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THERMODYNAMIC FUNCTIONS OF A PARTIALLY
DEGENERATE, FULLY IONIZED GAS

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ABSTRACT

The formalism of Glassgold, Heckrotte, and Watson for the expansion of the quantum-mechanical grand partition function has been applied to a gas of point charges. The expansion is shown to be closely related to Rayleigh-Schroedinger perturbation theory, and to give the results of Montroll and Ward in a simpler form. The theory has been extended to a multicomponent gas of fermions and bosons, and the ring diagrams have been summed to give an approximate expression for the equation of state valid for the entire temperature range. The near-classical limit (high temperature and low density so that the gas is only slightly degenerate) is discussed in detail, and useful formulae for numerical computation of pressure and internal energy are derived from the general ring approximation to the equation of state. By expanding the chemical potential in powers of the coupling constant e^2 , it is possible to eliminate the parametric dependence of pressure and density on the chemical potential and obtain the pressure as a function of density. The classical-limit Debye-Hückel results are obtained when β approaches 0. A general form of the screening length is obtained with the effective screening charge as $z_i e \theta_i$, where θ_i is a measure of the degeneracy of the particle species i .

The contribution to the pressure from the simplest exchange interaction valid for all temperature is evaluated exactly.

The temperature and density range for which the near-classical-limit formulae are valid is discussed.

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1. INTRODUCTION

A number of recent publications have developed general formalisms for dealing with the problems of quantum-statistical mechanics of interacting particles. These approaches involve the application of perturbation methods of quantum field theory to obtain a diagrammatic expansion of the grand partition function of an interacting many-body system. The present paper discusses the application of some of these methods to yield a fundamental and rigorous calculation of the thermodynamic functions (particularly, pressure and internal energy) of a system of point charges interacting only with Coulomb forces. The general theory of a one-component system of point charges obeying Fermi statistics, i.e., an electron gas in a continuous positive-charge background, has been given rather completely by Montroll and Ward.¹ In this paper, some general expressions similar to those obtained by Montroll and Ward are derived for a multicomponent gas composed of both electrons and positive point charges obeying either Fermi or Bose statistics. The primary aim of this work, however, is to obtain useful analytical results for the equation of state of a fully ionized gas at temperatures and densities for which deviations from the purely classical formulae due to quantum statistics are significant.

The starting point of any fundamental calculation of the thermodynamic functions of an interacting many-body system at finite temperature is the

¹ E. W. Montroll and J. C. Ward, *Physics of Fluids* 55 (1958).

calculation of the grand canonical partition function, expanded in powers of the coupling constant of the interaction. Matsubara has given an elegant field-theoretic treatment of the grand partition function of the electron-phonon system.² Yang and Lee have developed the binary-collision method and applied it to hard-sphere gases.³ Montroll and Ward have applied the Feynman propagator techniques of field theory to quantum-statistical mechanics and obtained an expansion of the grand partition function in terms of diagrams that are quantum generalizations of the Mayer cluster diagrams.¹ Bloch and de Dominicis have obtained an expansion in terms of linked diagrams closely related to Rayleigh-Schroedinger perturbation theory.⁴ More recently, Glassgold, Heckrotte, and Watson have obtained the results of Bloch and de Dominicis by using a theorem due to Hugenholtz.⁵ Brittin and Sakakura have obtained results similar to those of Montroll and Ward by more direct use of field-theory techniques.⁶ As a result of the work of these various investigators, the perturbation expansion of the grand partition function may be considered as well understood, and, consequently, this paper is concerned primarily with application of the theory.

The formalism of Glassgold, Heckrotte, and Watson will be used, since the fundamental result obtained by them is a convenient starting point for the calculation. They give an expansion of the grand partition function of a one-component system in terms of the sum of all possible linked diagrams:

² T. Matsubara, *Prog. Theoret. Phys.* 14, 351, (1955).

³ T. O. Lee and C. N. Yang, *Phys. Rev.* 113, 1165 (1959).

⁴ C. Bloch and C. de Dominicis, *Nuclear Phys.* 7, 459 (1959).

⁵ A. E. Glassgold, W. Heckrotte, and K. M. Watson, (To be published in *Phys. Rev.*).

⁶ W. E. Brittin and A. Sakakura, Unpublished work at the University of Colorado.

$$Z_G(\alpha) = \sum_{N=1}^{\infty} \text{Tr} e^{(\alpha N - \beta H_N)} = Z_0(\alpha) e^{\sum Q_L} \quad (1)$$

Each Q_L is obtained from a graph in which n particles are linked by interactions. Thus, for the Coulomb interaction with coupling constant e^2 , such a Q_L is proportional to e^{2r} , where r is the number of interactions; $Z_0(\alpha)$ is the grand partition function of a noninteracting system, but evaluated for $\alpha = \beta\mu$, where μ is the chemical potential per particle of the interacting system.

For application to ionized gases, we consider in this article only a limited set of diagrams out of the multitude of possible diagrams that comprise the expansion indicated by Eq.(1). This set consists of only the cycle or ring diagrams that are characterized by n particles interacting n times and exchanging momentum q at each interaction. The physical assumption on which this choice is based is that for very-long-range interactions, particularly the Coulomb interaction with its infinite range, the contribution to the sum $\sum Q_L$ in Eq.(1) from a cluster of n particles interacting cyclically, no matter how far apart, is more important than the contributions from clusters with more than n interactions. The retention of only the ring diagrams thus neglects the ladder diagrams between two particles, which give the all-important contribution for strong short-range forces. At zero temperature and high density, the ring diagrams give the Gell-Mann and Brueckner expression for the correlation energy of an electron gas,⁷ and this result has been shown to be equivalent to the random-phase approximation of Bohm and Pines.⁸

⁷ M. Gell-Mann and K. A. Brueckner, Phys. Rev. 106, 364 (1957).

⁸ K. Sawada, K. A. Brueckner, N. Fukada, and R. Brout, Phys. Rev. 108, 507 (1958).

In the high-temperature limit; the ring diagrams give the classical Debye-Hückel equation of state valid for low density.⁹ At any temperature, each ring diagram diverges as $O(-1/q^2)^N$ because of the infinite range of the Coulomb interaction. The sum of all ring diagrams, however, gives a finite result corresponding to a screened Coulomb interaction. The screening length is the same as that obtained from a linearized Thomas-Fermi type of equation, and which reduces to the Debye-Hückel theory in the classical limit.

In Sec. II, the Glasgold, Heckrotte, and Watson formalism has been extended to show that the Q_L corresponding to particular diagrams can be expressed as iterated temperature integrals similar to the time iterations of the S matrix in field theory. A temperature-dependent particle propagator is derived. It is then possible to show that this method gives results identical to those of Montroll and Ward. For the sum of the ring diagrams, a formal expression for the equation of state is obtained. This formal expression holds for the entire temperature range and gives the Gell-Mann and Brueckner theory and the Debye-Hückel theory as limiting cases for zero temperature and very high temperature, respectively. This result is identical with the Montroll and Ward expression for a one-component gas, but is obtained in a more compact, and possibly more useful, form.

In Sec. III, the complete expression for the sum of the ring diagrams is used to derive limiting results valid for the near-classical limit, for which the gas is slightly degenerate. The near-classical limit is essentially a high-temperature and low-density region, however, temperatures and densities are such that quantum statistics cause some deviation from the classical-limit results defined by $\hbar = 0$. Since the grand partition function

⁹ E. W. Montroll and J. E. Mayer, J. Chem. Phys. 18, 626 (1941).

has been used, the chemical potential appears in the theory as an independent variable in place of the density. Thus, in general, when the grand partition function is used, one obtains parametric equations for pressure and density as functions of $\alpha = \beta\mu$. In the near-classical limit, it is possible to eliminate the implicit dependence on α , and the final expressions obtained for the pressure and energy are functions of density.

In Sec. IV, the simplest exchange interaction is evaluated, and its contribution to the pressure and energy of an electron gas at all temperatures is obtained. In Sec. V the theory is extended to a multicomponent system of fermions and bosons, and the ring-diagram equation of state of this system is obtained. From this general expression, the thermodynamic functions of a real, fully ionized gas in the near-classical limit are derived in terms of density as the independent variable.

