sec^2 \frac{qA}{2kT}(z - z_0)\right], \qquad A \neq 0. \tag{58}$$

For $A = 0$, ϕ is logarithmic in z. In Section 4.6 we borrow this analysis for the cylindrically symmetrical case; a transformation relates the two geometries. The constants n, A, z_0 are determined from the consistency requirement (37) on n, and the two boundary conditions. Should A^2 be negative in (55), so that A is imaginary, then (57) remains real, and trigonometric functions are replaced by hyperbolic ones. Equation (58) remains real if z_0 is given an imaginary part $\pi kT/qA$, and $\sec^2$ is replaced by cosech^2. The integral in (37) is readily performed, and remarkably n cancels from the result. Nevertheless, provided we have three equations which are not completely decoupled, for the three unknowns all is still perfectly proper.

We apply this solution to investigate the distribution of a charged particle species confined between $z = \pm a$ in the absence of fixed charges; the distribution will not be uniform. Symmetry requires that the electric field be zero at $z = 0$ and we denote $\phi(0)$ by ϕ_c. From the first integral,

$$A^2 = \frac{2NnkT}{\varepsilon_0} \exp(-q\phi_c/kT), \tag{59}$$

and (58) becomes

$$\phi = \phi_c - \frac{kT}{q} \ln\left[\sec^2 \frac{qA}{2kT}(z - z_0)\right]. \tag{60}$$

The condition $\phi(0) = \phi_c$ tells us that

$$\frac{qAz_0}{2kT} = j\pi \tag{61}$$

where j is an integer, so that

$$\phi = \phi_c - \frac{kT}{q} \ln\left[\sec^2 \frac{qA}{2kT} z\right]. \tag{62}$$

Finally, condition (37) is

$$n^{-1} = \int_{-a}^{a} dz\, \zeta \tag{63}$$

$$= \exp\left(\frac{-q\phi_c}{kT}\right) \int_{-a}^{a} dz \sec^2\left(\frac{qAz}{2kT}\right) \tag{64}$$

$$= \frac{4kT}{qA} \exp\left(\frac{-q\phi_c}{kT}\right) \tan\left(\frac{qAa}{2kT}\right) \tag{65}$$

provided that

$$0 < \frac{qAa}{2kT} < \frac{\pi}{2}; \tag{66}$$

otherwise the integral diverges and makes no sense. Elimination of $n \exp(-q\phi_c/kT)$ between (59) and (65) gives a transcendental equation for A whose solution, substituted into (62), completely solves the problem. Instead of A let us work with

$$\gamma = \frac{2}{\pi} \frac{qAa}{2kT}; \tag{67}$$

then

$$\phi(z) = \phi_c - \frac{kT}{q} \ln\left[\sec^2\left(\frac{\pi}{2}\gamma \frac{z}{a}\right)\right], \tag{68}$$

where γ is the solution of

$$\frac{2}{NLa} \frac{\pi}{2}\gamma = \cot \frac{\pi}{2}\gamma, \qquad 0 < \gamma < 1, \tag{69}$$

the characteristic length L being defined as **I don't understand here**

$$L = q^2/2\varepsilon_0 kT. \tag{70}$$

L is linearly related to the Landau length of plasma theory, or the Bjerrum length of electrolyte theory. As required, (68) preserves gauge invariance.

In relating this solution to the inverse temperature expansion, we observe the limits

$$\frac{\pi}{2}\gamma \sim \begin{cases} (NLa/2)^{1/2}, & kT \gg Nq^2a/\varepsilon_0 \\ \dfrac{\pi}{2}\left(1 - \dfrac{2}{NLa}\right), & kT \ll Nq^2a/\varepsilon_0. \end{cases} \tag{71}$$

Despite the high-temperature result, half-integral powers of $(kT)^{-1}$ do not appear in the perturbation expansion.

Finally, we examine the concentration and the electric field. After some manipulation, the concentration is

$$q^{-1}\rho_p(z) = Nn\zeta = \frac{N}{2a}\,\frac{(\pi/2)\gamma}{\tan(\pi/2)\gamma}\,\sec^2\left(\frac{\pi}{2}\,\gamma\,\frac{z}{a}\right), \tag{72}$$

which integrates to N as required. The central region is depleted, and the regions close to the boundaries at $z = \pm a$ bear an excess of charge, in line with energetic arguments conerning repulsion of like charges. At high temperatures the concentration is asymptotically uniform, as expected, and at low temperatures (or large spacing $2a$), all the charge is asymptotically distributed on the boundaries.

The electric field within the plasma is

$$E(z) = \frac{Nq}{2\varepsilon_0}\tan\left(\frac{\pi}{2}\,\gamma\,\frac{z}{a}\right)\Big/\tan\left(\frac{\pi}{2}\,\gamma\right), \tag{73}$$

which reduces immediately to the linear form $(Nq/2\varepsilon_0)(z/a)$ at high temperatures, and to $\pm Nq/2\varepsilon_0$ at $z = \pm a$ in accordance with the limits of (72). Of course, the field outside the plasma is constant.

If there is a nonzero fixed charge distribution outside the plasma, one of $E(-a)$, $E(a)$ becomes a new parameter to be specified; only the difference $E(a) - E(-a) = Nq/\varepsilon_0$ remains unaltered. The new condition is to be incorporated by modifying the values of the integration constants A, z_0. Finally, if the boundaries at $\pm a$ are conductors, the solution is of the same form but the integration constants differ to allow for image charges.

4.5. *Two Species Planar Solutions*

Let us now consider a plasma with two species bearing equal and opposite charges $q_1 = -q_2 = q$, but not necessarily equal numbers of particles of each species. Within the plasma, in the absence of fixed charges, the first integral (53) of the Poisson–Boltzmann equation becomes

$$\frac{1}{2}\left(\frac{d\phi}{dz}\right)^2 = -\frac{1}{2}A^2 + \frac{2kT}{\varepsilon_0}(N_1N_2n_1n_2)^{1/2} \times\cosh\left[\frac{q\phi}{kT} + \frac{1}{2}\ln\left(\frac{N_2n_2}{N_1n_1}\right)\right] \tag{74}$$

$$= \frac{4kT}{\varepsilon_0}(N_1N_2n_1n_2)^{1/2} \times\sinh^2\left[\frac{1}{2}\frac{q\phi}{kT} + \frac{1}{4}\ln\left(\frac{N_2n_2}{N_1n_1}\right)\right] + B, \tag{75}$$

where B is a more concise way of writing the arbitrary constant. Transformation to polynomial form tells us that unless $B = 0$, the solution involves elliptic functions.

Although routine, we do not wish to pursue their technicalities here. We shall therefore reverse the usual procedure and deduce a posteriori the physical conditions corresponding to $B=0$. We shall also be guided by previous work on the two species planar problem.

Mathematically, the solution of (75) when $B=0$ poses no difficulty, and routine quadrature followed by reversion gives the solution

$$\phi(z) = -\frac{kT}{2q}\ln\left(\frac{N_2 n_2}{N_1 n_1}\right) + \frac{4kT}{q}\tanh^{-1}[\exp\{\pm 2(N_1 N_2 n_1 n_2)^{1/4} L^{1/2}(z-z_0)\}], \tag{76}$$

the ambiguity in sign arising from taking the square root of (75). The Landau length L is defined by (70). The sign ambiguity can be avoided if we replace the inverse hyperbolic function by its logarithmic form; after some manipulation (76) becomes

$$\phi(z) = \frac{kT}{q}\ln\left[\left(\frac{N_1 n_1}{N_2 n_2}\right)^{1/2}\coth^2\{(N_1 N_2 n_1 n_2)^{1/4} L^{1/2}(z-z_0)\}\right] \tag{77}$$

with associated field

$$E(z) = \left(\frac{8kT}{\varepsilon_0}\right)^{1/2}(N_1 N_2 n_1 n_2)^{1/4}\,\mathrm{cosech}\,[2(N_1 N_2 n_1 n_2)^{1/4} L^{1/2}(z-z_0)]. \tag{78}$$

Traditionally this solution has been associated with a semi-infinite plasma domain, when it has been given for finite $N_1 n_1 = N_2 n_2$ by many authors, for example, Clemmow and Dougherty [5]. In principle we can take this limit a posteriori; with the plasma confined in $a<z<b$, b finite, we have

$$n_1^{-1} = \int_a^b dz\,\exp(-q\phi/kT) \tag{79}$$

which eventually reduces to

$$(N_1 N_2 n_1 n_2)^{1/4} L^{1/2}[-(N_1/N_2 n_1 n_2)^{1/2} + (b-a)] = \tanh\{(N_1 N_2 n_1 n_2)^{1/4} L^{1/2}(b-z_0)\} - \tanh\{(N_1 N_2 n_1 n_2)^{1/4} L^{1/2}(a-z_0)\}. \tag{80}$$

Similarly, the equation

$$n_2^{-1} = \int_a^b dz\,\exp(q\phi/kT) \tag{81}$$

reduces to

$$(N_1 N_2 n_1 n_2)^{1/4} L^{1/2}[(N_2/N_1 n_2 n_1)^{1/2} - (b-a)] = \coth\{(N_1 N_2 n_1 n_2)^{1/4} L^{1/2}(a-z_0)\} - \coth\{(N_1 N_2 n_1 n_2)^{1/4} L^{1/2}(b-z_0)\}. \tag{82}$$

Equations (80) and (82) are to be solved simultaneously for $n_1 n_2$ and z_0. On substituting the solutions back into (78) we observe that the electric field is completely determined; the only ambiguity remaining in the potential is the gauge, which has no effect on the physics. The transcendental equation for the product $n_1 n_2$ is obtained by eliminating z_0 between (80) and (82). The result is

$$(N_1 N_2 n_1 n_2)^{1/4} L^{1/2} \coth\{(N_1 N_2 n_1 n_2)^{1/4} L^{1/2}(b-a)\}$$
$$= \frac{1}{-(N_1/N_2 n_1 n_2)^{1/2} + (b-a)} - \frac{1}{(N_2/N_1 n_2 n_1)^{1/2} - (b-a)}. \tag{83}$$

Clearly from (80) and (82), both denominators on the RHS are positive, while the RHS itself must also be positive. From these conditions we derive the inequalities

$$N_2 \geqslant N_1, \qquad (b-a)^2 n_1 n_2 \leqslant 1, \tag{84}$$

with equality corresponding to a singular case. In fact the latter inequality is always guaranteed by Schwarz' theorem.

