Relativistic Corrections in the Statistical Mechanics of Interacting Particles*

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In previous work on statistical mechanics, the consequences of the theory of relativity have only been investigated for the ideal gas. This study is concerned with relativistic effects for systems of interacting particles. The noninstantaneous nature of the forces leads to dynamical equations which cannot be treated by known mathematical methods; however, the interaction terms can be expanded to obtain a description of the system in terms of the positions and their derivatives of all orders at a single time. If one stops at the $(v/c)^2$ approximation, a specification in terms of positions and velocities is obtained; in electrodynamics this corresponds to the Darwin Hamiltonian. A system described by this Hamiltonian is investigated with the methods of equilibrium statistical mechanics. The cluster expansion with subsequent summation of diagrams as employed by Mayer for the Coulomb case is used; the modifications necessary due to the presence of momentum-dependent terms in the interaction are developed. In evaluating the lowest order nonvanishing (ring) approximation, mathematical difficulties peculiar to the relativistic interactions force restriction to calculation of the relativistic short-range correlation effects in the charged system. A modified Debye-Hückel law is obtained, including a relativistic correction term which is small compared to the static one. At the high temperatures required for appearance of relativistic effects, the static term is itself negligible except at very high densities. Thus the relativistic contribution can in effect be neglected in this approximation. The difficulty of extending our method to mesonic or gravitational interactions is discussed.

I. INTRODUCTION

THE modifications imposed on Newtonian mechanics by the requirements of the special theory of relativity are twofold: First, the mass of a body must depend on its velocity, and second, the forces between particles must be noninstantaneous. The second change, which is necessary because the concept of simultaneous positions is not a relativistic one, is far more drastic than the first. The equations of motion of a system of interacting particles cannot be treated rigorously by any known mathematical methods; even the two-body problem can not be solved exactly. Therefore, investigations in relativistic dynamics have mostly been restricted to a study of the motion of a single particle under the action of a given external force.[1] No relativistic statistical mechanics has been developed except for that of the ideal gas[2] in which the problem of interaction does not arise. This paper is devoted to a study of some of the modifications introduced into the usual classical statistical mechanics by the theory of relativity.

There are two general ways in which noninstantaneous interactions may be described, either by a theory containing only particle degrees of freedom, or by the introduction of fields, with their own degrees of freedom, in addition to the particles.

We will adhere to a formalism which contains only particle degrees of freedom, as is appropriate for a statistical mechanics of particles (as is well known, no satisfactory classical statistical mechanics of fields is possible because of the infinite number of degrees of freedom). The interactions are taken as time-symmetric. The treatment may be characterized as action at a distance, although for the case of electrodynamics an interpretation in terms of fields which is equivalent[3] may be given as far as the equations of motion are concerned. (However, there is no equivalence statistically, because no independent degrees of freedom associated with fields are considered.[4]) Time symmetry is required to allow formulation of a variational principle, as shown by Fokker.[5] It is also necessary because we shall be concerned with equilibrium, and hence energy-conserving, situations. If retarded (or advanced) interactions were used, the system of particles would lose (or gain) energy as a result of radiation.

This, however, does not in itself exclude consideration of radiation. It was first noted by Einstein[6] and further discussed by Wheeler and Feynman[7] that perhaps radiation arises from an otherwise time-symmetric theory as a statistical effect. This question is not investigated in the present work, however, since the relativistic approximation taken is of lower order than radiation effects.

Our main interest is in the study of the changes introduced in statistical mechanics by the presence of noninstantaneous interactions. Only equilibrium situations will be considered, although the greatest contributions from such interactions could reasonably be

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[1] For an extensive review see H. Arzeliès, *La Dynamique Relativiste et ses Applications* (Gauthier-Villars, Paris, 1957–8), 2 vols.
[2] F. Jüttner, Ann. Physik **34**, 856 (1911).
[3] In mesodynamics the equivalence is not complete. For a discussion of this and other points raised in the Introduction see P. Havas, in Argonne National Laboratory Summer Lectures on Theoretical Physics, 1958, ANL-5982 (unpublished), p. 124, and references given there.
[4] For this question compare G. Plass, Ph.D. thesis, Princeton University, 1947 (unpublished).
[5] A. D. Fokker, Z. Physik **58**, 386 (1929).
[6] A. Einstein, Physik Z. **10**, 323 (1909).
[7] J. A. Wheeler and R. P. Feynman, Revs. Modern Phys. **21**, 425 (1949).

expected for nonequilibrium systems. Unfortunately the difficulties encountered in introducing relativistic corrections to equilibrium theory are multiplied when one goes over to nonequilibrium theory.

We are then interested in deriving thermodynamic quantities for a stationary system which can be described by a conservative Hamiltonian for which an equilibrium probability density may be written. Since we wish to confine ourselves to a frame relative to which the system is macroscopically at rest, there is no need to introduce a covariant formulation which would include mass rotation and translation effects.

As noted before, no methods are available to treat the noninstantaneous interactions explicitly; we need a method which will give us a Hamiltonian involving particle variables taken at the same time, which can be done formally by a series expansion of the interaction terms. However, here another problem arises. The proper specification of the initial-value problem is not known for noninstantaneous forces. It may well be that for time-symmetric interactions a knowledge of the positions and velocities is sufficient, just as in Newtonian mechanics,[8] but this has not been established; on the other hand, a series expansion will introduce derivatives of all orders of the position vector, and if the approximation is carried up to nth order derivatives in the equations of motion, all derivatives up to the $(n-1)$st must be specified initially.[9] In the case of electromagnetic interactions, an expansion of the potentials up to order $(v/c)^2$ yields the Hamiltonian first obtained by Darwin,[10] for which the specification is of the usual type.