II. APPLICATION TO A ONE-COMPONENT GAS

In order to thoroughly illustrate the theory and minimize the complexity of the mathematical expressions, a complete discussion of the ring diagrams for a one-component gas will be given first. We consider N particles of charge $-e$ and spin s in a volume V , and, hence, a number density $\rho = N/V$. The total negative charge, $-Ne$, is balanced by an equal amount of positive charge smeared out continuously through the volume. The Hamiltonian of the system that enters (1) is:

$$H_N = T_N + U_N = -\frac{\hbar^2}{2m} \sum_i^N \nabla_i^2 + \sum_{i<j}^N U(r_{ij}), \quad (2)$$

where $U(r_{ij})$ is the Coulomb potential between point charges at r_i and r_j .

A few relations derived from the grand partition function will be noted here for future reference. The logarithm of the grand partition function gives

the pressure of the gas directly,¹⁰ since we have

$$Z_G(a) \approx \exp(PV/kT), \quad (3)$$

but Z_G is a function of a . Since PV obtained from (3) is a thermodynamic potential from which the other thermodynamic functions may be derived, it will be given a separate symbol:

$$\Omega(a) \equiv PV. \quad (4)$$

The internal energy is given by:

$$\begin{aligned} \frac{\bar{E}(a)}{kT} &= \frac{1}{Z_G} \sum_N \text{Tr } H_N \exp(aN - \beta H_N) \\ &= -\beta \frac{\partial}{\partial \beta} \log Z_G \Big|_a = -\beta \frac{\partial}{\partial \beta} \left(\frac{\Omega}{kT} \right)_a. \end{aligned} \quad (5)$$

and, similarly, the number of particles $\bar{N}$ is given by:

$$\bar{N} = \frac{\partial}{\partial a} \left(\frac{\Omega}{kT} \right)_a. \quad (6)$$

Since the density $\rho = \bar{N}/V$ is given, Eq. (6) determines the chemical potential a . Thus, (3), (5), and (6) are a set of parametric equations in a , from which the pressure and internal energy of the gas may be calculated for a given value of density. The potential energy of the interacting gas may be calculated by replacing the coupling constant with $e^2 = \eta e^2$, so that the pair potential in the Hamiltonian becomes $U_e(r_{ij}) = \eta U(r_{ij})$. One then obtains:

$$\begin{aligned} \frac{\bar{U}(a)}{kT} &= \frac{1}{Z_G} \sum_N \text{Tr} \left(e^{aN - \beta T_N} \beta U_N e^{-\beta U_N} \right) \\ &= \lim_{\eta \rightarrow 1} \eta \frac{\partial}{\partial \eta} \left(\frac{\Omega(a, \eta)}{kT} \right)_{\beta, a}. \end{aligned} \quad (7)$$

In terms of the diagrammatic expansion indicated by (1), the pressure of the gas is given by:

¹⁰ For a concise discussion of the grand canonical ensemble see L. O. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, 1958), pp. 105-7.

$$\frac{\Omega(a)}{kT} = \log Z_0(a) + Q_1 + \sum_{n=2} Q_n + \sum Q_{\text{non-ring}} \quad (8)$$

The first term of (8) is the quantum ideal-gas pressure, evaluated for the chemical potential of the interacting system. It should be noted that since a depends on the interaction, even the ideal-gas term depends implicitly on e^2 . The quantity Q_1 is the contribution to the pressure from two particles interacting once, and is analogous to the energy of two particles in first-order perturbation theory. As in perturbation theory when applied to interacting fermions or bosons, Q_1 is composed of two parts, a direct interaction and an exchange interaction. The third term is the sum of the ring-diagram contributions. It will be seen that Q_n corresponds to certain terms in the n^{th} -order Rayleigh-Schroedinger perturbation theory. All the non-ring terms indicated in the last term of (8) will be neglected. The non-ring contributions will be discussed in a later article.

The form of $\log Z_0(a)$, the pressure of an ideal quantum gas, is well known, but will be discussed briefly in order to establish notation that will be needed later. The usual form of the quantum ideal-gas grand partition function is for Fermi statistics:

$$Z_0(a_0) = \prod_i \left(1 + e^{a_0 - \beta p_i^2 / 2m} \right)^{2s+1} \quad (9)$$

where p_i are the momenta of free-particle states in a box of volume V , $2s+1$ arises from the spin degeneracy of each state, and a_0 is the chemical potential of the noninteracting gas. Using (9), we obtain:

$$\begin{aligned} \log Z_0(a_0) &= (2s+1) \sum_i \left(1 + e^{a_0 - \beta p_i^2 / 2m} \right) \\ &= \frac{(2s+1) 4\pi V}{(2\pi \hbar)^3} \int_0^\infty dp \, p^2 \log \left(1 + e^{a_0 - \beta p^2 / 2m} \right). \quad (10) \end{aligned}$$

If the variable of integration in (10) is changed to $x = p/\bar{p}$, where $\bar{p} = (2mkT)^{1/2}$, and if we integrate once by parts, we have:

$$\log Z_0(a_0) = N \frac{(2s+1)4\pi\bar{p}^3}{(2\pi\hbar)^3 \rho} \cdot \frac{2}{3} \int_0^\infty \frac{dx x^4}{1 + \exp(-a_0 + x^2)} \quad (11)$$

The integral in (11) is an example of a type that occurs repeatedly. Following Chandrasekhar,¹¹ we shall use the function:¹²

$$\mathcal{J}_\nu(a_0) = \frac{2}{\Gamma(\nu+1)} \int_0^\infty \frac{dx x^{2\nu+1}}{1 + \exp(-a_0 + x^2)} \quad (12)$$

where the coefficient has been chosen so that the series expansion of (12) begins with $z_0 = e^{a_0}$, the activity of the ideal gas. This series expansion, which converges for $z_0 < 1$, is:

$$\mathcal{J}_\nu(a_0) = z_0 - \frac{z_0^2}{2^{\nu+1}} + \frac{z_0^3}{3^{\nu+1}} - \dots \quad (13)$$

The $\mathcal{J}_\nu$ functions defined in this way have the convenient property, which will be used often, that:

$$\mathcal{J}'_\nu(a) = \mathcal{J}_{\nu-1}(a) \quad (14)$$

It is also convenient to collect the physical quantities that multiply the integral in (11) into a dimensionless parameter ζ , defined as:

$$\zeta = \frac{(2\pi\hbar)^3 \rho}{(2s+1)\pi^{3/2} \bar{p}^3} \quad (15)$$

¹¹ S. Chandrasekhar, An Introduction to Study of Stellar Structure (Dover, 1957), p. 400.

¹² Numerical values of the $\mathcal{J}_\nu$ functions may be obtained from the tables of J. McDougall and E. C. Stoner, *Phil. Trans.* 237, 67 (1938). In terms of the F_k functions tabulated by them for $k=3/2$ and $1/2$, the corresponding $\mathcal{J}_\nu$ functions are $\mathcal{J}_{3/2} = (2/3)(4/\sqrt{\pi})F_{3/2}$ and $\mathcal{J}_{1/2} = (4/\sqrt{\pi})F_{1/2}$. They also give values of $F_{-1/2}$ and $F_{-3/2}$, though to less accuracy. These tables have been extended to include the cases for $k=5/2, 7/2, 9/2$, and $11/2$ by A. C. Beerm, M. N. Chase, and P. F. Choquard, *Helv. Phys. Acta* 28, 529 (1955).