What of the limit $b \to \infty$? If the amount of plasma is kept finite, it is convenient to expand the potential—and of course the normalisation factor n^{-1}—in inverse powers of the "volume" $(b-a)$. The leading term is $\phi_{\text{ext}}(\mathbf{r})$. It is convenient to work with a new variable $\phi - \phi_{\text{ext}}$. We are more interested, however, in a nonzero mean plasma *density*, implying an infinite amount of each species, but with the net plasma charge finite. Thus the mean concentration of the species will be equal. The quantities

$$C = N_1/(b-a), \qquad \Delta = N_2 - N_1 \tag{85}$$

should be used to eliminate N_1 and N_2 before taking the limit; we should also use

$$n'_{1,2} = (b-a)\, n_{1,2} \tag{86}$$

instead of n_1, n_2. On making these substitutions in (83) and taking the limit, the hyperbolic cotangent goes to unity. Care must be taken with the RHS; defining

$$(n'_1 n'_2)^{-1/2} = 1 + \varepsilon/b + O(b^{-2}), \tag{87}$$

we find that ε satisfies the quadratic equation

$$\varepsilon^2 + 2(CL)^{-1/2}\varepsilon - (\Delta/2C)^2 = 0; \qquad \varepsilon > 0. \tag{88}$$

The term of order $O(b^{-1})$ is needed when calculating z_0. On substituting (87) into the ratio (80)/(82) and taking the limit, we have after some manipulation

$$\frac{\Delta/2C - \varepsilon}{\Delta/2C + \varepsilon} = \tanh(CL)^{+1/2}\,(a - z_0) \tag{89}$$

so that

$$(CL)^{1/2}(a-z_0)=\tfrac{1}{2}\ln(\Delta/2C\varepsilon). \tag{90}$$

It follows by substituting for ε from (88) that

$$\operatorname{cosech} 2(CL)^{1/2}(a-z_0)=\frac{\Delta}{2}\left(\frac{L}{C}\right)^{1/2}. \tag{91}$$

The electric field is

$$E(z)=\left(\frac{8CkT}{\varepsilon_0}\right)^{1/2}\operatorname{cosech}\left[2(CL)^{1/2}(z-a)+\operatorname{cosech}^{-1}\left(\frac{\Delta}{2}\left(\frac{L}{C}\right)^{1/2}\right)\right], \tag{92}$$

with values

$$E(a)=q\Delta/\varepsilon_0, \qquad E(\infty)=0 \tag{93}$$

in accordance with the divergence theorem: the plasma contains a total charge per unit area of $(N_1-N_2)q=-q\Delta$. An external electric field due to fixed charges $q\Delta/2\varepsilon_0$ must pervade the plasma. This could be due to a fixed charge per unit area of magnitude $+q\Delta$ placed anywhere in $z<a$. Observe that the fixed charge and plasma charge are equal and opposite, so that the field is zero on either side of the combination. Only now can we consider the limit $\Delta=0$, when there is no external field and the plasma is neutral. It is—as expected—undisturbed.

Traditionally this solution has been derived without regard to the limit $b\to\infty$: the concentrations have been taken as primitive, and set equal [5]. It is a subtle matter to appreciate how the concentrations of the two species can be equal, yet the plasma carries a net charge; it is only possible in an infinite domain. The role played by $\Delta=N_2-N_1$ clarifies this greatly:

$$C_1=N_1/V,\ C_2=N_2/V=(N_1+\Delta)/V\to C_1 \qquad \text{as } V\to\infty,\ C_1 \text{ finite}. \tag{94}$$

Armed with this, we can now answer two interesting questions: What happens when a slab of total charge σ per unit area (both sides included) is immersed in an infinite, overall neutral plasma; and when it bounds a semi-infinite overall neutral plasma? Ab initio analysis would need to take the infinite limits of the appropriate elliptic function solution; but we can at least gain a qualitative understanding. The system always arranges itself to have asymptotically zero field throughout the vast body of the plasma. In the first case, the slab sets up a fixed field of magnitude of $\sigma/2\varepsilon_0$ throughout the plasma on either side. This is neutralised by separating amounts of charge $\pm\frac{1}{4}\sigma$, the opposite charge being adjacent to the plate and the like charge at infinity, on either side. Thus the plate is only one-half neutralised in its vicinity. In the second case, the situation on the plasma side is identical, and the plate is one-quarter neutralised. The crucial fact is that the field of a charge does not alter with distance in one dimension. For this reason there is also nothing singular about the one dimensional "point charge" (in our three dimensional world, a thin charged plate).

4.6. *The Single Species Cylindrically Symmetrical Solution*

In this subsection we solve the problem of a single charged species confined between concentric insulating cylinders of radii a and b $(>a)$. Within $r<a$ are fixed charges distributed with cylindrical symmetry about the common axis; there is a total fixed charge Q'_{ext} per unit axial length. The radial electric field at $r=a$, by Gauss' law, is therefore $Q'_{\text{ext}}/2\pi\varepsilon_0 a$. It remains to specify the gauge; since $\phi = O(\ln r)$ at large distances, we cannot take $\phi(\infty)=0$. Instead we specify the potential at $r=a$ to be ϕ_a.

This problem is worth detailed consideration in addition to the slab geometry case, because shrinking a to zero gives us information on the screening of two dimensional point (i.e., line) charges.

Within the plasma, we have

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{d\phi}{dr}\right) = -\frac{Nqn}{\varepsilon_0}\exp\left(\frac{-q\phi}{kT}\right), \tag{95}$$

where N is the number of particles per unit axial length, and

$$n^{-1} = \int_a^b dr\, 2\pi r \exp(-q\phi/kT). \tag{96}$$

Equation (95) is invariant under a stretch of r and an appropriate translation of ϕ; on multiplying both sides by r^2, the transformation is clearly seen to leave the combination $r^2\exp(-q\phi/kT)$ invariant. We therefore seek a similarity solution, and denoting this combination by $\exp(-q\chi/kT)$, the equation becomes

$$\frac{d^2\chi}{d(\ln r)^2} = -\frac{Nqn}{\varepsilon_0}\exp\left(\frac{-q\chi}{kT}\right), \tag{97}$$

which is identical to the one dimensional equation. We borrow the results of the integration from Section 4.4; reverting from χ to ϕ, the first integral is

$$\frac{1}{2}\left(r\frac{d\phi}{dr} - \frac{2kT}{q}\right)^2 = -\frac{1}{2}A^2 + \frac{NnkT}{\varepsilon_0}r^2\exp\left(\frac{-q\phi}{kT}\right) \tag{98}$$

and the solution

$$\phi(r) = -\frac{kT}{q}\ln\left[\frac{\varepsilon_0 A^2}{2NnkTr^2}\sec^2\left(\frac{qA}{2kT}\ln\frac{r}{r_0}\right)\right]. \tag{99}$$

If A is imaginary the problem must be dealt with as in the planar case; replace sec by cosech again. The argument of the outer logarithm consequently contains only powers of r. Neither paper giving these solutions [25, 26] addresses the consistency condition for n, and their results—using only the two boundary conditions—are consequently not gauge invariant, indicating that something has gone wrong.

From (98) at $r=a$,

$$A^2 = \frac{2NnkTa^2}{\varepsilon_0} \exp\left(\frac{-q\phi_a}{kT}\right) - \left(aE_a + \frac{2kT}{q}\right)^2 \tag{100}$$

which is the difference of two nonnegative quantities. We can perfectly well choose E_a to make the second term vanish, or choose kT sufficiently large to make it dominant. It is therefore necessary to examine both $A^2 \gtreqless 0$. For $A=0$ we take the limit $A \to 0$ of the hyperbolic case, and find that ϕ behaves as $\ln(r \ln r)$. Let us now consider $A^2 > 0$ and put $r=a$ in (99) to give

$$\phi_a = -\frac{kT}{q} \ln\left[\frac{\varepsilon_0 A^2}{2NnkTa^2} \sec^2\left(\frac{qA}{2kT} \ln \frac{a}{r_0}\right)\right]; \tag{101}$$

eliminating n between this and (99) yields

$$\phi(r) = \phi_a - \frac{kT}{q} \ln\left[\frac{a^2}{r^2} \frac{\sec^2((qA/2kT)\ln(r/r_0))}{\sec^2((qA/2kT)\ln(a/r_0))}\right], \tag{102}$$

while substitution of $n \exp(-q\phi_a/kT)$ from (101) into (100) gives, on simplification,

$$\pm A = \left(aE_a + \frac{2kT}{q}\right) \cot\left(\frac{qA}{2kT} \ln \frac{a}{r_0}\right). \tag{103}$$

The normalisation equation (96) is readily evaluated using (99) for ϕ and integration variable $\ln(r/r_0)$, with the result

$$\frac{Nq}{2\pi\varepsilon_0 A} = \tan\left(\frac{qA}{2kT} \ln \frac{b}{r_0}\right) - \tan\left(\frac{qA}{2kT} \ln \frac{a}{r_0}\right) \tag{104}$$

provided that the interval

$$\left[\frac{qA}{2kT} \ln \frac{a}{r_0}, \frac{qA}{2kT} \ln \frac{b}{r_0}\right] \tag{105}$$

does not contain any half-integer multiple of π, at which points the integrand is singular. The strategy now is to use (103) and (104) to eliminate A and r_0 from (102), while resolving the ambiguity of sign in (103) and confirming the integrability condition for (104).

Instead of A and r_0, let us work with the combinations

$$\theta = \frac{qA}{2kT} \ln \frac{a}{r_0}, \qquad \psi = \frac{qA}{2kT} \ln \frac{b}{a}. \tag{106}$$

The potential (102) becomes

$$\phi(r)=\phi_a-\frac{q}{2\varepsilon_0 L}\ln\left[\frac{a^2\sec^2[\theta+\psi\ln(r/a)/\ln(b/a)]}{r^2\sec^2\theta}\right], \tag{107}$$

while (103) and (104) become respectively

$$\psi=\pm\left(1+\frac{qaE_a}{2kT}\right)\left(\ln\frac{b}{a}\right)\cot\theta \tag{108}$$

and

$$\tan(\theta+\psi)-\tan\theta=\frac{NL}{2\pi\psi}\ln\frac{b}{a}, \tag{109}$$

where L is again the Landau length (70); the interval $[\theta, \theta+\psi]$ shall not contain a half-integer multiple of π. On substituting (108) into (107) and differentiating, we have

$$E(r)=-\frac{q}{\varepsilon_0 Lr}\left[1\mp\left(1+\frac{qaE_a}{2kT}\right)\cot\theta\tan\left\{\theta\pm\left(1+\frac{qaE_a}{2kT}\right)\cot\theta\ln\frac{r}{a}\right\}\right],\qquad a<r<b. \tag{110}$$

By testing that $E(a)=E_a$, it is found that the upper sign must be taken in (110) and (108). It remains to substitute (108) into (109) and solve for θ in terms of two dimensionless parameters. The resulting transcendental equation is easily written, by multiplying (109) by ψ before substituting, as

$$\tan(\theta+\mu\cot\theta)=\nu\tan\theta,\qquad (j+\tfrac{1}{2})\,\pi\notin[\theta,\theta+\mu\cot\theta], \tag{111}$$

where

$$\mu=\left(1+\frac{qaE_a}{2kT}\right)\ln\frac{b}{a}\in(-\infty,\infty),\qquad \nu=1+\frac{NL}{2\pi\mu}\ln\left(\frac{b}{a}\right). \tag{112}$$

It is easy to confirm by eliminating θ between this and (110) with $r=b$ that

$$E(b)=(Nq+2\pi\varepsilon_0 aE_a)/2\pi\varepsilon_0 b, \tag{113}$$

in accordance with Gauss' law. This check also backs up a good deal of algebra. We quote the concentration

$$\begin{aligned} q^{-1}\rho_p(\mathbf{r}) &= Nn\exp\left(\frac{-q\phi}{kT}\right)\\ &=\frac{1}{Lr^2}\left(1+\frac{qaE_a}{2kT}\right)^2\cot^2\theta\sec^2\left\{\theta+\left(1+\frac{qaE_a}{2kT}\right)\cot\theta\ln\frac{r}{a}\right\}. \end{aligned} \tag{114}$$

Appearance of the external field E_a in the combination $(1+qaE_a/2kT)$ indicates that this field enhances (or competes with, depending on sign) an electrostatic repulsion effect away from the centre $r=0$. The repulsion effect will be more pronounced, the higher the dimensionality.