Here we shall confine ourselves to the study of a classical system described by the Darwin Hamiltonian. (There are difficulties in extending the method to systems interacting through gravitational and meson fields, which will be noted in Sec. VI.) Quantum effects can be neglected at high temperatures, except in the extreme of high densities; then degeneracy becomes more important. We will be concerned with densities for which the thermal DeBroglie wavelength is much smaller than the mean interparticle distance, and degeneracy is then unimportant.

The approximations used in statistical mechanics in evaluating the classical partition function for gases are primarily low-density ones. The technique usually used in such problems (which can be suitably modified for quantum problems[11]) is the cluster expansion theory of Mayer.[12] We shall use this method, taking into account the difficulties presented by the long range of the Coulomb interaction,[13] and introducing the modifications necessitated by the fact that the relativistic interaction is momentum dependent.[14]

Because of mathematical difficulties in applying the cluster expansion and summation techniques to the relativistic correction, it will be necessary to restrict our attention to the relativistic short-range correlations in a charged system; in effect this means that we consider a screened potential which is obtained from the relativistic interaction. No such difficulties occur for the static case, and thus the total static interaction will be treated.

Since the approximation taken requires neglect of long-range effects, they should be small compared to the short-range ones. For the nonrelativistic case Ichikawa[15] has shown in a collective treatment that in the high density limit their ratio is of the order of 0.22. While it is difficult to compare the collective and the cluster treatments because of the different approximations made, it might be hoped that a similar ratio of long-range to short-range effects exists for the relativistic interaction term.

In applying techniques developed in statistical mechanics for gases to a plasma, it should be noted that while the densities at which the interaction effects at relativistic temperatures are no longer negligible are high, in fact higher than liquid densities at ordinary temperatures, the methods developed for gases may still be applied since the density-limiting approximations made for the gas case hold for the completely ionized state.

A different approach to relativistic statistical mechanics is possible through the Boltzmann equation.[16] As this method is based on a consideration of collisions, it is not suitable for revealing the qualitatively new features of the problem introduced by the noninstantaneous nature of the forces, although it may be well suited for other purposes.

II. PROBABILITY DENSITY

The Darwin Hamiltonian for a system of n-charged particles, which is correct to order $(v/c)^2$ in the interaction term, is given by[10,17]

$$H_n=\sum_i m_ic^2[1+(p_i/m_ic)^2]^{1/2}+\sum_{i<j}\frac{e_ie_j}{r_{ij}} -\sum_{i<j}\frac{e_ie_j}{r_{ij}}\frac{1}{m_im_jc^2}\left(\mathbf{p}_i\cdot\mathbf{p}_j+\frac{\mathbf{p}_i\cdot\mathbf{r}_{ij}\,\mathbf{p}_j\cdot\mathbf{r}_{ij}}{r_{ij}^2}\right). \quad (2.1)$$

[8] P. Havas and J. Plebański, Bull. Am. Phys. Soc. **5**, 433 (1960); a detailed account is in preparation.

[9] One may, however, *select* some solutions specified in some way by positions and velocities and write a Hamiltonian of usual character; compare E. H. Kerner, J. Math. Phys. **3**, 35 (1962).

[10] C. G. Darwin, Phil. Mag. **39**, 537 (1920).

[11] E. W. Montroll and J. C. Ward, Phys. Fluids **1**, 55 (1958).

[12] J. Mayer and M. G. Mayer, *Statistical Mechanics* (J. Wiley & Sons, Inc., New York, 1940), p. 277.

[13] J. Mayer, J. Chem. Phys. **18**, 1426 (1950).

[14] For a treatment of electrolytes which differs from Mayer's, see T. H. Berlin and E. W. Montroll, J. Chem. Phys. **20**, 75 (1952).

[15] Y. H. Ichikawa, Progr. Theoret. Phys. (Kyoto) **20**, 715 (1958).

[16] Compare, P. Bergmann, "The Special Theory of Relativity," in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1962), Vol. 4, Sec. 29.

[17] L. D. Landau and E. M. Lifshitz, *Classical Theory of Fields* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1950), p. 180.

We have chosen to retain the first term in its unexpanded form, rather than use the term

$$H_0=\sum_i [p_i^2/2m_i-p_i^4/8c^2m_i^3]$$

given by the expansion, since otherwise we would have $H_0\to-\infty$ when $p_i\to\infty$, and thus we would have been led to an unnormalizable probability density; furthermore, by retaining this form we are able to make use of some of the results obtained in the relativistic free-particle case.[2]

With respect to the normalization of the probability density, we wish to use the grand canonical ensemble, for which we have, for a two-component system of unlike charges,[18]

$$W_{n_1n_2}=\exp[-q+n_1\nu_1+n_2\nu_2-\beta H_{n_1+n_2}]/n_1!n_2!, \quad (2.2)$$

which satisfies

$$\sum_{n_1,n_2}\int W_{n_1n_2}d\Omega=1. \quad (2.3)$$

It is apparent from (2.1) that the Hamiltonian has no lower bound and, consequently, (2.2) is not normalizable as it stands.[19] This difficulty is due to the presence of attractive interaction terms. Even in the static case such attractive terms force the inclusion of additional repulsive terms in the Hamiltonian, such as a hard sphere potential.

In the present case it is necessary to add a repulsive term which is both momentum and coordinate dependent since (2.1) is unbounded from below for attractive interactions when either $r\to 0$ or $p\to\infty$ (note that even if one assumed a fluid background model, it would still be necessary to introduce a repulsive term due to the presence of attraction in the relativistic interaction term). No explicit form for this function will be used, although such knowledge could possibly prove helpful in resolving a problem which arises when the relativistic interaction is considered, as will be discussed later.

Thus instead of (2.1) we will write

$$H=H_n+H_n^*+H_V, \quad (2.4)$$

where H_n is the Darwin Hamiltonian, H_n^* is the repulsive term, and H_V is a function which limits the system to finite configuration volume. This limitation is frequently omitted explicitly in the initial formulation of the problem, since ultimately one is concerned with the limiting process in which n, $V\to\infty$ such that the density is a constant. Although we will not consider this term in our calculations either, we include it initially to allow a proper definition of the probability density.