In terms of the $\mathcal{L}_\nu$ functions and ζ , the ideal Fermi-gas pressure (11) is:

$$\log Z_0(a_0) = N \zeta^{-1} \mathcal{L}_{1/2}(a_0) . \quad (16)$$

Noting that $\zeta \sim \beta^{-3/2}$ and using (5), we obtain, for the internal energy,

$$\frac{E_0}{kT} = \frac{3}{2} N \zeta^{-1} \mathcal{L}_{3/2}(a_0) . \quad (17)$$

The chemical potential, $a_0 = \beta \mu_0$, of the noninteracting gas is determined by normalization to the number of particles. If (16) is differentiated with respect to a_0 according to (6) and (14) is used, the defining relation for a_0 is given as:

$$\mathcal{L}_{1/2}(a_0) = \zeta . \quad (18)$$

The ideal gas with Bose-Einstein statistics is treated in the same way beginning with (9), but with the 1 replaced with -1. Corresponding to the $\mathcal{L}_\nu$ functions for Fermi statistics, the corresponding functions for Bose statistics will be denoted by $\mathcal{J}_\nu$ and defined as:

$$\begin{aligned} \mathcal{J}_\nu(a_0) &= \frac{2}{\Gamma(\nu+1)} \int_0^\infty \frac{dx x^{2\nu+1}}{e^{-a_0 + x^2} - 1} \\ &= z_0 + \frac{z_0^2}{2^{\nu+1}} + \frac{z_0^3}{3^{\nu+1}} + \dots \end{aligned} \quad (19)$$

The $\mathcal{J}_\nu$ functions also have the following useful property:

$$\mathcal{J}'_\nu(a) = \mathcal{J}_{\nu-1}(a) . \quad (20)$$

The pressure, energy, and defining relation for a_0 are given by:

$$\log Z_0(a_0) = N \zeta^{-1} \mathcal{J}_{1/2}(a_0) , \quad (21)$$

$$\frac{E_0}{kT} = \frac{3}{2} N \zeta^{-1} \mathcal{J}_{3/2}(a_0) , \quad (22)$$

$$J_{1/2}(a_0) = \zeta. \quad (23)$$

The corresponding results for Boltzmann statistics are obtained by retaining only the first term of either the J_v or J_v functions, i.e., only z_0 .

In terms of the preceding results, the ideal-gas term in (8) for the interacting quantum gas, i.e., $e^2 \neq 0$, is:

$$\log Z_0(a) = \begin{cases} N \frac{J_{3/2}(a)}{J_{1/2}(a_0)} & \text{F.D.} \\ N \frac{J_{3/2}(a)}{J_{1/2}(a_0)} & \text{B.E.} \end{cases} \quad (24)$$

according to the type of statistics. The chemical potential of the real gas may be written as $a = a_0 + \delta a$, where δa depends on e^2 . At sufficiently high temperature and low density such that $\zeta \ll 1$, (24) reduces to the Boltzmann form:

$$\log Z_0(a) = N(z/z_0). \quad (25)$$

The interaction portion of the grand partition function, when expanded as indicated by (1) requires the evaluation of the various Q_L , one for each topologically distinct linked diagram. For a diagram involving n particles initially in states $(p_1, \sigma_1), (p_2, \sigma_2), \dots, (p_n, \sigma_n)$ and making r interactions among themselves, the general form of the Q_L for Fermi statistics, as shown by the analysis of Glassgold, Heckrotte, and Watson, is:

$$Q_L = \sum_{\sigma \sigma' \sigma'' \dots} \sum_{p p' p'' \dots} f^-(p_1) f^-(p_2) \dots f^-(p_n) f^+(p'_1) \dots f^+(p'_n) f^+(p''_1) \dots$$

$$\frac{1}{2\pi i} \int_C \frac{dw e^{-\beta w}}{w^2} \frac{\langle u \rangle_{FI_{r-1}} \langle u \rangle_{I_{r-2}} \dots \langle u \rangle_{I_2 I_1} \langle u \rangle_{I_1 O}}{(w-D_{r-1})(w-D_{r-2}) \dots (w-D_1)} \quad (26)$$

where

$$f^-(p) = \frac{1}{1 + \exp(-\alpha + \beta p^2/2m)}$$

$$f^+(p') = 1 - f^-(p') = \frac{1}{1 + \exp(-\alpha + \beta p'^2/2m)} \quad (27)$$

The quantity $f^-(p)$ is the probability that the initial state p is occupied, and $f^+(p')$ the probability that the intermediate state p' is unoccupied. The transition from an initial state O to a final state F takes place through $r-1$ intermediate states denoted by $1_1, 1_2, \dots, 1_{r-1}$. The summation is over all initial and intermediate spin orientations, and over all allowed values of the initial- and intermediate-state momenta of the n particles. The $D_1, \dots, D_{r-1}$ are the usual energy denominators of Rayleigh-Schroedinger perturbation theory, namely, the difference of the particle energies in the intermediate and initial states. The integral over the complex variable w is taken over the contour shown in Fig. 1 and is chosen so as to enclose the positive real axis, thus giving contributions from the simple poles at $D_1 \dots D_{r-1}$ and the double pole at $w=0$. The matrix elements for the pair potential $U(r_{ij})$ have the usual form:

$$\langle p'_1 \sigma'_1 p'_2 \sigma'_2 | U | p_1 \sigma_1 p_2 \sigma_2 \rangle$$

$$= \delta_{\sigma_1 \sigma'_1} \delta_{\sigma_2 \sigma'_2} \langle p'_1 p'_2 | U | p_1 p_2 \rangle - \delta_{\sigma_1 \sigma'_2} \delta_{\sigma_2 \sigma'_1} \langle p'_1 p'_2 | U | p_2 p_1 \rangle \quad (28)$$

Both the direct and exchange interaction terms of (28) give rise to the Kronecker $\delta(p'_1 + p'_2 - p_1 - p_2)$ which expresses momentum conservation. If p'_1 is replaced by $p_1 + q$ and p'_2 by $p_2 - q$, where q is the momentum transfer in a momentum-conserving transition, (28) becomes:

$$u(q) = \delta_{\sigma_1 \sigma_2} u(|p_1 - p_2 + q|) .$$

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Fig. 1. Contour of integration C for the w integral of Q_L , Eq. (26).

with

$$u(q) = \frac{1}{V} \int d\mathbf{r} \exp(i\mathbf{q} \cdot \mathbf{r}/\hbar) U(r). \quad (29)$$

The corresponding Q_L for a cluster of Bose particles is obtained from (21) by replacing $f^-(p)$ and $f^+(p')$ with the analogous quantities for Bose statistics, which are:

$$b^-(p) = \frac{1}{1 + \exp(-a + \beta p^2/2m)}$$

$$b^+(p') = 1 - b^-(p') = \frac{1}{1 - \exp(-a + \beta p'^2/2m)}. \quad (30)$$

The simplest diagram shown in Fig. 2 involves one interaction between two particles with zero momentum transfer, i.e., direct and exchange forward scattering. The contribution to $\beta\Omega$ is:

$$Q_1 = \frac{1}{2!} \sum_{\substack{p_1 p_2 \\ \sigma_1 \sigma_2}} f^-(p_1) f^-(p_2) \frac{1}{2\pi i} \int_C \frac{dw e^{-\beta w}}{w^2} \langle p_1 p_2 \sigma_1 \sigma_2 | U | p_1 p_2 \sigma_1 \sigma_2 \rangle$$

$$= - \frac{\beta}{2!} (2s+1)^2 \sum_{p_1 p_2} f^-(p_1) f^+(p_2) \left\{ u(0) - \frac{1}{(2s+1)} u(|p_1 - p_2|) \right\}. \quad (31)$$

The factor of $1/2!$ must be present to avoid counting identical states twice. The direct part of (31) represents, essentially, the self energy of the total charge, Ne , of the particles when spread continuously over the volume V . This self energy must be cancelled by an equal contribution from the continuous positive background required for electrical neutrality. The second term of (31), which represents forward scattering with exchange, gives a finite non-classical contribution which will be dealt with in Sec. IV.