We now quote the results when the integration constant A^2 in (98) is negative:

$$\phi(r)=\phi_a-\frac{q}{2\varepsilon_0 L}\ln\left[\frac{a^2}{r^2}\frac{\operatorname{cosech}^2[\theta'-\mu\tanh\theta'\ln(r/a)/\ln(b/a)]}{\operatorname{cosech}^2\theta'}\right], \tag{115}$$

$$E(r)=-\frac{q}{\varepsilon_0 Lr}\left[1-\left(1+\frac{qaE_a}{2kT}\right)\tanh\theta'\coth\left\{\theta'-\frac{\mu\tanh\theta'\ln(r/a)}{\ln(b/a)}\right\}\right], \tag{116}$$

where

$$\coth(\theta'-\mu\tanh\theta')=\nu\coth\theta', \qquad 0\notin[\theta'-\mu\tanh\theta',\theta']; \tag{117}$$

and

$$q^{-1}\rho_p(\mathbf{r})=\frac{1}{Lr^2}\left(1+\frac{qaE_a}{2kT}\right)^2\tanh^2\theta'\operatorname{cosech}^2\left[\theta'-\frac{\mu\tanh\theta'\ln(r/a)}{\ln(b/a)}\right]. \tag{118}$$

An alternative method of matching the boundary conditions is given by Rubinstein [27].

It is quite common in the literature for special cases of complicated results to be examined without regard to the possibility of the conditions necessary for such simplifications being satisfied. For example, considerable simplification takes place when the coefficient of $\ln r$ within the hyperbolic functions equals ± 1:

$$\mu\tanh\theta'/\ln(b/a)=\mp 1. \tag{119}$$

Apart from the gauge, the potential is then proportional to the logarithm of an expression quadratic in r. This condition is, however, impossible to satisfy; for eliminating θ' between (117) and (119) gives, eventually,

$$\left(\frac{a}{b}\right)^2\left(1+\frac{4kT}{qaE_a}\right)=1+2\left(\frac{qaE_a}{2kT}+\frac{NL}{2\pi}\right)^{-1}, \tag{120}$$

which, on isolating a/b and demanding it be less than unity, reduces to the condition $qE_a>0$, or that the fixed and plasma charges are of like polarity. But the interval condition, which on choosing w.l.o.g. the root $\theta'>0$ (the two roots and intervals are mirror images) is just $\theta'-\mu\tanh\theta'>0$, reduces to

$$\left(\frac{a}{b}\right)^2\left(1+\frac{4kT}{qaE_a}\right)<1. \tag{121}$$

Clearly (120) and (121) are incompatible.

Next we examine the high-temperature limit $kT \to \infty$, $L \to 0$. The parameter ν approaches unity from above, and θ' becomes large; standard asymptotic analysis gives the result

$$2\exp(-2\theta') \approx \frac{NLa^2}{2\pi(b^2-a^2)}; \tag{122}$$

whence after careful manipulation,

$$\phi(r) \approx \phi_a - \frac{Nq(r^2-a^2)}{4\pi\varepsilon_0(b^2-a^2)} + \left[\frac{Nqa^2}{2\pi\varepsilon_0(b^2-a^2)} - aE_a\right]\ln\left(\frac{r}{a}\right), \tag{123}$$

$$E(r) \approx \frac{Nqr}{2\pi\varepsilon_0(b^2-a^2)} + \left[aE_a - \frac{Nqa^2}{2\pi\varepsilon_0(b^2-a^2)}\right] r^{-1}, \tag{124}$$

$$n^{-1} \approx \pi(b^2-a^2) \tag{125}$$

and

$$q^{-1}\rho_p(\mathbf{r}) \approx N/\pi(b^2-a^2). \tag{126}$$

The uniform concentration (126) could have been foreseen; (124) and (123) then follow immediately. The limit furnishes further confirmation of the algebra.

Let us now examine the singular limit $a \to 0$, with $aE_a = Q'_{\text{ext}}/2\pi\varepsilon_0$ constant, corresponding to a fixed line charge immersed in the plasma. Define

$$\eta = 1 + \frac{qQ'_{\text{ext}}}{4\pi\varepsilon_0 kT} = 1 + \frac{L}{2\pi}\frac{Q'_{\text{ext}}}{q} \tag{127}$$

which we suppose, for the time being, positive. We have

$$\mu = \eta \ln\left(\frac{b}{a}\right) \to +\infty, \qquad \nu = 1 + \frac{NL}{2\pi\eta} > 1, \tag{128}$$

and the solution of (117) for θ' is, asymptotically,

$$\theta' = \mu + \coth^{-1}\nu. \tag{129}$$

This is readily confirmed to be unique. On writing

$$\ln(r/a) = \ln(b/a) - \ln(b/r) = \eta^{-1}\mu - \ln(b/r) \tag{130}$$

and substituting (129) and (130) into (116), we have

$$E(r) = -\frac{q}{\varepsilon_0 Lr}\left[1 - \eta\coth\left(\coth^{-1}\nu + \eta\ln\left(\frac{b}{r}\right)\right)\right] \tag{131}$$

with limit

$$\lim_{r \to 0} 2\pi\varepsilon_0 r E(r) = 2\pi(\eta - 1)\, q/L \tag{132}$$

$$= Q'_{\text{ext}}. \tag{133}$$

There is no concentration of a finite amount of plasma charge in an infinitesimal volume at $r = 0$. Moreover,

$$q^{-1}\rho_p(r) = \frac{\eta^2}{Lr^2} \operatorname{cosech}^2\left(\coth^{-1} v + \eta \ln\left(\frac{b}{r}\right)\right) \tag{134}$$

$$\sim \frac{N}{\pi b^2} \frac{2\eta}{v+1} \left(\frac{r}{b}\right)^{2\eta - 2}, \qquad r \ll b. \tag{135}$$

The concentration of plasma charge behaves, as $r \to 0$, as the $LQ'_{\text{ext}}/\pi q$th power of r; the power may be positive or negative provided it is not less than -2 (when the fixed-to-plasma charge ratio qQ'_{ext}/Nq^2 is greater than $-2\pi/NL$). For positive powers at least, when the fixed and plasma charges have like polarity, this was predictable by a "decoupling" process: the potential is dominated at small r by the fixed charge and can be calculated from it to a good approximation; the concentration is then proportional to $\exp(-q\phi/kT)$, giving the form $r^{LQ'_{\text{ext}}/\pi q}$ immediately. For negative powers between 0 and -2, corresponding to fixed and plasma charges of opposite polarity, attraction of opposites is competing with the geometrical effect of plasma charge repulsion from the central line $r = 0$.

Should there be no fixed charge, so that $\eta = 1$, simplification results; for example, (131) becomes

$$E(r) = \frac{4kT}{qb} \frac{r/b}{1 + 4\pi/NL - (r/b)^2}. \tag{136}$$

This is precisely the simplification discussed after (118). For finite a it was impossible, but for $a = 0$ it is permissible. At low temperatures, with all the plasma asymptotically at $r = b$, the field does *not* fall off exponentially as r decreases from b, and the characteristic length is *not* the Debye length. This would apply only to predominantly neutral plasmas.

What happens if $\eta < 0$ and $\mu \to -\infty$ as $a \to 0$? We subdivide this case into two, drawing on (128): $0 < v < 1$ and $v < 0$. All values of v, and hence of charge ratio $qQ'_{\text{ext}}/Nq^2 = (v-1)^{-1} - 2\pi/NL$, are covered by these two cases and the one already considered. The uniqueness theorem guarantees that there is no overlap. For $0 < v < 1$ there are two "mirror image" solutions for θ':

$$\theta' = \pm\tanh^{-1}\mu. \tag{137}$$

They both yield the same physics. Substitution of the positive branch into (116) gives

$$E(r) = -\frac{q}{\varepsilon_0 L r}\left[1 - \eta\nu \coth\left(\tanh^{-1}\nu - \eta\nu \ln\left(\frac{r}{a}\right)\right)\right], \tag{138}$$

and taking the limit $a \to 0$ we have

$$E(r) = \frac{(\eta\nu - 1)q}{\varepsilon_0 L r} \tag{139}$$

$$= \frac{(Q'_{\text{ext}} + Nq)}{2\pi\varepsilon_0 r}. \tag{140}$$

This time the fixed charge has attracted all the plasma arbitrarily close to it in a delta function distribution; the plasma concentration elsewhere goes to zero. It is stressed that this phenomenon is taking place at nonzero temperatures. The conditions $0 < \nu < 1$ and $\eta < 0$ imply that

$$1 + \frac{2\pi}{NL} < \frac{-qQ'_{\text{ext}}}{Nq^2}, \tag{141}$$

so that the fixed and plasma charges are of opposite polarity, and the magnitude $|Nq|$ of the plasma charge is smaller by a nonzero amount than that of the fixed charge, $|Q'_{\text{ext}}|$; the case of equal and opposite charges cannot be approached through this branch. We can visualise the smaller plasma charge as vainly trying to neutralise the larger, oppositely polarised fixed charge. It is an altogether remarkable fact that charge condensation emerges from the equations in the appropriate limit. The nonlinear regime is crucially involved. Note the noncommutativity

$$Q'_{\text{ext}} + Nq = \lim_{r \to a} \lim_{a \to 0} 2\pi\varepsilon_0 r E(r) \neq \lim_{a \to 0} \lim_{r \to a} 2\pi\varepsilon_0 r E(r) = Q'_{\text{ext}}. \tag{142}$$

Of course, the plasma is an assembly of discrete particles, not a fluid as was assumed in deriving the Poisson–Boltzmann equation, and in practise condensation can never be complete.