[18] D. ter Haar, *Elements of Statistical Mechanics* (Rinehart and Company, Inc., New York, 1954), p. 135.

[19] For a discussion of this problem see R. Kurth, *Axiomatics of Classical Statistical Mechanics* (Pergamon Press, New York, 1960), p. 110.

III. ACTIVITY SERIES

The most striking difference between the nonrelativistic and relativistic approximations is that the relativistic interaction term has momentum dependence as well as coordinate dependence. This momentum dependence requires a departure from the usual method of dealing with the problem of interactions. Whereas in the static approximation one can integrate out the momentum dependence directly and deal with the so-called configuration integral, in the present case we must deal with the phase integral $Q_{n_1+n_2}$ which occurs in the expression obtained from (2.3),

$$e^q=\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\frac{e^{n_1\nu_1}}{n_1!}\frac{e^{n_2\nu_2}}{n_2!}\int\exp(-\beta H_{n_1+n_2})d\Omega_{n_1+n_2}, \quad (3.1)$$

which can be written

$$Q_{n_1+n_2}=\int\exp(-\beta H^0{}_{n_1+n_2})\times\exp[-\beta(H^*{}_{n_1+n_2}+H'{}_{n_1+n_2})]d\Omega_{n_1+n_2}.$$

Above we have split the Hamiltonian (2.4) into

$$H=H_n^0+H_n'+H_n^*,$$

where H_n^0 is the relativistic kinetic energy and H_n' is the interaction energy. Assuming that H_n' and H_n^* are small compared to H_n^0, we proceed to use the cluster expansion[12]

$$Q_{n_1+n_2}=\int\exp(-\beta H^0{}_{n_1+n_2})\prod_{i<j}(f_{ij}+1)d\Omega_{n_1+n_2}, \quad (3.2)$$

where

$$f_{ij}=\exp[-\beta(H_{ij}'+H_{ij}^*)]-1, \quad (3.3)$$

which may also be written

$$f_{ij}=g_{ij}+(g_{ij}+1)\sum_{\alpha\geq 1}\frac{(-\beta H_{ij}')^\alpha}{\alpha!},\qquad g_{ij}=\exp(-\beta H_{ij}^*)-1. \quad (3.4)$$

From (3.1) one can obtain the activity series for a two-component system[20]

$$q=V\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}b_{n_1n_2}z_1^{n_1}z_2^{n_2}. \quad (3.5)$$

The derivation of this series requires no particular assumption on the form of the interaction, except that a cluster expansion of the type given in (3.2) be possible.[21] In order to see how the coefficients $b_{n_1n_2}$ are defined for the present case, we must first investigate the activity z, which is defined[22] so that in the limit $n/V\to 0$, in

[20] J. Mayer, J. Phys. Chem. **43**, 71 (1939).

[21] G. E. Uhlenbeck, Physica **26**, S17 (1960).

[22] T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), p. 130.

which the interaction can be neglected, it approaches the density ρ.

If we define

$$z_\alpha = e^{\nu_\alpha}\Lambda_\alpha, \quad \Lambda_\alpha = \int \exp(-\beta H_{1\alpha}^0) d^3p_\alpha, \quad \alpha = 1, 2, \tag{3.6}$$

then in this limit it follows from (3.1) that

$$e^q = \sum\sum \frac{(e^{n_1\nu_1}\Lambda_1 V)^{n_1}}{n_1!} \frac{(e^{n_2\nu_2}\Lambda_2 V)^{n_2}}{n_2!},$$

and thus the grand potential equals

$$q = (z_1 + z_2)V.$$

From this we get

$$\rho_\alpha = \bar{n}_\alpha / V = (z_\alpha / V)(\partial q / \partial z_\alpha) = z_\alpha, \quad \alpha = 1, 2,$$

as required.

In passing we note that in the limit considered the equation of state obtained from q is just the perfect gas law, in agreement with Jüttner.[2]

From the form of q in the low-density limit we see that the appropriate definition of the cluster coefficient is

$$b_{n_1n_2} = \frac{1}{n_1!n_2!V\Lambda_1^{n_1}\Lambda_2^{n_2}} \int \exp(-\beta H^0{}_{n_1+n_2}) \times \sum \prod f_{ij} d\Omega_{n_1+n_2}, \tag{3.7}$$

where the sum is over all products consistent with given n_1, n_2.

It is to be noted that up to this point no particular form of the momentum dependence in the interaction terms has been invoked (apart from the behavior assumed which required the assumption of additional repulsive terms).

IV. IRREDUCIBLE CLUSTERS

In the usual Mayer treatment[12] for the static approximation it is possible to express the reducible cluster integrals in terms of irreducible ones. For the case where the interaction is momentum dependent it is not possible to do this in an analogous manner, since we can not break up the reducible forms into suitably defined, momentum-dependent irreducible forms.

We can, however, proceed in the following manner. First, we assume that the g_{ij} in (3.4) may be ignored (thus limiting ourselves to systems where roughly the mean interparticle distance is much greater than the repulsive core of the particles). In addition we take the lowest order approximation of (3.4)

$$f_{ij} \cong -\beta H_{ij}'. \tag{4.1}$$

In the static approximation this step is taken after the irreducible forms are derived. Here it is necessary to make the approximation in order to get an irreducible integral form.