The ring diagrams, which are expected to give the principle contribution to the correlation pressure and energy, are shown in Fig. 3 for clusters of

Fig. 2. Diagrammatic representation of a single interaction between two particles; a) is the direct interaction, and b) the exchange interaction. The vertical lines represent the propagation of particles in β space, the statistical-mechanical analogue of time.

a) $n=2$

b) $n=3$

c) $n=4$

d)

e)

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Fig. 3. The ring diagrams for clusters of 2, 3, and 4 particles. In the quantum-mechanical case the particles propagate along the vertical lines, which are connected by horizontal interaction lines that show the time ordering of the interactions. In the classical Mayer diagrams shown below each quantum diagram, the time order of the interactions is indicated by the letters a, b, c, and d.

2, 3, and 4 particles. Momentum conservation requires that the momentum transfer be the same for each interaction, and the last interaction returns the cluster of n particles to the states $p_1, \dots, p_n$ from which they started. In the cases of $n = 2$ and $n = 3$ there is only one distinct diagram, but in general there are $(n-1)!/2$ topologically different diagrams corresponding to the different time orderings of the interactions.¹³ The particle lines shown in each of the diagrams of Fig. 3 may be thought of as lines evenly spaced on the outside of a vertical cylinder. The diagrams used to represent the classical Ursell-Mayer cluster expansion are obtained from this cylindrical representation by looking down the cylinder. The particle lines then become points and are shown as the corners of polygons below the quantum-mechanical diagrams of Fig. 3. The interaction lines in the classical representation encircle the cylinder as a ring. The $3!/2 = 3$ quantum diagrams for $n = 4$. Figure 3, c., d., and e) can be shown in the classical Mayer representation only by writing in the order of the interactions as shown on the diagrams. Only the direct-interaction diagrams are shown in Fig. 3. The contribution of exchange interactions in the ring diagrams will be treated in detail in a later article.

If the general form (26) is used, the one diagram for $n = 2$ gives the contribution:

$$Q_2 = \frac{1}{2} \sum_{\substack{p_1 p_2 q \\ \sigma_1 \sigma_2}} f^-(p_1) f^+(p_1') f^-(p_2) f^+(p_2') u(q)^2 R_2(\beta) \quad (32)$$

¹³ Gell-Mann and Brueckner (*loc. cit.* 7.) use a different diagrammatic representation, and in their Fig. 1 for $n=4$ show $3! = 6$ diagrams, and, in general, count $(n-1)!/2$ pairs of diagrams. Each member of a pair represents one of the two directions around the ring in the Mayer diagrams. The two diagrams of a pair differing only by opposite directions around the ring are not topologically distinct, and of course give equal contributions.

where

$$R_2(\beta) = \frac{1}{2\pi i} \int_C \frac{dw e^{-\beta w}}{w^2} = \frac{1}{w - D_1} \quad (33)$$

$$\begin{aligned} D_1 &= \epsilon(p'_1) + \epsilon(p'_2) - \epsilon(p_1) - \epsilon(p_2) \\ &= \frac{1}{2m} \left[(p'_1)^2 - p_1^2 + (p'_2)^2 - p_2^2 \right]. \end{aligned}$$

Converting the sums to integrations, we have:

$$Q_2 = \frac{(2\pi+1)^2}{2} \left(\frac{V}{(2\pi\hbar)^3} \right)^3 \int dq u(q)^2 \int dp_1 f^-(p_1) f^+(p'_1) \int dp_2 f^-(p_2) f^+(p'_2) R_2(\beta). \quad (34)$$

The contour integral (33) is elementary, and gives:

$$\begin{aligned} R_2(\beta) &= \frac{e^{-\beta D_1}}{D_1^2} = \frac{1}{D_1^2} + \frac{\beta}{D_1} \\ &= \frac{\beta^2}{2!} - \frac{\beta^3 D}{3!} + \frac{\beta^4 D^2}{4!} - \dots \quad (35) \end{aligned}$$

The first term of the series expansion of $R_2(\beta)$ gives the classical result for Q_2 , valid at high temperature, i.e., β approaches 0.

For $n > 2$ there are $(n-1)!/2$ time orderings of the interactions among the n particles. A particular diagram for a time ordering will be denoted by the subscript α , and the contribution to $\beta\Omega$ from a cluster of n particles will be:

$$Q_n = \sum_{\alpha=1}^{(n-1)!/2} Q_{n\alpha}.$$

The combinatorial factor for each diagram for $n > 2$ is $n!/n! = 1$. The $1/n!$ is required to remove the degeneracy for identical states, i.e., when $p_1 = p_2 = \dots = p_n$, while the $n!$ is the number of ways the n particles may be placed on the ring. For $n = 2$ however, the factor is $1/2!$, since there is only one possible diagram. The $Q_{n\alpha}$ for a given diagram is:

$$Q_{na} = \sum_{\substack{q p_1 \dots p_n \\ \sigma_1 \dots \sigma_n}} \tilde{f}(p_1) f^*(p'_1) \dots \tilde{f}(p_n) f^*(p'_n) u(q)^n R_n(\beta) \quad (36)$$

$$= (2\pi)^n \left(\frac{V}{(2\pi\hbar)^3} \right)^{n+1} \int dq u(q)^n \int dp_1 \tilde{f}(p_1) f^*(p'_1) \dots \int dp_n \tilde{f}(p_n) f^*(p'_n) R_n(\beta) ,$$

where

$$R_n(\beta) = \frac{1}{2\pi i} \int_C \frac{dw e^{-\beta w}}{w^2} \prod_{i=1}^{n-1} \frac{1}{(w - D_{ai})} . \quad (37)$$

The complex integral may be evaluated conveniently by expanding the product in (37) in partial fractions. The result, as shown in Appendix A, is:

$$R_n(\beta) = \sum_{i=1}^{n-1} \frac{a_i}{D_{ai}} \left(e^{-\beta D_{ai}} - 1 \right) + (-1)^n \beta \prod_{i=1}^{n-1} \frac{1}{D_{ai}} , \quad (38)$$

where

$$a_i = \prod_{j \neq i}^{n-1} \frac{1}{(D_{ai} - D_{aj})} ,$$

and has the series expansion:

$$R_n(\beta) = (-1)^n \left\{ \frac{\beta^n}{n!} - \frac{\beta^{n+1}}{(n+1)!} \sum_i D_{ai} + \frac{\beta^{n+2}}{(n+2)!} \left(\sum_i D_{ai}^2 + \sum_{i < j} D_{ai} D_{aj} \right) - \dots \right\} \quad (39)$$

From (38) and (39), the zero-temperature-limit and the classical-limit forms of Q_n may be easily seen. In the very-high-temperature case, which gives the classical limit only the first term of (39) remains. Also, the probability functions $\tilde{f}(p)$ and $f^*(p')$ become:

$$\begin{aligned} \tilde{f}(p) &\rightarrow z e^{-\beta p^2/2m} \\ f^*(p') &\rightarrow 1 , \end{aligned}$$

so that

$$(2s+1) \frac{V}{(2\pi\hbar)^3} \int dp f^-(p) = N(z/z_0),$$

since (18) reduces to $z_0 = 1$. Hence, the classical form for Q_n with the use of (36), becomes:

$$Q_n^{\text{classical}} = \frac{(-1)^n}{2^n} \left(\frac{z}{z_0} \right)^n \beta^n \rho^n \frac{V}{(2\pi\hbar)^3} \int dq (V u(q))^n. \quad (40)$$

Equation (40) agrees with the classical form of the ring-diagram contribution obtained by Montroll and Ward. This result is similar to the ring-cluster-integral contribution of the Mayer cluster expansion.¹⁴ Note that (40) does not actually depend directly on density, since $(z/z_0)\rho = z/\lambda_{th}^3$, where λ_{th} is the thermal de Broglie wavelength defined as $\lambda_{th} = \hbar/\bar{p}$. It is evident from the expansion (39) that the Q_{na} are equal to $O(\beta^n)$ for every time ordering, and that quantum-mechanical effects enter when the $O(\beta^{n+1})$ term must be retained. Since, for the Coulomb potential, $u(q)$ is proportional to $1/q^2$, the leading term of Q_n diverges as dq/q^{2n} , and the Debye-Hückel theory is obtained by formally summing the divergent terms before doing the q integration. The second term of (39) is of order q^2 ; hence, the retention of higher-order terms in (39), to obtain quantum corrections to the classical result, corresponds to summing lesser divergences.