The criterion for condensation is not merely $|Nq/Q'_{\text{ext}}| < 1$, but, from (141), depends also on the plasma temperature. How can this be understood? The answer is that the plasma concentration is proportional to $\exp(-q\phi/kT)/\langle\exp(-q\phi/kT)\rangle$, which reduces to the delta function whenever $\exp(-q\phi/kT)$ has a nonintegrable nonoscillatory singularity: by definition the expression integrates to unity and is pulled to zero by the denominator at all points except the singularity. Upon integrating (140) to give ϕ, it is found that $\exp(-q\phi/kT) = O(r^p)$ where $p = (qQ'_{\text{ext}} + Nq^2)/2\pi\varepsilon_0 kT < 0$. This is then multiplied by the element $2\pi r\,dr$ and integrated; nonintegrability at $r = 0$ corresponds to $p \leqslant -2$, immediately giving condition (141). Condensation has been viewed as a peculiar form of second order phase transition [27].

For $\eta < 0$, $\nu < 0$, corresponding to

$$1 + \frac{2\pi}{NL} > \frac{-qQ'_{\text{ext}}}{Nq^2} > \frac{2\pi}{NL}, \tag{143}$$

it is easy to show there is no real solution for θ' in the limit $\mu \to -\infty$. The interval (143) does not necessarily include the case of equal and opposite fixed and plasma charges. The trigonometric form (107) rather than the hyperbolic form (115) is now the appropriate expression to examine as $a \to 0$. The solution of (111) for θ is, asymptotically,

$$\theta = \left(j + \tfrac{1}{2}\right)\pi - \frac{m\pi}{\mu} - \left(1 - \frac{1}{\nu}\right)\frac{m\pi}{\mu^2} + O(\mu^{-3}), \qquad m \neq 0 \tag{144}$$

so that the interval

$$[\theta, \theta + \mu \cot \theta] = \left[\left(j + \frac{1}{2}\right)\pi - \frac{m\pi}{\mu} + O(\mu^{-2}), \left(j + \frac{1}{2}\right)\pi + \frac{m\pi}{\mu} - \frac{m\pi}{\nu\mu} + O(\mu^{-2})\right]. \tag{145}$$

Provided that $m = \pm 1$, this does not include a half-integer multiple of π. (Recall that $\mu \to -\infty$ and that $\nu < 0$.) Before taking the limit it is convenient to write the field (110) as

$$E(r) = -\frac{q}{\varepsilon_0 Lr}\left\{1 - \eta \cot \theta \tan\left[\theta + \mu \cot \theta - \eta \cot \theta \ln\left(\frac{b}{r}\right)\right]\right\}, \tag{146}$$

which reduces, on substituting for θ and taking $\mu \to \infty$, to

$$E(r) = -\frac{q}{\varepsilon_0 Lr}\left(1 - \frac{\eta\nu}{1 + \eta\nu \ln(b/r)}\right), \tag{147}$$

independent of the integer j and the sign of m. This corresponds to a central line charge per unit length

$$\lim_{r \to 0} 2\pi\varepsilon_0 r E(r) = -2\pi q/L, \tag{148}$$

independent of Q'_{ext}. The concentration (114) reduces to

$$q^{-1}\rho_p(r) = \frac{1}{Lr^2}\left(\frac{\eta\nu}{1 + \eta\nu \ln(b/r)}\right)^2, \tag{149}$$

which integrates over the plasma volume to give a volume charge

$$\int_a^b dr\, 2\pi r \rho_p(\mathbf{r}) = Nq + Q'_{\text{ext}} + \frac{2\pi q}{L}. \tag{150}$$

Added to the central charge, this gives precisely the total charge $Nq + Q'_{ext}$, as expected. It is readily confirmed from (143) that

$$1 > \frac{1}{Nq} \int_a^b dr\, 2\pi r \rho_p(r) > 0, \tag{151}$$

so that a portion of the plasma charge condenses onto the fixed line charge, but, from the sign of (148), not enough to neutralise it. Strictly, the concentration should be written as the sum of (149) and a singular term corresponding to the condensed charge.

The explanation of partial condensation in terms of singularities of the potential and of $\exp(-q\phi/kT)$ is now rather subtle. This exponential is proportional to $r^{-2}(1 + \eta v \ln(b/r))^{-2}$, which on multiplication by $2\pi r\, dr$ is "just" integrable at $r = 0$: there is no margin of safety in the power index, and convergence is a consequence of the logarithmic term, (150) being proportional to its coefficient, ηv.

In all three cases, condensation is never sufficient to neutralise the fixed charge, even when there is enough oppositely polarised plasma charge to do the job. Condensation has been extensively studied in two (oppositely charged) species plasmas, particularly in cylindrical geometry. The absence of exact solutions has led to alternative means of attack. Details are given in the next subsection; we can say though, that condensation should certainly be no greater when a second species of similar polarity to the fixed charge is added, for the fixed charge then must compete with this species for the opposite charges.

These results could have been derived more directly from the boundary condition $a = 0$ ab initio. The equation is unchanged, with again solutions of the form (99) (with hyperbolic functions as necessary) in terms of n and two integration constants. The latter are easily disposed of in favour of $E(b)$, given by Gauss' law as $(Q'_{ext} + Nq)/2\pi\varepsilon_0 b$, and $\phi(b)$. The integral giving n yields a concentration which integrates to Nq less any condensate; combining this with the requirement that $-\lim_{r \to 0} 2\pi\varepsilon_0 r\, d\phi/dr$ equals the fixed charge plus any condensate enables the amount of condensate, if any, to be found.

4.7. *The Two Species Cylindrically Symmetrical Problem*

Let us now consider a plasma containing two species of equal and opposite charges ($q_1 = -q_2 = q$) confined in $a < r < b$, and, as in the preceding subsection, a coaxial cylindrically symmetrical fixed charge distribution in $r < a$. In appropriate limits, the solutions of the preceding subsection will be approached. We do not insist that there be equal numbers of the two species; the plasma need not be overall neutral. When we come to take $b \to \infty$, however, we shall insist that the net plasma charge be finite. The Poisson–Boltzmann equation in the plasma may be written

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{d\phi}{dr}\right) = \frac{2q}{\varepsilon_0}(N_1 N_2 n_1 n_2)^{1/2} \sinh\left[\frac{q\phi}{kT} + \frac{1}{2}\ln\left(\frac{N_2 n_2}{N_1 n_1}\right)\right]. \tag{152}$$

Not even a first integral is known, and no similarity transformation exists; however, (152) is reducible to a particular case of Painlevé's third transcendent PIII. The appropriate variables are $L^{1/2}(N_1N_2n_1n_2)^{1/4}r$, $-\exp[\frac{1}{2}q\phi/kT+\frac{1}{4}\ln(N_2n_2/N_1n_1)]$ [21]. Clearly this is but a power law transformation of the usual polynomial form. This equation also arises in connection with the Ising model in two dimensions [28, 29]. Painlevé's form guarantees that any branch points or essential singularities are fixed, independent of the integration constants. The reason for testing for the Painlevé property is that detailed classification of such equations already exists in the literature [17, 30]. McCoy *et al.* [31] have studied the particular case of PIII arising from (152) and give the one parameter family of solutions bounded at $r=\infty$ as an infinite series involving quadratures (take their parameter $\nu=0$); however, if the plasma is bounded the full two parameter solution is needed. The general two species problem ($q_2\neq -q_1$) may also be reduced to this case of PIII [21]. It has been studied as the Dodd–Bullough equation [32], at least for overall neutrality; generalisation to charged plasmas consists, before boundary conditions are imposed, of nothing more than a change of gauge, at least before the n_1, n_2 factors are determined by self-consistency.

Can anything be done with differential equations this nonlinear? Numerical solutions are available [20, 21, 33]; see also further references cited in these. High- and low-temperature behaviour can be predicted immediately (Sections 4.1 and 4.2); but in general, the nonlinearity brings to mind soliton solutions of nonlinear partial differential equations. Assuredly it should be easier to tackle an ordinary than a partial differential equation; but the handling of the boundary conditions by inverse scattering appears to depend crucially on the equation containing two variables: x, and an evolution variable t such that the solution at $t=0$ is known. Lax's reformulation, given in standard soliton texts, instead regards the nonlinear equation as a compatibility condition for existence of a solution to a system of linear homogeneous first order differential equations; just as the condition for existence of a solution to a system of linear homogeneous algebraic equations is that the determinant of coefficients must vanish. The coefficients in the system of linear differential equations involve the dependent variable and certain of its derivatives. For nonlinear partial differential equations the usual inverse scattering techniques operate on the linear system, but for nonlinear ordinary differential equations the solutions to the nonlinear system are characterised completely by their behaviour at singular points (and analyticity elsewhere): the *monodromy data.* A good deal of progress can therefore be made without need to solve the problem completely: see McCaskill and Fackerell [21], in particular their Appendix A, and the further references given therein.

Just as the high- and low-temperature limits can be obtained without consideration of the full solution, so can a certain amount of analytical progress be made on the line charge limit $a\to 0$. The delta-function argument set out in the paragraph following (142) serves to show that condensation of opposite charges must occur on to a fixed line charge Q'_{ext} of magnitude greater than $2\pi\,|q|/L$. The proof is elementary: suppose condensation does *not* occur. Then, sufficiently close to the fixed charge, $\phi \sim -(Q'_{\text{ext}}/2\pi\varepsilon_0)\ln r$, and the concentration factor $\exp(-q\phi/kT)$ for the opposite charges behaves as the $-|Q'_{\text{ext}}L/\pi q|$th power of radius. But this has a nonintegrable singularity at $r=0$, corresponding to condensation, when the power is -2 or more negative. The like charges have a density increasing as a positive power ($\geqslant 2$) of radius and can be asymptotically neglected as $r \to 0$; the desired result now follows by equating powers. We again expect the amount of condensed charge to be that which just reduces the power index to the convergent value -2, provided that there is sufficient plasma. Complete condensation should occur if there is not. This conclusion is independent of the distribution of plasma charge of the same polarity as Q'_{ext}, which then arranges itself as best it can with repulsion away from $r=0$.

What of the limit $b \to \infty$? Traditionally the n factors are ignored for infinite plasmas. This process might seem to do little harm in two (and higher) dimensions when the mean concentrations of the two species are equal, because the difference in the total amount of charge of each species within any radius is finite. Any finite charge may always be banished to $r=\infty$, where it has no effect—a result which conspicuously fails in one dimension. However, we suspect the problems of unbounded oscillations in the potential (cf. [21, formula 27]) can be traced to this factor.