Noting the form of the interaction potential in (2.1), we write

$$\begin{aligned} H_{ij}' &= V_{ij}{}^S + V_{ij}{}^R, \\ V_{ij}{}^S &= \frac{e_ie_j}{r_{ij}}, \\ V_{ij}{}^R &= -\frac{e_ie_j}{r_{ij}} \frac{1}{2m_im_jc^2}\left(\mathbf{p}_i\cdot\mathbf{p}_j + \frac{\mathbf{p}_i\cdot\mathbf{r}_{ij}\,\mathbf{p}_j\cdot\mathbf{r}_{ij}}{r_{ij}^2}\right). \end{aligned} \tag{4.2}$$

Thus (3.7) becomes

$$b_{n_1n_2} = \frac{1}{n_1!n_2!V\Lambda_1^{n_1}\Lambda_2^{n_2}} \int \exp(-\beta H^0{}_{n_1+n_2}) \times \sum \prod (-\beta H_{ik}') d\Omega_{n_1+n_2} \tag{4.3}$$

We now restrict our attention to the lowest nonvanishing approximation (known as the ring approximation[13]). From the condition of electrical neutrality the terms defined in (4.3) which involve products of static contributions alone and are not of the ring form will vanish. Also any products involving the relativistic terms except those which contain only $V_{ij}{}^R$ and are of the ring form will vanish, as a consequence of the particular symmetry of the momentum dependence (which is such that integration over momentum angular variables causes the vanishing of certain products).[23]

Thus we obtain an irreducible form from the previous reducible one and (4.3) becomes

$$b^o{}_{n_1n_2} = \frac{1}{n_1!n_2!V\Lambda_1^{n_1}\Lambda_2^{n_2}} \int \exp(-\beta H^0{}_{n_1+n_2}) \times \{\sum_{\text{rings}} [\prod(-\beta V_{ij}{}^S) + \prod(-\beta V_{ij}{}^R)]\} d\Omega_{n_1+n_2}, \tag{4.4}$$

where the superscript o denotes the ring approximation. We note that such a reduction could have been effected for an over-all neutral system by any interaction where the momentum dependence enters as $f(r)\mathbf{p}_1\cdot\mathbf{p}_2$ or $f(r)\mathbf{p}_1\cdot\mathbf{r}\,\mathbf{p}_2\cdot\mathbf{r}$. In addition, a form such as $f(r)\mathbf{p}_1\cdot\mathbf{r}$, which is linear in only one momentum vector, would have the necessary properties; a function which would depend on the magnitude, but not direction, of momentum would not give the requisite behavior, however.

We shall ignore the relativistic interaction contribution from the proton component, since with even one proton contained in the ring, the ring product obtained is of the order $(m_e/m_p)^2 = O(10^{-6})$ smaller than if only electrons composed the ring. The activity series now becomes

$$q = V \sum_{\substack{n,n_1,n_2 \\ (n=n_1+n_2)}} \frac{z_1^{n_1}}{n_1!}\frac{z_2^{n_2}}{n_2!} \int \sum_{\text{rings}} \prod(-\beta V_{ij}{}^S) \frac{dV_{n_1+n_2}}{V} + \sum_{n_1} \frac{z_1^{n_1}}{n_1!} \int \sum_{\text{rings}} \prod(-\beta V_{ij}{}^R) \frac{d\Omega_{n_1+n_2}}{V}.$$

[23] For details of this and subsequent calculations see John E. Krizan, Lehigh University thesis, 1962 (unpublished).

Replacing the sum over rings by a factor $\frac{1}{2}(n-1)!$, which represents the number of independent rings, and using the binomial theorem this may be written as

$$q=V\{(z_1+z_2)+\sum_{n\geq 2}(\beta_{n-1}{}^{oS}/n)(z_1+z_2)^n + \sum_{m\geq 2}(\beta_{m-1}{}^{oR}/m)z_1{}^m\}, \quad (4.5)$$

where we have defined

$$\beta_{n-1}{}^{oS}=\frac{(-\beta e^2)^n}{2V}\int \prod_{\text{rings}}(V_{ij}{}^S)dV_n \quad (4.6)$$

and

$$\beta_{n-1}{}^{oR}=\frac{(-\beta e^2)^n}{2V\Lambda^n}\int \exp(-\beta H_n{}^0)\prod_{\text{rings}}(V_{ij}{}^R)d\Omega_n. \quad (4.7)$$

These integrals are evaluated in the Appendix. Finally we may put the grand potential in the form

$$q=V(z_1+z_2)\left\{1+\frac{1}{z_1+z_2}\int_0^{z_1+z_2}S^S(z_1+z_2)d(z_1+z_2)\right\} +V\int_0^{z_1}S^R(z_1)dz_1, \quad (4.8)$$

where

$$S^M(z)=\sum_{n\geq 1}\beta_n{}^{Mo}z^n, \quad M=S,R. \quad (4.9)$$

As is well known, the individual cluster terms in this series diverge in the static case due to the long range of the Coulomb interaction. Similarly our coefficients, given by Eqs. (A11) and (A12), diverge. Nevertheless, following Mayer,[13] we will sum up the series in the hope of obtaining a reasonable result. We get

$$S^S(z)=\sum_{n\geq 1}\left\{\frac{(-\beta)^{n+1}}{2(2\pi)^3}\int[(2\pi)^{\frac{3}{2}}u^S(t)]^{n+1}d^3t\right\}z^n, \quad (4.10)$$

and

$$S^R(z)=\sum_{n\geq 1}\left\{\frac{(-\beta)^{n+1}}{2(2\pi)^3}(-\kappa)^{n+1} \times\int[(2\pi)^{\frac{3}{2}}u^S(t)]^{n+1}d^3t\right\}z^n, \quad (4.11)$$

with $u^S(t)$ defined by (A3) and κ by (A8). Summation of (4.10) leads to a well-defined integral and to the Debye-Hückel terms. On the other hand, summation of (4.11) leads to an undefined integral (since analytic continuation of the geometric series, in contrast to the alternating geometric series, introduces singularities along the path of the transform integration).

If one knew the form of the repulsive term $H_{ij}{}^*$ assumed in Sec. II, and combined it with the relativistic term, one might get a sensible result upon analytic continuation. There is a possibility that the singularity introduced indicates that the problem might be one of stability and as such would be intimately connected with the necessity of introducing repulsive terms.