At zero temperature ($\beta \rightarrow \infty$), only the second term of (38) contributes to Q_n . The probability functions $f^-(p)$ and $f^+(p')$ reduce to:

$$f^-(p) = \begin{cases} 1 & p < p_F \\ 0 & p > p_F \end{cases}$$

$$f^+(p') = \begin{cases} 0 & p' < p_F \\ 1 & p' > p_F \end{cases}.$$

¹⁴(loc. cit. 9) For a comparison with the ring-cluster integrals of the Mayer expansion, see Appendix B of the paper by Montroll and Ward.

where p_f is the Fermi momentum of the interacting system. (The chemical potential as $T \rightarrow 0$ is $\alpha = \beta p_F^2/2m$.) The contribution to Ω from a cluster of n particles is:

$$\lim_{\beta \rightarrow \infty} Q_n/\beta = (-1)^n (2s+1)^n \left(\frac{V}{(2\pi\hbar)^3} \right)^{n+1} \int d\mathbf{q} u(\mathbf{q})^n \int_{\substack{p_1 \dots p_n \\ p_i < p_F \\ |\mathbf{p} + \mathbf{q}| > p_F}} d\mathbf{p}_1 \dots d\mathbf{p}_n \sum_{a=1}^{(n-1)/2} \prod_{i=1}^{n-1} \frac{1}{D_{ai}} \quad (41)$$

Equation (41) is the form of Rayleigh-Schroedinger perturbation theory used by Gell-Mann and Brueckner in their calculation of the correlation energy of a completely degenerate electron gas.

The Q_L , as defined by (26), is a term of a perturbation expansion of the grand partition function using plane waves as the basis functions, and is valid at every temperature. To obtain a more convenient form for intermediate temperatures, we use an iterated expression for the complex integral

$R_n(\beta)$:

$$R_{na}(\beta) = (-1)^n \int_0^\beta d\beta_n \int_0^{\beta_n} dt_{n-1} e^{-D_{an-1}t_{n-1}} \int_0^{\beta_n - t_{n-1}} dt_{n-2} e^{-D_{an-2}t_{n-2}} \dots \int_0^{\beta - t_{n-1} - \dots - t_2} dt_1 e^{-D_{a1}t_1} \quad (42)$$

which may be proved by induction to give (38). Next, we want a change of integration variables that will separate the particle momenta in the D_{ai} so that only one momentum appears in each integral. To effect this separation a set of intermediate temperatures analogous to interaction times are introduced according to the scheme indicated in Fig. 4 for one of the diagrams (Fig. 3, e) of a cluster of four particles. The temperatures $\beta_1, \beta_2, \beta_3$, and β_4 indicate the "times" of the interactions subject to the restriction for the diagram of Fig. 4 that $\beta > \beta_4 > \beta_2 > \beta_3 > \beta_1$. The t variables in (42) are thus the "time" differences between interactions:

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Fig. 4. One of the diagrams for a cluster of four particles showing the intermediate temperatures corresponding to interaction "times." Also shown are the energy denominators for each of the intermediate states.

$$\begin{aligned}t_1 &= \beta_3 - \beta_1 \\t_2 &= \beta_2 - \beta_3 \\t_3 &= \beta_4 - \beta_2\end{aligned}\quad (43)$$

and indicate the duration of the three intermediate states with energy denominators D_1 , D_2 , and D_3 , respectively. The energy denominators are sums of particle excitation energies:

$$\Delta = \epsilon(p') - \epsilon(p) = (p'^2 - p^2)/2m = (q^2 + 2q \cdot p)/2m \quad (44)$$

In terms of the β variables of (43), $R_{4a}(\beta)$ for this diagram becomes:

$$\begin{aligned}R_{4a}(\beta) &= \int_0^\beta d\beta_4 \int_0^{\beta_4} dt_3 e^{-(\Delta_1 + \Delta_4)t_3} \int_0^{\beta_4 - t_3} dt_2 e^{-(\Delta_1 + \Delta_2 + \Delta_3 + \Delta_4)t_2} \int_0^{\beta_4 - t_3 - t_2} dt_1 e^{-(\Delta_1 + \Delta_2)t_1} \\&= \int_0^\beta d\beta_4 \int_0^{\beta_4} d\beta_2 \int_0^{\beta_2} d\beta_3 \int_0^{\beta_3} d\beta_1 e^{-(\beta_4 - \beta_1)\Delta_1 - (\beta_2 - \beta_1)\Delta_2 - (\beta_2 - \beta_3)\Delta_3 - (\beta_4 - \beta_3)\Delta_4}\end{aligned}\quad (45)$$

For any diagram, $R_{na}(\beta)$ may be written down by inspection in the same fashion. By interchanging the order of the temperature and momentum integrations, we may further write the Q for the diagram shown in Fig. 4 as:

$$\begin{aligned}Q_{4a} &= \frac{V}{(2\pi\hbar)^3} \int d\mathbf{q} u(\mathbf{q})^4 H_{4a}(\mathbf{q}, \beta) \\H_{4a}(\mathbf{q}, \beta) &= \int_0^\beta d\beta_4 \int_0^{\beta_4} d\beta_2 \int_0^{\beta_2} d\beta_3 \int_0^{\beta_3} d\beta_1 G(\beta_4 - \beta_1) G(\beta_2 - \beta_1) G(\beta_2 - \beta_3) G(\beta_4 - \beta_3) \quad (46)\end{aligned}$$

where

$$\begin{aligned}G(\mathbf{q}, \tau) &= \frac{(2s+1)V}{(2\pi\hbar)^3} \int d\mathbf{p} f^-(\mathbf{p}) f^+(\mathbf{p}') e^{-\tau\Delta} \text{ for } 0 < \tau < \beta \\&= 0 \quad \text{for } \tau < 0, \tau > \beta\end{aligned}\quad (47)$$

The quantity $G(\mathbf{q}, \tau)$ is the temperature-dependent particle propagator after excitation by the momentum transfer $\mathbf{q}$. If the product $f^-(\mathbf{p}) f^+(\mathbf{p}')$ is

expanded in powers of the activity, $z = e^a$, one obtains for (47):

$$G(q, \tau) = \frac{(2s+1)V}{(2\pi\hbar)^3} \sum_{r=1}^{\infty} (-1)^{r+1} z^r \sum_{j=0}^{r-1} \int dp \exp - \frac{p^2}{2m} [(r-j)\beta - \tau] \exp \left[- \frac{(p+q)^2}{2m} (j\beta + \tau) \right], \quad (48)$$

which is identical to the fermion propagator obtained by Montroll and Ward (their Eq. 5.17). When the momentum integration is carried out, (48) becomes:

$$G(q, \tau) = \frac{(2s+1)V}{(2\pi\hbar)^3} \sum_{r=1}^{\infty} (-1)^{r+1} z^r \sum_{j=0}^{r-1} \left(\frac{2\pi m}{\beta r} \right)^{3/2} \exp \left[- \frac{q^2}{2m\beta r} (j\beta + \tau) (r\beta - j\beta - \tau) \right]$$

$$= N \zeta^{-1} \sum_{r=1}^{\infty} \frac{(-1)^{r+1} z^r}{r^{3/2}} \sum_{j=0}^{r-1} \exp \left[- (q/\beta)^2 (j + \tau/\beta) (r - j - \tau/\beta) / r \right]. \quad (49)$$

If (49) is used, a useful symmetry property of the propagator may be proved.