The condensation phenomenon is again best discussed using the criterion of whether or not $n\exp(-q\phi/kT)$ is a delta function. Arguments pertaining to infinite plasma which ignore the n factors, no matter how ingenious, handicap themselves [34–37].

Bounds on the solution, invariably for unbounded plasmas with $b \to \infty$, have been established by MacGillivray [6, 38, 39] and by Lampert and Crandall [36]. Asymptotic approximations to the solution for a slightly more general plasma have been derived [7, 8, 27]. At small r the solution is asymptotic to the single species solution, whereas at large r, it is asymptotic to that of the linearised (Debye–Hückel) equation. Connection of the solution at small r to that at large r has been established [20, 21, 40]. Reference [21] uses techniques of isomonodromy theory to establish the connection even when matching of asymptotic expansions fails.

A related problem of interest concerns the charge seen by an observer at infinity. At great distances the potential behaves like the solution of the Debye–Hückel equation, screening fixed charges exponentially. However, the Debye–Hückel approximation becomes progressively worse closer in, and we can ask: What is the relaton between Q'_{ext} and the charge which would give rise to the same potential at large distances were the Debye–Hückel approximation exact? Clearly the nonlinear phenomenon of condensation is but one complicating factor in this analysis. Bounds are of course related to those found for solutions, and the matching problem is crucial. The above references are therefore relevant; see also [33, 41].

4.8. *The Single Species Problem in Two Dimensions*

The general solution of the Poisson–Boltzmann equation for this case was first found by Liouville [42] in another context. We present a more modern method of solution using Bäcklund transformations, following the text of Drazin [43]. For convenience the equation

$$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)\phi = -\frac{Nnq}{\varepsilon_0}\exp\left(\frac{-q\phi}{kT}\right) \tag{153}$$

is cast into dimensionless form via the transformations

$$(x', y') = (2NnL)^{1/2}(x, y), \qquad \Phi^- = -q\phi/kT; \tag{154}$$

as usual, n is calculated a posteriori. The notation Φ^- is used for later convenience. The equation is now put into characteristic form: on defining

$$u = \tfrac{1}{2}(x' + iy'), \qquad v = \tfrac{1}{2}(x' - iy'), \tag{155}$$

the result is

$$\nabla'^2\Phi^- \equiv \frac{\partial^2\Phi^-}{\partial u\,\partial v} = \exp\Phi^-. \tag{156}$$

Introduce the coupled first order equations [43]

$$\frac{\partial\Phi^-}{\partial u}+\frac{\partial\Psi}{\partial u} = \sqrt{2}\exp\frac{1}{2}(\Phi^- - \Psi), \tag{157}$$

$$\frac{\partial\Phi^-}{\partial v}-\frac{\partial\Psi}{\partial v} = \sqrt{2}\exp\frac{1}{2}(\Phi^- + \Psi); \tag{158}$$

these constitute a Bäcklund transformation between Φ^- and Ψ. By differentiating (157) with respect to v, (158) with respect to u, eliminating first derivatives using the other equation, and adding and subtracting results, we recover (156) together with

$$\frac{\partial^2\Psi}{\partial u\,\partial v} = 0. \tag{159}$$

Transformations (157), (158) imply (156) and (159); since differentiation is involved the converse is not automatically true. Our scheme is nevertheless to solve (159) and substitute the result into (157) and (158). If these can then be solved consistently together for Φ^-, a solution of (156) will have been generated. The general solution of (159) is, immediately,

$$\Psi = F(u) + G(v) \tag{160}$$

for arbitrary once differentiable functions F and G. Substitution into (157) gives

$$\exp(F)\frac{\partial}{\partial u}(\Phi^- + F - G) = \sqrt{2}\exp\frac{1}{2}(\Phi^- + F - G) \tag{161}$$

with solution

$$-\sqrt{2}\exp[-\tfrac{1}{2}(\Phi^- + F - G)] = U(u) + f(v), \tag{162}$$

where

$$U(u) = \int^u du' \exp[-F(u')]. \tag{163}$$

Similarly, substitution of (160) into (158), and integration, gives

$$-\sqrt{2}\exp[-\tfrac{1}{2}(\Phi^- + F - G)] = V(v) + g(u), \tag{164}$$

where f and g denote arbitrary functions. Compatibility of (164) and (162) forces us to take $f = V$, $g = U$. We have therefore generated a solution of (156) which, since it contains two arbitrary functions, is the general solution. On eliminating F and G in favour of U and V we find from either equation that

$$\Phi^-(u, v) = \ln\left[\frac{2U'(u)\, V'(v)}{[U(u) + V(v)]^2}\right], \tag{165}$$

where a prime denotes differentiation with respect to argument. The essence of the method lies in factorising the Laplacian as $(\partial_x + i\partial_y)(\partial_x - i\partial_y)$. Factorisation in higher dimensions necessarily involves nonscalar coefficients of $\partial/\partial x_j$ [44], as in the Dirac equation of quantum mechanics. Stoyanov [45] has found an ingenious spinorial reduction giving the general scalar solution in four dimensions in terms of an arbitrary analytic function of two complex variables.

Physically, we demand that U and V must be such that the solution is real whenever $v = u^*$, corresponding to real x and y. Clearly therefore

$$V(\xi) = U^*(\xi), \qquad \forall \xi. \tag{166}$$

There are of course still two arbitrary functions in the solution, but now these must be real.

It is generally easier to specify the Green's integral form of the Poisson–Boltzmann equation than the boundary conditions, because boundary conditions and the Green's function are likely to be far more readily available for a point charge than for a charge distribution not known in advance. Recall that $\nabla^2 G(\mathbf{r}, \mathbf{r}') = -\delta(\mathbf{r} - \mathbf{r}')$ (Eq. (14)), and write the Poisson–Boltzmann equation momentarily as $\nabla^2\phi(\mathbf{r}) = -\rho_{\text{ext}}(\mathbf{r})/\varepsilon_0 - v(\mathbf{r})\, F[\phi(\mathbf{r})]$. Then

$$\phi(\mathbf{r}) = \varepsilon_0^{-1} \int_{V_p} d\mathbf{r}'\, G(\mathbf{r}, \mathbf{r}')\, \rho_{\text{ext}}(\mathbf{r}') + \int_{V_p} d\mathbf{r}'\, G(\mathbf{r}, \mathbf{r}')\, F[\phi(\mathbf{r}')]. \tag{167}$$

Now suppose we already have the general solution of the differential version (e.g., (165)). This information can be combined with the integral formulation (167) to generate a simpler equation for the arbitrary functions of integration. Write the LHS of (167) as

$$\phi(\mathbf{r}) = \int_{V_p} d\mathbf{r}'\, \phi(\mathbf{r}')\, \delta(\mathbf{r}-\mathbf{r}'), \qquad \mathbf{r} \in V_p \tag{168}$$

$$= -\int_{V_p} d\mathbf{r}'\, \phi(\mathbf{r}')\, \nabla^2_{r'} G(\mathbf{r}, \mathbf{r}') \tag{169}$$

$$= -\int_{V_p} d\mathbf{r}'\, G(\mathbf{r}, \mathbf{r}')\, \nabla^2_{r'} \phi(\mathbf{r}') - \int_{\partial V_p} d\mathbf{S}' \cdot [\phi(\mathbf{r}')\, \nabla_{r'} G(\mathbf{r}, \mathbf{r}') - G(\mathbf{r}, \mathbf{r}')\, \nabla_{r'} \phi(\mathbf{r}')] \tag{170}$$

using the symmetry of $G(\mathbf{r}, \mathbf{r}')$, and Green's vector identity. On substituting back into (167), the volume integrals over the plasma charge cancel because ϕ satisfies the Poisson–Boltzmann equation, leaving only the *linear* condition

$$\int_{\partial V_p} d\mathbf{S}' \cdot [\phi(\mathbf{r}')\, \nabla_{r'} G(\mathbf{r}, \mathbf{r}') - G(\mathbf{r}, \mathbf{r}')\, \nabla_{r'} \phi(\mathbf{r}')]$$
$$= -\int_{\bar{V}_p} d\mathbf{r}'\, G(\mathbf{r}, \mathbf{r}')\, \rho_{\text{ext}}(\mathbf{r}'), \qquad \mathbf{r} \in V_p. \tag{171}$$

$\bar{V}_p$ is the complement of the plasma volume with respect to the arena of the problem; the RHS of (171) is an integral over fixed charge residing *outside* the plasma. For a conducting boundary it is necessary to put $\bar{V}_p = 0$. Equation (171) is linear in ϕ, and a surface integral: a great simplification on both counts. It is the sought-for boundary condition inducing a unique solution for the potential.

If the plasma boundary is conducting and contains a net nonzero charge, then the potential at infinity is Q_p/C where C is the capacitance of the boundary (fixed charges are presumed absent), since the potential on the boundary is chosen as zero in this formulation. This quantity can be subtracted off if desired.

It would be interesting to apply these ideas to a single species within the rectangle $-a < x < a$, $-b < y < b$, using (165) and (167), with both insulating and conducting boundaries. For the insulating case as $b \to \infty$ with N/b constant, the one dimensional results of Section 4.4 would be recovered. The Green's function in two dimensions is the sum of $-(1/2\pi) \ln |\mathbf{r} - \mathbf{r}'|$ and a harmonic function chosen to ensure that the potential be zero at infinity. For the conducting case, the Green's function is a double sum over a lattice of image charges. These problems are not addressed further here. We do, however, examine how the general two dimensional solution reduces to the cylindrically symmetrical solutions of Section 4.6 when dependence only on $uu^* \propto r^2$ is demanded. We then have the functional equation

$$\frac{2U'(u)\, V'(u^*)}{[U(u) + V(u^*)]^2} = f(uu^*); \tag{172}$$

it has not been assumed that $V = U^*$ since the constants of integration of the cylindrical problem may, from a mathematical point of view, perfectly well be complex. One of the remarkable facets of the theory of functional equations is that equations as seemingly arbitrary as (172) may perfectly well possess unique solutions. Finding them, or proving uniqueness indirectly, is no easy matter and the reader is referred to the standard authority on the topic [46]. We content ourselves with verifying that, for the real case with $V = U^*$, (172) is satisfied by

$$U(\xi) = V(\xi) = KC^{-1} \tanh[\tfrac{1}{2} C \ln(\xi/\xi_0)], \qquad K, C, \xi_0 \text{ real} \tag{173a}$$

$$f(\zeta) = \tfrac{1}{2} C^2 \zeta^{-1} \operatorname{cosech}^2[\tfrac{1}{2} C \ln(\zeta/\xi_0^2)]. \tag{173b}$$

Solution (173) corresponds immediately to solution (99) of the cylindrical problem. We know in advance that (173) is unique when $V = U^*$, apart from a replacement of hyperbolic functions by trigonometric ones.