We may, however, treat an important part of the relativistic interaction without a knowledge of these repulsive terms. The possibility for doing this follows from the fact that a finite range of sufficient size can allow an analytic continuation which leads to a reasonable result.

A charged system can exhibit long-range and short-range modes for the Coulomb interaction; the short-range part arises from interactions within the Debye sphere, and the long-range correlations add up to produce collective oscillations.

In the following discussion we will restrict our attention to the short-range relativistic effects and neglect the long-range ones. We would expect the short-range relativistic effects to predominate at high densities, and for high temperatures it is in this region that the interaction effects will be most pronounced. With respect to the static terms we will continue to treat the total interaction. We shall discuss the validity of the procedures used in Sec. VI.

The calculations are outlined in the Appendix. We obtain the same expression (4.10) for $S^S(z)$ as before, but in place of (4.11) we get

$$S^R(z)=\sum_{n\geq 1}\left\{\frac{(-\beta)^{n+1}}{2(2\pi)^3}(-\kappa)^{n+1} \times\int[(2\pi)^{3/2}U^S(t)]^{n+1}d^3t\right\}z^n, \quad (4.12)$$

where

$$U^S(t)=(2/\pi)^{1/2}[\epsilon^2/(R_D{}^2+t^2)]$$

is the transform of the shielded Coulomb potential.

Upon summation of the series (4.10) and (4.12) and integration over the transform variable, we get

$$S^S(z)=z^{1/2}\beta^{3/2}\pi^{1/2}\epsilon^3, \quad (4.13)$$

$$S^R(z)=z^{1/2}\beta^{3/2}\pi^{1/2}\epsilon^3\kappa[1-(1-\kappa)^{1/2}], \quad (4.14)$$

and thus

$$S(z)\equiv S^S(z)+S^R(z)=z^{1/2}\beta^{3/2}\pi^{1/2}\epsilon^3K(\kappa),$$
$$K(\kappa)\equiv 1+\kappa[1-(1-\kappa)^{1/2}]. \quad (4.15)$$

Before using these results in deriving the thermodynamic functions we first evaluate the parameter κ. The integral involved is given by Watson[24] and thus

$$\kappa=8\pi(mc)^3K_3(mc^2\beta)/(mc^2\beta)^2\Lambda,$$

where the $K_n(x)$ are modified Bessel functions of the second kind. Since Λ in (3.5) equals[2]

$$\Lambda=4\pi(mc)^3\frac{K_2(mc^2\beta)}{mc^2\beta}, \quad (4.16)$$

we have

$$\kappa=\frac{2K_3(mc^2\beta)}{mc^2\beta K_2(mc^2\beta)}. \quad (4.17)$$

[24] G. N. Watson, *Theory of Bessel Functions* (Cambridge University Press, New York, 1944), 2nd ed., p. 172.

The $(v/c)^2$ approximation serves to limit the values that κ can take and still give a valid approximation. Thus, e.g., for $v/c=\frac{1}{3}$ the argument in the Bessel functions will be large, and we have asymptotically $K_3(x) \cong K_2(x) \propto e^{-x}/\sqrt{x}$. As $\beta=(kT)^{-1}$, we can then write (4.17) as

$$\kappa \cong 2kT/mc^2.$$

Thus κ is at most of $O(10^{-1})$. Examination of (4.15) reveals that $K(\kappa)$ varies as κ^2. Therefore, the relativistic correction is small compared to the static one.

V. THERMODYNAMIC FUNCTIONS

We now calculate the equation of state, the average energy, and the fugacity from Eqs. (4.8) and (4.15). Noting that $S^S(z)$ and $S^R(z)$ are proportional to $z^{\frac{3}{2}}$, (4.8) may be written as

$$q=V\{(z_1+z_2)[1+\tfrac{2}{3}S^S(z_1+z_2)]+\tfrac{2}{3}z_1S^R(z_1)\}. \quad (5.1)$$

The average numbers of particles are then

$$\bar{n}_1=z_1\partial q/\partial z_1=Vz_1[1+S^S(z_1+z_2)-S^S(z_1)+S(z)]$$

and

$$\bar{n}_2=Vz_2[1+S^S(z_1+z_2)].$$

Solving for the activities, we obtain to the first order

$$\begin{aligned} z_1&=\rho[1-S^S(2\rho)+S^S(\rho)-S(\rho)],\\ z_2&=\rho[1-S^S(2\rho)]. \end{aligned} \quad (5.2)$$

Thus the equation of state is to the same order

$$\begin{aligned} p/kT&=(z_1+z_2)[1+\tfrac{2}{3}S^S(z_1+z_2)]-\tfrac{2}{3}z_1[S^S(z_1)-S(z_1)]\\ &\cong 2\rho\{1-\tfrac{1}{3}S^S(2\rho)+\tfrac{1}{2}[S^S(\rho)-S(\rho)]\}, \end{aligned}$$

or

$$\begin{aligned} p/2kT\rho=1-\tfrac{1}{3}(2\rho)^{1/2}\beta^{3/2}\pi^{1/2}\epsilon^3\\ \times\{1-(3/2\sqrt{2})[1-K(\kappa)]\}, \end{aligned} \quad (5.3)$$

which in the nonrelativistic limit $[K(\kappa)\to 1]$ reduces to the Debye-Hückel law.