One notes that $G(\tau)$ is equal to $\sum_r G_r(\tau)$ and that $G_r(\tau)$ has the form:

$$G_r(\tau) = \sum_{j=0}^{r-1} f \left[(j + \tau/\beta) (r - j - \tau/\beta) \right]. \quad (50)$$

If we change the summation variable from j to $j' = r - j - 1$, then (50) becomes:

$$G_r(\tau) = \sum_{j'=0}^{r-1} f \left[(r - j' - 1 + \tau/\beta) (j' + 1 - \tau/\beta) \right] = G_r(\beta - \tau), \quad (51)$$

and consequently:

$$G(q, \beta - \tau) = G(q, \tau). \quad (52)$$

The Q_{na} for any time ordering may be written in the following form, similar to (46):

$$H_{na}(\beta) = \int_0^\beta \dots \int_0^\beta d\beta_n \dots d\beta_1 G(\beta_n - \beta_1) G(\beta_2 - \beta_1) \dots G(\beta_n - \beta_{n-1}). \quad (53)$$

A particular time ordering is expressed by choosing the upper limits of the integrations in (53) as a permutation of the intermediate temperatures, $\beta_n \dots \beta_2$.

For example, with $n=4$, the contributions of the three diagrams of Fig. 3 are obtained by choosing the limits of the temperature integrations, respectively, so that $\beta > \beta_4 > \beta_3 > \beta_2 > \beta_1$, $\beta > \beta_1 > \beta_3 > \beta_2 > \beta_4$, and $\beta > \beta_4 > \beta_2 > \beta_3 > \beta_1$. Finally, the sum of the $(n-1)!/2$ diagrams for an n -particle cluster may be conveniently written as a single iterated integral:

$$Q_n = \frac{V}{(2\pi\hbar)^3} \int d\mathbf{q} u(\mathbf{q})^n H_n(\mathbf{q}, \beta)$$

$$H_n(\mathbf{q}, \beta) = \sum_{a=1}^{(n-1)!/2} H_{na}$$

$$= \frac{(-1)^n}{2^n} \int_0^\beta \dots \int_0^\beta d\beta_1 \dots d\beta_n G(|\beta_n - \beta_1|) G(|\beta_2 - \beta_1|) \dots G(|\beta_n - \beta_{n-1}|) \quad (54)$$

The iterated temperature integral of (54) may be reduced to a sum of the n^{th} power of the eigenvalues of a homogeneous Fredholm integral equation with the propagator as a kernel:

$$\lambda_k(\mathbf{q}) \psi_k(\beta') = \int_0^\beta d\beta'' \psi_k(\beta'') G(\mathbf{q}, |\beta' - \beta''|) \quad (55)$$

The solutions of (55), $\psi_k(\beta')$, form a complete, normalized, orthogonal set of functions corresponding to the eigenvalues $\lambda_k(\mathbf{q})$. Using Mercers' theorem, we may expand the propagator as:¹⁵

$$G(\mathbf{q}, |\beta' - \beta''|) = \sum_{k=-\infty}^{\infty} \lambda_k(\mathbf{q}) \psi_k^*(\beta') \psi_k(\beta'') \quad (56)$$

If (56) and the orthonormality of $\psi_k(\beta')$ are used, the iterated integral of (54) becomes:

$$H_n(\mathbf{q}, \beta) = \frac{(-1)^n}{2^n} \sum_{k=-\infty}^{\infty} \lambda_k^n(\mathbf{q}) \quad (57)$$

¹⁵ F. G. Tricomi, Integral Equations (Interscience Publishers, 1957), p. 124-7.

The $\lambda_k(q)$ are obtained from the integral equation, (55). The procedure is to use an assumed form of the eigenfunctions, namely:

$$\psi_k(\beta') = \beta^{-1/2} e^{2\pi i k \beta' / \beta} \quad (58)$$

and verify that this choice satisfies the integral equation. The right-hand side of (55) may be written in two parts as:

$$\int_0^\beta d\beta' \psi_k(\beta') G(\beta' - \beta'') + \int_{\beta'}^\beta d\beta'' \psi_k(\beta'') G(\beta' - \beta'') .$$

By changing variables to $\tau = \beta' - \beta''$ in the first part and $\beta - \tau = \beta' - \beta''$ in the second part, and using the assumed sinusoidal form of $\psi_k(\beta')$, one verifies that (58) does satisfy the integral equation, and one is left with the eigenvalue as:

$$\lambda_k(q) = \int_0^\beta d\tau e^{-2\pi i k \tau / \beta} G(\tau) + \int_\beta^\beta d\tau e^{-2\pi i k \tau / \beta} G(\beta - \tau) \quad (59)$$

Using the symmetry property of the propagator, Eq. (52), we find that the eigenvalue reduces to a single integral:

$$\lambda_k(q) = \int_0^\beta d\tau e^{-2\pi i k \tau / \beta} G(q, \tau) \quad (60)$$

which agrees with the Montroll and Ward result, but has been derived differently.¹⁶ The eigenvalue for bosons is also given by (60), but the boson propagator is:

¹⁶ In the present derivation it was not necessary to assume a periodic extension of the propagator, i.e., $G(\tau + \beta) = G(\tau)$, as they did. The proof of the symmetry relation, Eq. (52), was shown to the author by Howard Levine. It was also pointed out by Dr. Levine that the propagator is a function of $|\beta' - \beta''|$ only when both β' and β'' are in the range 0 to β , and since the propagator is zero for β' or β'' outside of this range, the same is true for $\psi_k(\beta)$. Thus, $\psi_k(\beta)$ is a sinusoidal function with only one period; it is given by (58) for $0 < \beta' < \beta$ but is otherwise zero.

$$G(q, \tau) = \frac{(2s+1)V}{(2\pi\hbar)^3} \int d\mathbf{p} \, b^-(\mathbf{p}) \, b^+(\mathbf{p}') \, e^{-\tau\Delta} \quad (61)$$

Equation (61) has a power-series expansion in z given by the fermion propagator expansion (49), but with the $(-1)^{r+1}$ replaced by 1.

Changing the variable of the temperature integration in (60) to $x = \tau/\beta$, and the momentum integration in the propagator to $y = \mathbf{p}/\mathbf{p}$, and multiplying and dividing by ζ , we may rewrite the eigenvalue expression as:

$$\lambda_k(q) = V \rho \beta \mathcal{L}(q/\mathbf{p}, 2\pi k) \quad (62)$$

where

$$\mathcal{L}(q/\mathbf{p}, 2\pi k) = \int \frac{dy}{\pi^{1/2}} \frac{f^-(y)f^+(y)}{\zeta} \int_0^1 dx \, e^{-x(y'^2 - y^2) + 2\pi i k x} \quad (63)$$

If the expansion of the propagator (49) is used, an expansion of the dimensionless function $\mathcal{L}(q/\mathbf{p}, 2\pi k)$ in powers of $(q/\mathbf{p})^2$ may be obtained, convergent for all values of q . For large values of the momentum transfer, the asymptotic form of $\mathcal{L}(q/\mathbf{p}, 2\pi k)$ is $O(\mathbf{p}^2/q^2)$ for all k . For small q , the $k=0$ eigenvalue behaves as $\mathcal{L}(q/\mathbf{p}, 0) \propto \text{const.} - O(q^2)$, whereas for $k \neq 0$, it begins with $O(q^2)$. It should be noted that the eigenvalue as given by (62) is still a function of the activity z , not the density ρ , since ρ/ζ is independent of density. The misleading way of writing λ_k in (62) is, however, convenient for later work.