A further functional equation could be derived for dependence only on x, or (by rotation) on $\mathbf{k} \cdot \mathbf{r}$, where $\mathbf{k} \cdot \mathbf{k} \neq 0$, and would lead to the one dimensional solution of Section 4.4. The variable $u = \frac{1}{2}(x' + iy')$ is precisely that linear combination which cannot be rotated to this form, having $\mathbf{k} \cdot \mathbf{k} = 0$. Similarly, functional equations can be set up to reduce Stoyanov's four dimensional solution [45] to three or fewer dimensions.

4.9. *The Two Species Problem in Two Dimensions*

Again we consider only the solution away from fixed charges, and with particle species of equal and opposite charge: $q_1 = -q_2 = q$. The Poisson–Boltzmann equation reduces, under the transformations

$$\mathbf{r}' = \left[\frac{2(N_1 N_2 n_1 n_2)^{1/2} q^2}{\varepsilon_0 kT}\right]^{1/2} \mathbf{r}, \qquad \Phi = \frac{q\phi}{kT} + \frac{1}{2} \ln\left(\frac{N_2 n_2}{N_1 n_1}\right) \tag{174}$$

and the same characteristic transformation as in the previous section, to

$$\nabla'^2 \Phi \equiv \frac{\partial^2 \Phi}{\partial u\, \partial v} = \sinh \Phi. \tag{175}$$

This equation also arises in connection with the two dimensional Ising model [28, 29]. Introduce the Bäcklund transformation pair [43]

$$\frac{\partial \Phi}{\partial u} + \frac{\partial \Psi}{\partial u} = 2\lambda \sinh \frac{1}{2} (\Phi - \Psi), \tag{176}$$

$$\frac{\partial \Phi}{\partial v} - \frac{\partial \Psi}{\partial v} = 2\lambda^{-1} \sinh \frac{1}{2} (\Phi + \Psi), \tag{177}$$

which is equivalent to (175) together with

$$\frac{\partial^2 \Psi}{\partial u\, \partial v} = \sinh \Psi. \tag{178}$$

This is identical to (175) and is (of course) no easier to solve, in sharp contrast to the single species problem. Bäcklund transformations exist only for the single species and two species equal and oppositely charged cases [47]. We expect the polynomial form of (175) to have the Painlevé property generalised for partial differential equations [48].

Despite (178) being identical to (175), progress can still be made: *any* solution of (178) for which (176) and (177) can be solved consistently for Φ will generate a solution of (175). Let us try the trivial solution $\Psi = 0$; it leads successfully to the nontrivial potential

$$\Phi(u, v) = 4 \tanh^{-1}[C \exp(\lambda u + \lambda^{-1} v)]. \tag{179}$$

This is not in fact a true two dimensional solution: it depends only on a linear combination of u and v, and hence of x and y. An axis rotation reduces it to a function of a single (possibly complex) cartesian variable, and indeed it is the one dimensional solution (58) in disguise. However, if (179) is now taken as the solution of (178) for Ψ, and substituted back into the transformation equations, a new solution for Φ is generated which *is* intrinsically two dimensional. This can itself be substituted back and so on to generate a family of solutions, although never the general solution. Indeed, with one of the spatial coordinates imaginary and representing time, (175) is nothing other than the sine-Gordon equation, and this family of solutions is a hierarchy of zero, one, two, etc., soliton solutions [43]. Equation (175) is called the sinh-Gordon or sinh-Poisson equation [11]. Solution (179) when written in terms of x and y, and a good many other solutions besides, may be derived by the following direct method: transform to a new variable $\tanh(\frac{1}{4}\Phi)$, and take a trial separable solution $X(x)/Y(y)$ of the resulting equation. (Note the asymmetry: the quotient and *not* the product of X and Y is involved.) X and Y may be expressed as elliptic functions. Details are given by Drazin [43], where a good deal of concise information can also be found on the sine-Gordon equation; problem 6.6, for example, demonstrates how solutions depending on $r^2 \propto uv$ alone obey the requisite ordinary differential equation.

Ting *et al.* [11] obtain the general solution of the sinh-Poisson equation using the inverse scattering transform and some impressive complex analysis. They consider only $kT < 0$ (in a different physical context), although generalisation to positive temperatures is only a matter of detail. As is usual with the method of inverse scattering, the solution is left in implicit form: at this level, reduction to a linear equation counts as victory. That the solution remains implicit can be foreseen: if the cylindrically symmetrical case requires Painlevé transcendents to solve it, the full two dimensional problem will be no easier. Generalisation to higher dimensions has not been successful [47], although cylindrical and spherical solitons are known [49].

4.10. *The Single Species Problem with Spherical Symmetry*

In this subsection we consider a single species, spherically symmetrical plasma confined to $a<r<b$ in three dimensions. Within the sphere $r=a$ is a fixed charge density distributed with spherical symmetry about $r=0$; without loss of generality in $r>a$, it can be taken to reside at $r=0$. For $a=0$ we recover (at last) the result of immersing a point charge in a three dimensional plasma.

We argue first that the results found here differ in important respects from the two and one dimensional cases, but are essentially unchanged in higher dimensions. Suppose a fixed point charge of magnitude Q_{ext} is surrounded ($a=0$) by a single species of like charge. We anticipate that the plasma density near the fixed charge will be small, so that $\phi \sim Q_{\text{ext}}/4\pi\varepsilon_0 r$. The density varies as $\exp(-q\phi/kT) \sim \exp(-K/r)$, $K>0$. More generally in $D \geqslant 3$ dimensions, the density varies as $\exp(-K/r^{D-2})$; this form is nonanalytic in r and highly singular at $r=0$. In two dimensions, by contrast, $\phi \sim \ln r$ and the density behaves as a power of r (expression (135)). This observation acts as a warning that the effect of dimensionality is crucial. We shall work with arbitrary dimensionality D for the sake of generality and put $D=3$ later.

The relevant Poisson–Boltzmann equation is

$$\frac{1}{r^{D-1}} \frac{d}{dr}\left(r^{D-1} \frac{d\phi}{dr}\right) = -\frac{Nnq}{\varepsilon_0} \exp\left(\frac{-q\phi}{kT}\right), \tag{180}$$

which is clearly invariant under a translation of ϕ and a stretch of r which leaves the combination $r^2 \exp(-q\phi/kT)$ invariant. According to similarity concepts (Lie group theory) this is chosen as a convenient function of a new dependent variable. Define

$$R=(2NnL)^{1/2} r, \qquad \xi = \ln R, \qquad \exp\chi = R^2 \exp(-q\phi/kT). \tag{181}$$

Then (180) becomes

$$\frac{d^2\chi}{d\xi^2} + (D-2)\left(\frac{d\chi}{d\xi} - 2\right) - \exp\chi = 0. \tag{182}$$

A particular solution is $\chi = \ln(4-2D)$; no other solution for ϕ of the form of an ascending power series in R plus a term in $\ln R$ exists. Equation (180) is equivalent to the pair of consecutive first order differential equations

$$\eta \frac{d\eta}{d\chi} + (D-2)(\eta-2) - \exp\chi = 0, \tag{183}$$

$$\frac{d\xi}{d\chi} = \eta^{-1}. \tag{184}$$

Once (183) has been solved for $\eta(\chi)$, the solution is substituted into (184) and integrated to give ξ in terms of χ. Reversion then yields the solution. Equation (183) is simplified to algebraic form on defining $\mu = \exp \chi$ as independent variable. Also write $\sigma = D - 2$, to give

$$\mu\eta \frac{d\eta}{d\mu} + \sigma(\eta - 2) - \mu = 0. \tag{185}$$

This is a special case of the second kind of Abel equation, and, taking η^{-1} as dependent variable, of the first kind [50]. It is not reducible to Ricatti form and consequently does not possess the Painlevé property [17]. It can be rewritten as

$$\frac{d}{d\mu}\left[\mu^{(1/2)\sigma}(\eta-2)\exp\left[\frac{1}{2}(\eta-2)\right]\right] = -\frac{1}{2}\mu^{(1/2)\sigma}\exp\left[\frac{1}{2}(\eta-2)\right]. \tag{186}$$

Other canonical forms are given by Murphy [50]. None of the special cases listed by Murphy corresponds to (185). The technique of isolating one of μ or η in terms of the other and the differential coefficient, and differentiating to give a new first order equation, leads again to Abel's form.

One possible route to a solution remains. For $D = 1$, $\sigma = -1$, the problem has been solved completely in Section 4.4. Adapting the result to the present choice of variables gives the solution of (185) as

$$2\theta - \sqrt{2\mu}\cos\theta = \text{constant}, \qquad \eta = 2 + \sqrt{2\mu}\sin\theta. \tag{187}$$

This is easily confirmed by direct substitution. The point is that this problem *also* defeats Murphy's tool box of special cases, because the transformation reducing (185) to the Poisson–Boltzmann equation is not seen as having any value; incorrectly, for $D = 1$, $\sigma = -1$. Equation (187) opens a new class of solutions of Abel's equations; suitable generalisation might yield the solution for $D = 3$, $\sigma = 1$, and beyond. Unfortunately the trial form

$$\theta + F_1(\mu)\cos\theta = \text{constant}; \qquad \sin\theta = F_2(\mu)\eta + F_3(\mu) \tag{188}$$

is insufficient, accounting only for the trivial generalisation of (185) in which both variables are rescaled. Clearly the nature of the nonlinear transformation from η to θ is crucial. The best hope lies now in a judicious mixture of intuition and computer algebra.