By a similar procedure we get for the average energy

$$\begin{aligned} \bar{E}=-\pi^{1/2}\beta^{1/2}\epsilon^3 2\bar{n}(2\rho)^{1/2}\{1+(1/2\sqrt{2})[1-K(\kappa)]\}\\ -\bar{n}[(\partial\Lambda_1/\partial\beta)(1/\Lambda_1)+(\partial\Lambda_2/\partial\beta)(1/\Lambda_2)], \end{aligned} \quad (5.4)$$

where the last term in brackets is the contribution from the relativistic free-particle kinetic energy.[2] In the nonrelativistic limit (5.4) becomes[25]

$$\bar{E}=-\pi^{1/2}\beta^{3/2}\epsilon^3 2\bar{n}(2\rho)^{1/2}+\bar{n}[(3/\beta)+(m_p+m_e)c^2].$$

The fugacities are

$$\begin{aligned} \nu_1=-\ln\Lambda_1+\ln\rho-\pi^{1/2}\beta^{3/2}\epsilon^3(2\rho)^{1/2}\\ \times\{1-(1/\sqrt{2})[1-K(\kappa)]\}, \end{aligned} \quad (5.5)$$

$$\nu_2=-\ln\Lambda_2+\ln\rho-\pi^{1/2}\beta^{3/2}\epsilon^3(2\rho)^{1/2},$$

which again reduce to the nonrelativistic results[26] for $K(\kappa)\to 1$.

VI. DISCUSSION

Equations (5.3), (5.4), and (5.5) show the relativistic modifications of the Debye-Hückel theory resulting from the Darwin Hamiltonian, with only the short-range relativistic correlations taken into account. We saw that our inability to treat the more general case involving long-range relativistic correlations may be due to incomplete knowledge of the total interaction required for allowing statistical equilibrium. However, it may also be that the difficulties encountered in the relativistic case are only due to the failure of the customary mathematical methods of the nonrelativistic one. The short-range correlations may be expected to be the most important ones under certain conditions, as at high densities. Thus, while the treatment is deficient in its neglect of long-range effects, the results in terms of short-range effects may be of interest by themselves.

In considering the nonrelativistic case alone, if one were to decompose the static interaction term into two parts and discard the long-range part, one would obtain only about half the usual result. If we extended this argument to the relativistic terms, then one might say that by neglect of long-range correlations we will not appreciably change the expectation that the total relativistic effect would be small [in fact, smaller than one might expect from the magnitude of $(v/c)^2$]. The small correction obtained is of the same form as the electrostatic one; no unusual effects (which one might have expected from the unusual forces) are apparent in the result.

The consideration of only the short-range relativistic terms had the effect of introducing a shielding parameter. It may appear that the restriction to short-range relativistic interactions with subsequent summation of ring terms is somewhat redundant since in the static case it is known that the summation of diagrams in the lowest approximation for the average potential leads to Debye shielding; if an attempt is made to investigate whether an analogous statement can be made for the relativistic term, it is found that the equivalent summation leads to an undefined result, as discussed in Sec. IV, and thus no definite conclusion can be reached.

Beyond the restriction discussed above, the problem is of formal interest for statistical mechanics because of the inclusion of velocity-dependent interactions. This velocity dependence required a departure from the usual reduction of reducible clusters to irreducible ones by necessitating an expansion of the f_{ij} early in the treatment rather than after the irreducible integral forms are obtained. Related to this requirement was our restriction to the activity series, rather than use of the virial series.

[25] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), p. 232.

[26] S. Ono and Sohei Kondo, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1960), Sec. 40, p. 224.

Although the particular tensor form of the relativistic interaction term was of no importance up to Eq. (3.7), it became critical for the steps involving integration over momentum. It was only because of this form that we were able to get a simple product term which could be easily summed.

The system is necessarily restricted to electrical neutrality, and the approximations introduced somewhat limit the possibility of taking higher approximations. In addition, in extending the treatment to systems other than electrodynamic ones there appear to be insurmountable difficulties. We have restricted ourselves to the ring approximation; this is justified because treatments extending the Debye-Hückel theory in the nonrelativistic approximation by taking into account higher order clusters show that these corrections are small compared to those of the rings. Bowers and Salpeter[27] have shown this to be the case for a low density gas, and Ichikawa[15] for high densities; while Ichikawa attributed these higher order effects to the long-range oscillation mode, it has not been shown that at lower densities certain higher order clusters are equivalent to the plasma oscillation mode.

We have not considered the effects of suitable repulsive terms which could be considerable but for which we have no explicit form. Apart from the fact that these terms might have influence on the problem of treating the total interaction, the bypassing of these terms is not feasible in computing higher order corrections.[28]

Our approximations impose restrictions on the density. For usual plasma densities at high temperatures the Debye-Hückel terms are quite small compared to the kinetic energy contribution. At higher densities, such as those found in stars, these terms become larger. However, for these higher densities, degeneracy plays an important role and thus we shall first estimate the expected limitations of the classical result. The thermal DeBroglie wavelength $\lambda=h(2\pi mkT)^{-1/2}$ is of the order of 10^{-10} cm for $T\sim10^8$ °K, so that for densities below about 10^{30} cm^{-3} the classical treatment is applicable. At a density of 10^{30} cm^{-3} and temperature of $T=10^8$ °K, the static Debye-Hückel term is of $O(10^{-3}-10^{-4})$.

The approximation made when the f_{ij} in (3.3) are expanded and retained in the first order in (4.1) leads to an upper limit on the density for a given temperature regardless of the classical limit restriction. Thus $kT\gg H_{ij}'$ leads to a good approximation. We see that roughly (using only the static approximation for this order-of-magnitude calculation) $r\gg\epsilon^2/kT$. We have actually used this condition in Sec. V in linearizing expressions by treating $S(\rho)$ as small compared with unity. Thus the limit of approximation on the density, considering a fixed high temperature (and excluding the classical limit criterion), is $\rho\ll(kT/\epsilon^2)^3$. For $T=10^8$ °K the limit is $\rho\ll10^{36}$ cm^{-3}, which is less restrictive than the classical criterion $\rho\ll10^{30}$ cm^{-3} obtained before. If the densities appropriate to the problem are extended to $O(10^{36})$, the static-classical Debye-Hückel term approaches unity for $T\sim10^8$ °K. Treatment of the quantum case would probably decrease the size of this term relative to the kinetic energy, owing to the increasing degeneracy which will tend to diminish the effects of interaction.

It is to be noted that the density limit criterion prevents one from taking a high-density limit in the sense of Ichikawa. Nevertheless, the densities are high.