Returning now to the ring-integral contribution to $\beta\Omega$, we find:

$$\begin{aligned} (\beta\Omega)_{\text{ring}} &= \sum_{n=2}^{\infty} Q_n \\ &= \frac{V}{(2\pi\hbar)^3} \sum_{n=2}^{\infty} \frac{(-1)^n}{2^n} \int d\mathbf{q} \sum_{k=-\infty}^{\infty} \left(u(q) \lambda_k(q) \right)^n \end{aligned} \quad (64)$$

Equation (64) is well defined for any pair potential $U(r)$ that has a Fourier transform; however, the ring diagrams are a sensible choice for the physical problem only when $U(r)$ has an extremely long range. The Coulomb potential has a Fourier transform when defined as $U(r) = (e^2/r)e^{-\epsilon r}$, with the result using (29).

$$u(q) = \frac{4\pi e^2 \hbar^2}{V(q^2 + \epsilon^2)} \quad (65)$$

If the limit $\epsilon \rightarrow 0$ is taken, then each Q_n in (64) diverges. However, by retaining $\epsilon \neq 0$, Q_n is formally finite and the interchange of the q integration and n summation may be justified. The n summation is convergent only for q and ϵ large enough so that $u(q)\lambda_k(q) < 1$, but nevertheless represents the integrand correctly for all q . After interchanging the order of the k and n summations, we find that (64) becomes:

$$(\beta\Omega)_{\text{ring}} = \frac{1}{2} \cdot \frac{V4\pi}{(2\pi\hbar)^3} \int_0^\infty dq q^2 \sum_k \left\{ u(q)\lambda_k(q) - \ln(1 + u(q)\lambda_k(q)) \right\} \quad (66)$$

For the Coulomb potential, using (65) and (62), we have:

$$u(q)\lambda_k(q) = \frac{(4\pi e^2 \beta p) \hbar^2 \mathcal{L}(q/\bar{p}, 2\pi k)}{q^2 + \epsilon^2} \quad (67)$$

After taking the limit $\epsilon \rightarrow 0$, we find that the integrand of (66) is still finite at $q = 0$. It is convenient to rewrite (67) in terms of the dimensionless parameter y :

$$y^2 = \frac{(4\pi e^2 \beta p) \hbar^2}{\bar{p}^2} = \left(\kappa_{\text{th}} / \lambda_D \right)^2 \quad (68)$$

where $\lambda_D = (4\pi e^2 \beta p)^{-1/2}$ is the classical Debye screening length for a one-component gas. After changing the integration variable in (66) to $v = q/\bar{p}$, and adding the ideal gas term, we find the ring-integral approximation to the equation of state of a one-component gas to be:

$$\frac{\Omega(\alpha)}{kT} = \bar{N} \frac{\mathcal{L}_{3/2}(\alpha)}{\zeta} + \frac{1}{2} \cdot \frac{4\pi V p^3}{(2\pi\hbar)^3} \int_0^\infty dv v^2 \sum_k \left\{ (\gamma^2/v^2) \mathcal{L}(v, 2\pi k) - \ln \left(1 + (\gamma^2/v^2) \mathcal{L}(v, 2\pi k) \right) \right\} \quad (69)$$

The chemical potential α is determined by normalization to the number of particles $\bar{N}$ in the volume V ; when (69) is differentiated with respect to α according to (6) and $\bar{N}$ is cancelled, the following remains as the defining equation for α :

$$1 = \frac{\mathcal{L}_{1/2}(\alpha)}{\zeta} + \frac{1}{2} \frac{4\pi p^3}{(2\pi\hbar)^3} \int_0^\infty dv \sum_k \frac{\gamma^4 \mathcal{L}(v, 2\pi k)}{[v^2 + \gamma^2 \mathcal{L}(v, 2\pi k)]} \frac{\partial \mathcal{L}}{\partial \alpha} \quad (70)$$

In the limit of no interaction, $e^2 = 0$, (70) reduces to (18).

At any temperature, (69) and (70) are parametric equations in α for the equation of state of a one-component gas of fermions or bosons, for densities such that the non-ring and exchange diagrams may be neglected. In the zero-temperature limit, Montroll and Ward have shown that the Gell-Mann and Brueckner expression of the correlation energy of an electron gas of high density may be derived from (69) and (70). Similarly, in the opposite limit of very high temperature and low density, they obtained from (69) and (70) the classical-limit result of Debye and Hückel. For temperatures and densities between these two extreme limits, the mathematical analysis required for the v integration and k summation in (69) is very much more difficult. The evaluation of (69) for a very degenerate gas at finite temperature and the criterion for the validity of the ring-diagram approximation will be deferred to a later article.

III. THE NEAR-CLASSICAL LIMIT

The general expression for the sum of the ring diagrams (66) may be used to obtain useful analytical formulae for a slightly degenerate gas for

which the density is high enough so that there are some corrections due to quantum statistics. The true classical limit is obtained by setting $\hbar = 0$ in the near-classical-limit formulae.

The significant contribution to the q integration of (66) comes from $q \sim 0$, and corresponds to interactions between particles at great distances. The classical limit and near-classical-limit form of (66) may be obtained by neglecting terms of $O(q^2)$. Since only the $k = 0$ eigenvalue has a nonzero value at $q = 0$, this approximation simplifies the k summation to one term. To find the $q = 0$ value of λ_0 , we note that the $f^-(y)f^+(y')$ factor in the eigenvalue expression (63) may be written as:

$$\begin{aligned} f^-(y)f^+(y') &= f^-(y)(1-f(y)) - f^-(y)(f^-(y') - f^-(y)) \\ &= \frac{d}{da} f^-(y) + O(q^2/p^2), \end{aligned}$$

and, consequently,

$$\mathcal{L}(q/p, 0) = \frac{1}{\zeta} \frac{d}{da} \mathcal{J}_{1/2}(a) - O(q^2/p^2) = \zeta^{-1} \mathcal{J}_{-1/2}(a) - \dots \quad (71)$$

Since the quantity $\zeta^{-1} \mathcal{J}_{-1/2}(a)$ occurs fairly often and always in connection with e^2 , it is convenient to denote it by a separate symbol:

$$\theta^2(a) \equiv \zeta^{-1} \mathcal{J}_{-1/2}(a). \quad (72)$$

Using (71) and dropping quantities of $O(q^2)$, we have, for the ring-integral contribution to $\beta\Omega$,

$$(\beta\Omega)_{\text{ring}} \approx \frac{1}{\zeta} - \frac{4\pi V}{(2\pi\hbar)^3} \int_0^\infty dq q^2 \left\{ x_0(q) - \ln(1 + x_0(q)) \right\}. \quad (73)$$

with

$$x_0(q) = u(q) \lambda_0(q) \approx (\hbar/\lambda_D q)^2 \theta^2(a).$$

The q integral is elementary in this approximation and gives:

$$\begin{aligned}
 (\beta\Omega)_{\text{ring}} &\approx \frac{2\pi V}{(2\pi\hbar)^3} \cdot \frac{\pi}{3} \left(\frac{\hbar\theta(a)}{\lambda_D} \right)^3 \\
 &= \frac{2}{3} N \Lambda \theta^3(a) = \frac{V\theta^3(a)}{12\pi\lambda_D^3} ,
 \end{aligned} \tag{74}$$

where

$$\Lambda = \frac{e^2/2\lambda_D}{kT} = \sqrt{\pi} e^3 \beta^{3/2} \rho^{1/2} . \tag{75}$$

The dimensionless parameter Λ is the ratio of the classical Debye-Hückel potential energy per electron, $e^2/2\lambda_D$, to the thermal energy kT . In the near-classical limit it may be expected that the ring diagrams give the leading contribution to the thermodynamic functions of a gas when Λ is small.

If the ideal gas term and (74) are retained, the logarithm of the grand partition function is given by:

$$\beta\Omega(a) = \bar{N} \left\{ \zeta^{-1} \mathcal{Q}_{3/2}(a) + \frac{2}{3} \Lambda \theta^3(a) \right\} . \tag{76}$$

Noting that $\Lambda \zeta^{-3/2}$ has a temperature dependence of $\beta^{-3/4}$, we find for the internal energy:

$$\frac{\bar{E}(a)}{kT} = -\beta \frac{\partial}{\partial \beta} \left(\frac{\Omega}{kT} \right)_a = \bar{N} \left\{ \frac{3}{2} \zeta^{-1} \mathcal{Q}_{3/2}(a) + \frac{1}{2} \Lambda \theta^3(a) \right\} . \tag{77}$$

Similarly, the potential energy due to the correlation of the interacting particles is found by using (7), thus:

$$\beta \bar{U}(a) = -\bar{N} \Lambda \theta^3(a) . \tag{78}$$

The chemical potential is determined by:

$$\bar{N} = \frac{\partial}{\partial a} \left(\frac{\Omega}{kT} \right)_\beta = \bar{N} \left\{ \frac{\mathcal{Q}_{1/2}(a)}{\zeta} + \Lambda \left(\frac{\mathcal{Q}_{1/2}(a)}{\zeta} \right)^{1/2} \left(\frac{\mathcal{Q}_{3/2}(a)}{\zeta} \right) \right\} . \tag{79}$$