A power series solution of (180) can successfully be sought. Rescale r to R as in (181), denote differentiation with respect to R by a prime, and work again with $\Phi = q\phi/kT$, to give

$$\Phi'' + (D-1)R^{-1}\Phi' + \exp(-\Phi) = 0. \tag{189}$$

We seek a series solution

$$\Phi = \sum_{m=0}^{\infty} a_m R^{m+s}, \qquad a_0 \neq 0; \tag{190}$$

whence on substitution

$$\sum_{m=0}^{\infty} (m+s)(m+s+D-2)\, a_m R^{m+s-2} + \exp\left(-\sum_{m=0}^{\infty} a_m R^{m+s}\right) = 0. \quad (191)$$

This is only possible at small R if $s=2$, from which it follows immediately that

$$a_0 = -1/2D, \qquad a_1 = 0. \quad (192)$$

(For the two species case, incidentally, it is impossible to find an index allowing cancellation of the smallest power of R.) Next, write the exponential term as

$$\exp(-\Phi) \equiv G(R) = 1 + \sum_{m=1}^{\infty} g_m R^m, \quad (193)$$

from which we have

$$G' = -G\Phi', \quad (194)$$

wth a corresponding relation among the coefficients

$$(m+2)\, g_{m+2} = -\sum_{l=0}^{m} (m-l+2)\, g_l a_{m-l}; \qquad g_1 = 0. \quad (195)$$

On substituting (193) into (191), with $\sigma = 2$, it follows immediately that

$$(m+2)(m+D)\, a_m + g_m = 0, \qquad n \geqslant 2. \quad (196)$$

When this is used to eliminate the g's from (195) in favour of the a's, the result is

$$a_{m+2} = -[(m+2)(m+4)(m+D+2)]^{-1} \sum_{l=0}^{m} (l+2)(l+D)(m-l+2)\, a_l a_{m-l}. \quad (197)$$

This is a nonlinear recurrence relation giving successive coefficients, with starting values given by (192). It is readily shown that coefficients with m odd must vanish; the remainder can be simplified, giving finally

$$\Phi = -\sum_{m=0}^{\infty} \frac{e_m}{2m+2} \left(\frac{R}{2\sqrt{D}}\right)^{2m+2}, \quad (198)$$

where

$$e_{m+1} = \frac{2(m+D)}{(m+1)(2m+D+2)} \sum_{l=0}^{m} e_l e_{m-l}, \qquad e_0 = 1, \quad (199)$$

are the coefficients in an expansion of the electric field; l appears only as a suffix in

(199). Clearly the coefficients e_m are unique, and $e_m \sim 2^m$ for $D \gg 2m$. For $D = 3$ the related coefficients g_m in an expansion of $\exp(-\Phi)$ have been tabulated and numerical solutions given [18].

This series solution contains no arbitrary constants; it cannot be used in solving problems with arbitrary boundary conditions. It corresponds to $\Phi = \Phi' = 0$ at $R = 0$ (even if $R = 0$ should be physically inaccessible) and is therefore appropriate for enclosure of the single species plasma within $r = b$, with no inner boundary and no central fixed charge. As usual, n is determined a posteriori; it is to be eliminated in favour of b. More precisely, the dimensionless combination NLb^2n is a function of D and NLb^{2-D} alone. The singularity of potential noted by Lampert and Martinelli [18] is always beyond $r = b$ and is unphysical.

Assuredly it is no coincidence that for the only tractable cases, $D = 1$ and 2, the numerator $(m + D)$ in (199) cancels in the denominator. It is easy to confirm that the $D = 2$ analysis with these boundary conditions, formula (136), corresponds to (198) with $e_m = 1$, $\forall m$. Convergence is assured for $r < b(1 + 4\pi/NL)$, which includes all of the region of physical interest $r \leqslant b$. We do not study convergence for general dimensionality. For $D = 1$, (198) is the solution $\Phi = 2 \ln(\cos R/\sqrt{2})$, so that, by differentiating (198) once, the e_m are related to the coefficients in a power series expansion of the tangent function. These are themselves related to the Bernoulli numbers (Ref. [51, formula 4.3.67]); the recurrence relation (199) expresses a relation among these numbers wnich may be derived directly from their definition. Perhaps the general solution of (199) can be expressed simply in terms of Bernoulli and Euler polynomials of particular arguments.

In the absence of analytical solutions, the problem must be studied numerically. Qualitative features can still be predicted. In particular, the fate of a point charge immersed in oppositely charged plasma in three dimensions is known. If there is insufficient plasma charge to neutralise the fixed charge, the potential is $O(1/r)$ with the same sign as Q_{ext}, and the concentration factor $\exp(-q\phi/kT)/\langle \exp(-q\phi/kT)\rangle$ is a delta function centred at the origin; all the plasma charge condenses on to the fixed charge. If there is excess opposite plasma charge, the fixed charge is neutralised precisely: the assumption that $\phi = O(1/r)$ with the same sign as Q_{ext} would lead again to complete condensation, and consequent contradiction of the assumption concerning the sign of ϕ. Similarly the assumption $\phi = O(1/r)$ with *opposite* sign to Q_{ext} leads to inconsistency. Thus ϕ is not $O(1/r)$, $E = -d\phi/dr$ is not $O(1/r^2)$, and $Q_{\text{central}} = -4\pi\varepsilon_0 \lim_{r\to 0} r^2\, d\phi/dr$ (assuming the limit exists) is zero: neutralisation is complete. Thus the series solution can equally well include a fully neutralised fixed charge at the centre. This proof is substantially different from that in cylindrical geometry, where $\phi \propto \ln r$ near a bare charge. Building on this, one would expect complete neutralisation of fixed point charges to take place in three or more dimensions no matter how asymmetrical the rest of the problem, since the potential of a point charge is both singular and spherically symmetrical. Because the equation is nonlinear, proof of this assertion would be a formidable task; this degree of difficulty indicates the great capacity of nonlinearity for giving birth to new and unusual effects.

4.11. *The Two Species Problem with Spherical Symmetry*

The Poisson–Boltzmann equation with spherical symmetry, irrespective of the details of the plasma species, is called an Emden equation [17]. As usual, we consider only $q_1 = -q_2 = q$, when the Poisson–Boltzmann equation reduces to

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\phi}{dr}\right)=\frac{2q}{\varepsilon_0}(N_1N_2n_1n_2)^{1/2}\sinh\left[\frac{q\phi}{kT}+\frac{1}{2}\ln\left(\frac{N_2n_2}{N_1n_1}\right)\right]. \tag{200}$$

As in the cylindrical case, when we come to take the outer radius $b \to \infty$ we shall insist that the net plasma charge, proportional to $(N_1 - N_2)$, remains finite. Under transformations (174), equation (200) reduces to

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\Phi}{dr}\right)=\sinh\Phi. \tag{201}$$

Even after transformation to polynomial form (taking $\exp(\pm\Phi)$ as new variable) this cannot be reduced to an equation of Painlevé type: Ince [30] shows how to confirm this. It therefore has movable critical points, and conjecture has it that the monodromy approach is inapplicable. We have already broadcast a warning (Section 4.10) that highly transcendental behaviour and movable critical points should come as no surprise in three dimensions.

Numerical solutions for two species with spherical symmetry have been given in [19, 23, 33].

For matching of small r to large r solutions in unbounded plasmas, see [52]. The related problem of the charge seen at infinity in the Debye–Hückel approximation is considered in [33, 41].

We consider only the fate of a fixed point charge in such a plasma. Following the argument of the previous subsection, it is easily seen that the charge will attract an equal and opposite charge arbitrarily close to itself if sufficient exists, and if not, all the opposite charge available. If the potential is postulated to be that of a bare charge near the origin, the plasma species of opposite polarity condenses at $r=0$ and modifies the value of the bare charge; consistency can be maintained only by neutralisation. This proof is substantially simpler than that of Lampert and Crandall [35], who established bounds on the potential of an extended fixed charge distribution, using geometrical arguments to relate the three dimensional solution to the exact solution for $q_2 = -q_1$ in one dimension, and then shrank the fixed charge down to $r=0$. Analogy with one dimension, in which the effect of charge does not diminish with distance, is questionable. Moreover it is assumed that the n factor can be ignored because the plasma is infinite in extent; from our standpoint this complicates rather than simplifies matters: the two limits $a \to 0$, $b \to \infty$ compete, with consequences difficult to analyse. The present proof has no need to take any limit a posteriori and is immediately generalisable to multi-species plasmas with different charges. Nor does it assume global spherical symmetry.

If there are two fixed point charges of like polarity, and insufficient plasma charge to neutralise both, the problem of the extent to which each is neutralised is mathematically undetermined, for if the charges were taken as extended and then shrunk to zero the result depends on details of the shrinking process.

That condensation is a singular effect is easily seen in this picture. Write the Poisson–Boltzmann equation is

$$\varepsilon_0 \nabla^2 \phi = -Q_{\mathrm{ext}}\, \delta(\mathbf{r}-\mathbf{r}') - \sum_s N_s q_s \frac{\exp(-q_s\phi/kT)}{\langle \exp(-q_s\phi/kT)\rangle}. \tag{202}$$

The fixed charge term can be viewed as "driving" the potential. Usually the differential term is taken as responding to it, and other terms treated as perturbations; but here, nonlinearity causes the plasma charge terms to be more singular, and it is appropriate instead to view the $\nabla^2\phi$ term as a perturbation in the neighborhood of the fixed charge.

4.12. *Condensation in Multi-species Plasmas*

Generalise briefly to the case in which there are many species of opposite polarity to the fixed charge, with total charge more than sufficient to neutralise it. What are their proportions in the condensate? The answer is that the most highly charged species will be used up first, then the next most highly charged, and so on, until neutralisation is complete. Until now this has been assumed on heuristic grounds [27]. The rigorous argument involves the variational principle (43) from which the Poisson–Boltzmann equation can be derived. Write this as $\delta I[\phi; Q_{\mathrm{ext}}; N_1, ..., N_l] = 0$, where N_i denotes the ith species of opposite polarity to Q_{ext}; there are l of these. Next, consider the Poisson–Boltzmann equation with the same boundary conditions but with the fixed charge absent; write the solution as $\phi(\mathbf{r}; N_1, ..., N_l)$. Let γ_i denote the amount of the ith species in the condensate. Now minimise the variand I over all proportions of the l species making up the condensate:

$$\frac{d}{d\gamma_i} I[\phi(\mathbf{r}; N_1-\gamma_1, ..., N_l-\gamma_l); 0; N_1-\gamma_1, ..., N_l-\gamma_l] = 0, \qquad \sum_{i=1}^{l} \gamma_i q_i = -Q_{\mathrm{ext}}. \tag{203}$$

Now

$$\frac{dI}{d\gamma_i} = \frac{\delta I}{\delta\phi}\frac{\partial\phi}{\partial\gamma_i} + \frac{\partial I}{\partial\gamma_i} \tag{204}$$

$$= -kT \ln\left[V^{-1}\int dV\, v(\mathbf{r}) \exp(-q_i\phi/kT)\right], \tag{205}$$

from (43), since the $\delta I/\delta\phi$ term vanishes by construction. According to the method of Lagrange multipliers we require

$$-kT \ln\left[V^{-1}\int dV\, v(\mathbf{r}) \exp(-q_i\phi/kT)\right] - \omega q_i = 0, \qquad i = 1, ..., l, \tag{206}$$

where ω is the Lagrange multiplier associated with the constraint that the condensed charge precisely neutralises the fixed charge. Dependence of (206) on the set of γ's is implicit, through ϕ. Rewrite (206) as

$$V^{-1} \int dV\, v(\mathbf{r}) \exp(-q_i \phi/kT) = \exp(-q_i \omega/kT), \qquad i = 1, ..., l. \tag{207}$$

This can be satisfied only if $\phi(\mathbf{r})$ is everywhere constant, and ω takes the value of that constant. The proof is given in Appendix B. Unless the net plasma charge fortuitously cancels the fixed charge exactly, ϕ is not constant, no solution of (207) exists, and consequently there is no minimum of I in γ-space on the plane $\sum_i \gamma_i q_i = -Q_{\text{ext}}$. We are restricted to the hypercube $0 \leqslant \gamma_l \leqslant N_j$; the smallest value of I on its boundary must be taken. This must correspond to $\gamma_j = N_j$ for some species j. The argument that $\exp(-q_i \phi_{\text{ext}}/kT)/\langle \exp(-q_i \phi_{\text{ext}}/kT)\rangle$ is "more singular" than $\exp(-q_j \phi_{\text{ext}}/kT)/\langle \exp(-q_j \phi_{\text{ext}}/kT)\rangle$ for $|q_i| > |q_j|$ is now employed to show that these will be the most highly charged species of opposite polarity to the fixed charge.