The relativistic correction is small, and generally negligible. At extremely high temperatures of $O(10^{10}$ °K) it can become comparable to the static Debye-Hückel term, although this result is not reliable since the $(v/c)^2$ approximation is plainly violated in this region. At temperatures of $O(10^{10}$ °K), κ approaches 1, and by (4.15) $K(\kappa)$ becomes imaginary when $\kappa>1$. This point roughly corresponds to a temperature at which the mean thermal energy is equal to the electron rest energy, a region in which pair production processes (which can not be treated classically) become important. It is to be expected that radiation effects become important at somewhat lower temperatures; the problems involved in a treatment of these effects were discussed in the Introduction.

The fact that the meson field is short ranged might lead one to expect that the treatment used here for electric charges could be applied *mutatis mutandis* to nucleons. Several features of the nuclear problem appear to vitiate such an attempt, however. First, no condition of neutrality can be imposed in this case, while such a condition was critical for our earlier argument leading to a separation of momentum and coordinate terms.

Another difficulty comes to the fore when we examine the form of the interaction. If one retains terms of order $(v/c)^2$ in the solutions of the Klein-Gordon equation and substitutes these in the Hamiltonian for scalar mesons, one obtains interaction terms of the form

$$-\frac{g_ig_j}{r}\exp(-\chi r)+\frac{g_ig_j}{2m^2c^2}\exp(-\chi r)\left[\chi(\mathbf{p}_i\cdot\mathbf{r})^2+\frac{\mathbf{p}_j\cdot\mathbf{p}_j}{r}\right].$$

This form does not permit reduction of the general cluster integral to a product form [as in (A6) for electrodynamics]. Similar difficulties exist for vector mesons. These difficulties are not related to the fact, mentioned in the Introduction, that in the meson case action at a distance and symmetric field theory are not entirely equivalent[3]; the difference does not show up in the approximation considered here.

Instead of using the potential above, one might attempt to use the Werle[29] "equivalent potential."

[27] D. L. Bowers and E. E. Salpeter, Phys. Rev. **119**, 1180 (1960).

[28] E. Meeron, in *Plasma Physics*, edited by J. E. Drummond (McGraw-Hill Book Company, Inc., New York, 1961), Chap. 3, p. 88.

[29] J. Werle, Bull. acad. polon. sci. Classe III, **1**, 281 (1953).

This is obtained by approximation from the relativistic Hamilton-Jacobi equation and has the form

$$-g^2 \exp(-\chi r)/r+(g^4/2mc^2)[\exp(-2\chi r)/r^2].$$

This term is exclusively r dependent and so the reduction of the activity series to irreducible form (due to p dependence) is unnecessary. Hence we do not need the condition of neutrality, and we may use the virial expansion of Mayer directly. If this is done, the cluster integrals β_n $(n\geq 1)$ will all converge in the ring approximation. However, the Fourier transform of the interaction term is

$$V_t=4\pi g^2[(t^2+\chi^2)^{-1}-(g^2/2mc^2)t^{-1}\tan^{-1}(t/2\chi)],$$

and when the general term

$$\beta_n(n\geq 2)=\int_0^\infty (V_t)^{n+1}d^3t$$

is summed over $n\geq 2$, the resulting integral over the t variable will diverge to the $1/t$ dependence of V_t.

An extension of the methods used to the case of gravitational forces also is not feasible. First, no invariant subspace of positive finite measure has been found which would allow definition of a probability density even for the nonrelativistic case.[30] In addition a requirement of neutrality is needed in the case of long-range forces in order to cause certain infinite terms to vanish. Even assuming that a repulsive term could be defined in order to legitimately write an equilibrium probability density, there would be a failure of the cluster approximation due to the infinities introduced by the long range of the force.

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APPENDIX

The integrals (4.6) and (4.7) are of the form

$$\int V_{12}{}^S V_{23}{}^S\cdots V_{n+1\,1}{}^S d^3r_1 d^3r_2\cdots d^3r_{n+1},$$

and

$$\int \exp(-\beta H_{n+1}{}^0)V_{12}{}^R V_{23}{}^R\cdots V_{n+1\,1}{}^R d^3r_1 d^3r_2\cdots \times d^3r_{n+1}d^3p_1d^3p_2\cdots d^3p_{n+1}.$$

These integrals have a convolution form as far as the r coordinates are concerned, and it has been shown[31] that they can be expressed in terms of Fourier transforms. Then Eqs. (4.6) and (4.7) become

$$\beta_n{}^{So}=\frac{(-\beta)^{n+1}}{2(2\pi)^3}\int[(2\pi)^{3/2}u^S(t)]^{n+1}d^3t \tag{A1}$$

and

$$\beta_n{}^{Ro}=\frac{(-\beta)^{n+1}}{2(2\pi)^3\Lambda^{n+1}}\int \exp(-\beta H_{n+1}{}^0)\times\{[(2\pi)^{3/2}u_{12}{}^R(t)][(2\pi)^{3/2}u_{23}{}^R(t)]\times\cdots\times[(2\pi)^{3/2}u_{n+1\,1}{}^R(t)]\}d^3p_1d^3p_2\cdots d^3p_{n+1}d^3t, \tag{A2}$$

with the transforms

$$u^S(t)=\frac{1}{(2\pi)^{3/2}}\int V^S(\mathbf{r})e^{i\mathbf{t}\cdot\mathbf{r}}d^3r, \tag{A3}$$

and

$$u^R(t)=\frac{1}{(2\pi)^{3/2}}\int V^R(\mathbf{p},\mathbf{r})e^{i\mathbf{t}\cdot\mathbf{r}}d^3r. \tag{A4}$$

Since the $u^R(t)$ are momentum dependent the integrand in (A2) can not be written in the form of that in (A1).