So much for the fate of a fixed point charge. What of a fixed point dipole, or quadrupole, immersed in the plasma? The answer can be foreseen by a limiting process of regarding the dipole as made up of two point charges $\pm D/\sigma$, with separation σ, and letting $\sigma \to 0$. The magnitude of the charges increases without bound, and asymptotically all of the plasma is attracted to one or other of them. (Quadrupoles are obtained by a like process with dipoles, and so on.) This result is in line with the greater singularity of the radial part of the dipole field (r^{-2}) than the field of a charge (r^{-1}). It follows incontrovertibly from the Poisson–Boltzmann equation, and its absurdity stems solely from the violation of conditions necessary for the equation's validity. The plasma is *not* ultimately a continuous fluid, and effects of discreteness cut in to make hazy the very concept of condensed charge; certainly the amount of plasma charge in any finite volume containing the multipole is finite. Consistent refinement involves a good deal of nontrivial kinetic theory.

5. Conclusions

The Poisson–Boltzmann equation is of special importance for three reasons:

1. Its correct derivation using the Maximum Entropy Principle requires a nonlinear constraint. Conventional linear derivations, while fortuitously giving the same result, are erroneous.

2. It is a nonlinear equation whose solutions consequently exhibit great richness of structure. Inverse scattering and other modern techniques are in the forefront of its solution.

3. It predicts condensation of opposite charge on to a point (line) charge, partially neutralising the charge in two dimensions and completely neutralising it in three dimensions. This startling result demonstrates vividly the restrictions of the linearised theory.

APPENDIX A: THE BOLTZMANN DISTRIBUTION FOR MANY CHARGED SPECIES

Suppose we have N_s particles of the sth species. The entropy to be maximised is

$$-\int \left(\prod d\Gamma_s\right) p(\Gamma_1, \Gamma_2, \ldots) \ln p(\Gamma_1, \Gamma_2, \ldots), \tag{A1}$$

where

$$\Gamma_s = (\mathbf{r}_1, \mathbf{v}_1)^{(s)} \otimes (\mathbf{r}_2, \mathbf{v}_2)^{(s)} \otimes \cdots \otimes (\mathbf{r}_{N_s}, \mathbf{v}_{N_s})^{(s)}. \tag{A2}$$

This is the full Liouville function of all the coordinates of all the particles. It is assumed already to have been made symmetrical in the coordinates of all particles of any one species. The assumption that the particles are uncorrelated is now made,

$$\begin{aligned} p(\Gamma_1, \ldots, \Gamma_s, \ldots) &= p^{(1)}(\mathbf{r}_1^{(1)}, \mathbf{v}_1^{(1)}) \cdots p^{(1)}(\mathbf{r}_{N_1}^{(1)}, \mathbf{v}_{N_1}^{(1)}) \\ &\quad \times \cdots p^{(s)}(\mathbf{r}_1^{(s)}, \mathbf{v}_1^{(s)}) \cdots p^{(s)}(\mathbf{r}_{N_s}^{(s)}, \mathbf{v}_{N_s}^{(s)}) \cdots, \end{aligned} \tag{A3}$$

following which (A1) reduces to the sum of the entropies for each particle:

$$-N_1 \int d\mathbf{r} \int d\mathbf{v}\, p^{(1)}(\mathbf{r}, \mathbf{v}) \ln p^{(1)}(\mathbf{r}, \mathbf{v}) \cdots - N_s \int d\mathbf{r} \int d\mathbf{v}\, p^{(s)}(\mathbf{r}, \mathbf{v}) \ln p^{(s)}(\mathbf{r}, \mathbf{v}) - \cdots. \tag{A4}$$

The analysis in the main text, with only a single species, is of course a special case. The assumption of uncorrelated particles was not mentioned there explicitly.

The entropy (A4) is to be maximised subject to normalisation of each $p^{(s)}$, and the energy constraint

$$\begin{aligned} U_{\mathrm{TOT}} &= \sum_s N_s \int d\mathbf{r} \int d\mathbf{v}\, \frac{1}{2} m_s v^2 p^{(s)}(\mathbf{r}, \mathbf{v}) + \sum_s N_s q_s \int d\mathbf{r} \int d\mathbf{v}\, \phi_{\mathrm{ext}}(\mathbf{r})\, p^{(s)}(\mathbf{r}, \mathbf{v}) \\ &\quad + \frac{1}{2} \varepsilon_0^{-1} \int d\mathbf{r} \int d\mathbf{r}'\, G(\mathbf{r}, \mathbf{r}')\, \rho_p(\mathbf{r})\, \rho_p(\mathbf{r}'), \end{aligned} \tag{A5}$$

where

$$\rho_p(\mathbf{r}) = \sum_s N_s q_s \int d\mathbf{v}\, p^{(s)}(\mathbf{r}, \mathbf{v}). \tag{A6}$$

Details of the normalisation are routine; the final term of (A5) again contributes a term ϕ_p to be added to ϕ_{ext}, and we emerge with the condition

$$\sum_s N_s \left[-\ln\left(\frac{p^{(s)}}{Z^{(s)}}\right) + \lambda \left(\frac{1}{2} m_s v^2 + q_s \phi\right)\right] = 0, \tag{A7}$$

where $Z^{(s)}$ is the sth normalisation Lagrange multiplier, and λ the multiplier for the energy constraint. Since $p^{(s)}$ must not depend on any parameters of the other particle species, each term in this sum must separately be constant, the constants summing to zero. In fact the constants can be absorbed into $Z^{(s)}$, and we have without further ado

$$p^{(s)}(\mathbf{r}, v) = Z^{(s)-1} \exp[-(\tfrac{1}{2}m_s v^2 + q_s\phi)/kT], \tag{A8}$$

where λ has been put equal to $1/kT$. From (6)

$$\rho_p(\mathbf{r}) = \sum_s N_s q_s n_s \exp(-q_s\phi/kT), \tag{A9}$$

where

$$n_s^{-1} = \int d\mathbf{r} \exp(-q_s\phi/kT). \tag{A10}$$

We do not consider generalisation to separate conserved energies, and distinct temperatures for each species, since the electrostatic component of the energy is irrevocably a multi-species phenomenon allowing interchange of kinetic energy between the species, even if interspecies collision cross-sections are zero.

It is often stated that the neglect of particle correlations corresponds to smearing out the charges into a "jellium" (see, for example, [5, Sect. 12.4.3]). Appearance of the unit of charge q_s for each species in (A9) demonstrates the falsehood of this assertion. What our analysis in fact corresponds to is smearing in such a way that the smeared parts of each particle are correlated with each other, but not with elements of other smeared particles. Onsager [53] has pointed out the inconsistency of this scheme; nevertheless our results should be accurate when plasma potential energy is small compared to kinetic energy. Fixman [54] indicates how to correct for correlations. The correction is necessarily heuristic, since a full maximum entropy analysis fails as we now indicate. Consider the total energy $\bar{U}$ in three dimensions:

$$\bar{U}(\mathbf{v}_i, \mathbf{r}_i) = \sum_i \left[\frac{1}{2} m_i v_i^2 + q_i \phi_{\mathrm{ext}}(\mathbf{r}_i)\right] + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{q_i q_j}{4\pi\varepsilon_0 |\mathbf{r}_i - \mathbf{r}_j|}, \tag{A11}$$

where summations and indices momentarily run over all particles, irrespective of species. As usual we multiply (A11) by the probability density in the full phase space, integrate over it, and take the result as a conserved quantity. This is then employed as a constraint in maximising the entropy over the phase space, giving for the probability in the full phase space the expression

$$Z^{-1} \exp[-\lambda \bar{U}(\mathbf{v}_i, \mathbf{r}_i)]. \tag{A12}$$

The partition function Z is determined by normalisation. Unfortunately the singularity at $\mathbf{r}_i = \mathbf{r}_j$ for particles of opposite polarity renders it divergent [22] and the probability (A12) a delta function at the singularity. Resolution involves quantum theory: instead of approaching each other arbitrarily closely, oppositely charged particles form bound states (atoms), and if the energy is sufficiently great most of these ionise. Unless we are dealing with true point particles, van der Waals' and other polarisation forces should also be taken into account.

APPENDIX B: Proportions of Species in the Point Charge Condensate

Here we prove the impossibility of satisfying (207),

$$V^{-1} \int dV\, v(\mathbf{r}) \exp(-q_i\phi/kT) = \exp(-q_i\omega/kT), \qquad i=1, ..., l \qquad (207), (B1)$$

for nonconstant $\phi(\mathbf{r})$. This result is needed in determining which species are represented in the condensate onto a fixed point charge. All of the q_i are the same sign; order them such that $|q_1| \leqslant |q_2| \leqslant \cdots |q_m|$, and put $q_i = l_i q_1$. Clearly $l_1 = 1$, and the l_i's are rationals no smaller than one. Now take $f(\mathbf{r}) = v(\mathbf{r}) \exp(-q_1\phi/kT)$, and eliminate ω in (B1), to give

$$\left[V^{-1} \int dV\, f(\mathbf{r})^{l_i}\right]^{1/l_i} = \text{constant}, \qquad \forall i \qquad (B2)$$

$$= V^{-1} \int dV\, f(\mathbf{r}), \qquad (B3)$$

on choosing $i=1$ on the RHS. But the LHS is readily shown, by differentiation, to be a nondecreasing function of l_i and is stationary only for $f(\mathbf{r}) = \text{constant}$ (Ref. [51, formula 3.2.4]). The result follows immediately.

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Note added in proof. The argument concerning nonlinear constraints in maximum entropy analysis (equations (5)–(12)) is published as [55]. The proof of charge condensation in Section 4.12 is reproduced in [56]. References to the Poisson–Boltzmann equation applied to gravitating particles, as mentioned in Section 3, are given in [57]. Bounds on solutions of the equation can be calculated using methods given in [58].

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