Using the definition (4.2) we can perform the integration over the coordinate variables in (A4) and we get

$$u_{12}{}^R(t)=-\frac{1}{(2\pi)^{1/2}}\int\frac{e^2}{r}\frac{p_1p_2}{2m^2c^2}[(A+B)\cos\Theta_1\cos\Theta_2+\tfrac{1}{2}(3A-B)\sin\Theta_1\sin\Theta_2\cos(\Phi_1-\Phi_2)]r^2dr, \tag{A5}$$

where Θ, Φ refer to momentum angles and θ, φ to coordinate angles, with

$$A(r,t)=\int_0^\pi e^{itr\cos\theta}\sin\theta d\theta,$$

and

$$B(r,t)=\int_0^\pi e^{itr\cos\theta}\cos^2\theta\sin\theta d\theta.$$

There are terms analogous to (A5) for the other pairs of variables. Substituting (A5) into (A2) and performing the integration over the angular variables of momentum we obtain

$$\beta_n{}^{Ro}=\frac{[-(\beta\kappa/2)]^{n+1}}{2(2\pi)^3}\int\{[(2\pi)^{3/2}u^R{}_{A+B}(t)]^{n+1}+[(2\pi)^{3/2}u^R{}_{\frac{1}{2}(3A-B)}(t)]^{n+1}\}d^3t, \tag{A6}$$

where

$$u^R{}_{A+B}(t)=-\frac{1}{(2\pi)^{1/2}}\int_0^\infty\frac{e^2}{r}[A(r,t)+B(r,t)]r^2dr,$$
$$u^R{}_{\frac{1}{2}(3A-B)}(t)=-\frac{1}{(2\pi)^{1/2}}\int_0^\infty\frac{e^2}{r}\frac{1}{2}[3A(r,t)-B(r,t)]r^2dr \tag{A7}$$

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[30] R. Kurth, *Introduction to the Mechanics of Stellar Systems* (Pergamon Press, New York, 1957), p. 58.

[31] See, e.g., E. Meeron, J. Chem. Phys. 28, 630 (1958).

and

$$\kappa = \frac{8\pi}{3\Lambda} \int_0^\infty \exp(-\beta H_1{}^0) \frac{p^4}{2m^2c^2} dp. \tag{A8}$$

Evaluating (A3) and (A7) by the formal device of adding a convergence factor $\exp(-\chi r)$ and taking the limit as $\chi \to 0$ after the integration is performed, we obtain

$$\begin{aligned} u^R{}_{A+B}(t) &= 0, \\ u^R{}_{\frac{1}{2}(3A-B)}(t) &= -2u^S(t), \end{aligned} \tag{A9}$$

where

$$u^S(t) = (2/\pi)^{1/2} t^{-2}. \tag{A10}$$

Substituting these expressions into Eqs. (A1) and (A6), we get

$$\beta_n{}^{So} = \frac{(-\beta)^{n+1}}{2(2\pi)^3} \int \left(\frac{4\pi}{t^2}\right)^{n+1} d^3t \tag{A11}$$

and

$$\beta_n{}^{Ro} = \frac{[(\beta\kappa/2)]^{n+1}}{2(2\pi)^3} \int \left(\frac{8\pi}{t^2}\right)^{n+1} d^3t. \tag{A12}$$

To separate the long- and short-range interactions, we first Fourier-analyze (4.2) in a box of volume V using (A5), (A7), (A9), and (A10), to get

$$\sum_{i<j} H_{ij}' = (1/V) \sum_{i<j} \sum_k [F^S(k) + F^R(k,p)] \exp(i\mathbf{k}\cdot\mathbf{r}_{ij}),$$

where

$$F^S(k) = 4\pi\epsilon^2/k^2,$$

$$F^R(k,p) = -\frac{8\pi\epsilon^2}{k^2} \frac{p_i p_j}{m^2c^2} \sin\Theta_i \sin\Theta_j \cos(\Phi_i - \Phi_j).$$

Now we divide the interaction into two parts

$$\sum_{i<j} H_{ij}' = H_{SR+S} + H_{LR},$$

where

$$H_{SR+S} = \frac{1}{V} \sum_{i<j} \Big[\sum_{k>k_D} F^R(k,p) \exp(i\mathbf{k}\cdot\mathbf{r}_{ij}) + \sum_{\text{all } k} F^S(k) \exp(i\mathbf{k}\cdot\mathbf{r}_{ij}) \Big],$$

where k_D is the reciprocal of the Debye radius, and

$$H_{LR} = (1/V) \sum_{i<j} \sum_{k<k_D} F^R(k,p) \exp(i\mathbf{k}\cdot\mathbf{r}_{ij}).$$

Following the previous discussion we shall absorb H_{LR} into the unknown term H^* and the remainder of the argument will go through as before with H_{SR+S} instead of the exact potential.

Now by summing over k in H_{SR+S}, we get[32]

$$H_{SR+S} = \sum_{i<j} (\epsilon_i\epsilon_j/r_{ij}) \{1 - [(2p_ip_j/m_im_jc^2) \sin\Theta_i \sin\Theta_j \times \cos(\Phi_i - \Phi_j)][1 - (2/\pi)\,\mathrm{Si}(k_Dr_{ij})]\},$$

where $\mathrm{Si}(y) \equiv \int_0^y (x^{-1} \sin x) dx$. As shown in reference 32, the last term in square brackets is equivalent to a screened potential of range k_D and thus

$$H_{SR+S} \cong \sum_{i<j} (\epsilon_i\epsilon_j/r_{ij}) \times [1 - \exp(-k_Dr_{ij})(2p_ip_j/m_im_jc^2) \sin\Theta_i \sin\Theta_j \times \cos(\Phi_i - \Phi_j)].$$

Next we repeat all the steps leading up to (4.10) and (4.11), as the form of the interaction allows the same reduction of reducible to irreducible integrals, and obtain the results (4.10) and (4.12) discussed in Sec. IV.

[32] D. Bohm and D. Pines, Phys. Rev. 92, 609 (1953).