The previous four equations give the thermodynamic functions of a one-component gas in the near-classical limit. For convenience in numerical calculations, it would be desirable if the dependence on a could be

eliminated, and the pressure and energy written as functions of density. To accomplish this end, we may treat a as a sum of two parts, $a = a_0 + \delta a$, where a_0 is the chemical potential of the noninteracting gas defined by (18), and δa is the modification due to the interaction. To find δa , at least to the lowest order of the coupling constant, we expand the $\mathcal{Q}_v$ functions (or the $\mathcal{Q}$ functions, for Bose statistics) in a Taylor series in δa about a_0 . Equation (79) becomes:

$$1 = \zeta^{-1} \left[\mathcal{Q}_{1/2}(a_0) + \delta a \mathcal{Q}_{-1/2}(a_0) + \dots \right] + \Lambda \left(\frac{\mathcal{Q}_{-1/2}(a_0 + \delta a)}{\zeta} \right)^{1/2} \left(\frac{\mathcal{Q}_{-1/2}(a_0 + \delta a)}{\zeta} \right) \quad (80)$$

Solving for δa from (80), we have:

$$\delta a = - \Lambda \theta_0 \frac{\mathcal{Q}_{-3/2}(a_0)}{\mathcal{Q}_{-1/2}(a_0)} + O(\Lambda^2), \quad (81)$$

where

$$\theta_0^2 \equiv \theta^2(a_0) = \frac{\mathcal{Q}_{-1/2}(a_0)}{\mathcal{Q}_{1/2}(a_0)} = 1 - \frac{z_0}{2^{3/2}} + \left(\frac{2}{3^{3/2}} + \frac{1}{8} \right) z_0^2 - \dots \quad (82)$$

The quantity θ_0^2 is a measure of the degeneracy of a Fermi gas. In the high-temperature limit $\theta_0 \rightarrow 1$, and in the zero-temperature limit $\theta_0 \rightarrow 0$.

Similarly, for a Bose gas the degeneracy parameter is:

$$\theta_0^2 = \frac{\mathcal{Q}_{-1/2}(a_0)}{\mathcal{Q}_{1/2}(a_0)} = 1 + \frac{z_0}{2^{3/2}} + \left(\frac{2}{3^{3/2}} + \frac{1}{8} \right) z_0^2 + \dots \quad (83)$$

and is greater than 1 for any deviation from classical statistics. The quantity

δa may be conveniently written as:

$$\delta a = - \Lambda \theta_0^3 + \Lambda \theta_0 \eta, \quad (84)$$

where

$$\begin{aligned} \eta &= \frac{\mathcal{Q}_{-1/2}(a_0)}{\mathcal{Q}_{1/2}(a_0)} - \frac{\mathcal{Q}_{-3/2}(a_0)}{\mathcal{Q}_{-1/2}(a_0)} \\ &= \frac{z_0}{2^{3/2}} - \left(\frac{4}{3^{3/2}} + \frac{3}{8} \right) z_0^2 + \dots \end{aligned} \quad (85)$$

for Fermi statistics, and

$$\begin{aligned}\eta &= \frac{\mathcal{J}_{-1/2}(a_0)}{\mathcal{J}_{1/2}(a_0)} - \frac{\mathcal{J}_{-3/2}(a_0)}{\mathcal{J}_{-1/2}(a_0)} \\ &= -\frac{a_0^2}{2^{3/2}} - \left(\frac{4}{3^{3/2}} + \frac{3}{8}\right)a_0^2 - \dots\end{aligned}\quad (86)$$

for Bose statistics. In the near-classical limit η is small, since $a_0 \sim \zeta \ll 1$.

After expanding $\mathcal{J}_{3/2}(a_0 + \delta a)$ and using (84) in (76) and (77), we have, for the pressure and energy of a one-component gas in terms of density through a_0 to order e^3 in the coupling constant,

$$\begin{aligned}\frac{PV}{kT} &= N \left\{ \zeta^{-1} \mathcal{J}_{3/2}(a_0) - \frac{1}{3} \Lambda \theta_0^3 + \Lambda \theta_0 \eta + O(\Lambda^2) \right\} \\ \frac{E}{kT} &= N \left\{ \frac{3}{2} \zeta^{-1} \mathcal{J}_{3/2}(a_0) - \Lambda \theta_0^3 + \frac{3}{2} \Lambda \theta_0 \eta + O(\Lambda^2) \right\} \\ \frac{U}{kT} &= -N \Lambda \theta_0^3 + O(\Lambda^2).\end{aligned}\quad (87)$$

There is no point in calculating the $O(\Lambda^2)$ terms until some of the non-ring terms that may also give $O(\Lambda^2)$ are evaluated. These expressions give the thermodynamic functions for temperatures and densities for which deviations from the purely classical expressions ($\theta_0^2 = 1$ and $\eta = 0$), using Boltzmann statistics, first begin to appear. They are valid for values of θ_0^2 between 1 and some lower limit of the order of 0.9. For a more degenerate gas (i. e., $\theta_0^2 < 0.9$), the approximation of neglecting $O(\Lambda^2)$ terms in the evaluation (69) is no longer valid. The complete evaluation of (69) will give (74), plus non-classical terms involving higher powers of γ^2 .

The pressure and energy formulae (87) satisfy the virial theorem, $PV = (2/3)T + (1/3)U$, where $E = T + U$. The average kinetic energy is given by:

$$T/kT = N \left\{ \frac{3}{2} \zeta^{-1} \mathcal{J}_{3/2}(a_0) + \frac{3}{2} \Lambda \theta_0 \eta \right\}.\quad (88)$$

The η term is seen to be a nonclassical correction to the ideal-gas form of $\bar{T}$, due to the change of probability $f(p)$ from

$$\left\{ 1 + \exp \left[-a_0 + \beta p^2/2m \right] \right\}^{-1} \quad \text{to} \quad \left\{ 1 + \exp \left[-(a_0 + ba) + \beta p^2/2m \right] \right\}^{-1}$$

as the interaction between particles is turned on.

IV. EXCHANGE PRESSURE AND ENERGY

We consider now the contribution to the pressure from the exchange interaction in the simplest diagram, Q_1 , i.e., forward scattering with exchange as shown in Fig. 2a. From (31) of Sec. II, this contribution is given by:

$$Q_{1x} = \frac{1}{2} \beta (2s+1) \sum_{p_1 p_2} f^-(p_1) f^-(p_2) u(p_1 - p_2). \quad (89)$$

After converting the summations to integrations and using the Fourier transform of the Coulomb potential, we have:

$$\begin{aligned} Q_{1x} &= \frac{1}{2} \frac{\beta}{(2s+1)} \left(\frac{(2s+1)V}{(2\pi\hbar)^3} \right)^2 \frac{4\pi e^2 \hbar^2}{V \bar{p}^2} \iint \frac{dp_1 dp_2}{\bar{p}^6} f^-(p_1) f^-(p_2) \frac{\bar{p}^2}{(p_1 - p_2)^2} \\ &= \frac{1}{2} \frac{N}{(2s+1)} V^2 \zeta^{-2} \mathcal{J}_x(a), \end{aligned} \quad (90)$$

where

$$\mathcal{J}_x(a) = \iint \frac{dy_1 dy_2}{\pi^3} \cdot \frac{f^-(y_1) f^-(y_2)}{(y_1 - y_2)^2}. \quad (91)$$

The steps of performing the integration of (91) are indicated in Appendix B.

The result is:

$$\mathcal{J}_x(a) = 2 \sum_{\substack{r_1=1 \\ r_2=1}} \frac{(-1)^{r_1+r_2} (r_1+r_2)^a}{\sqrt{r_1 r_2} (r_1+r_2)} = 2 \int_{-\infty}^{\infty} da' \mathcal{J}_{-1/2}(a')^2. \quad (92)$$

Considering only the ideal-gas term and the direct exchange interaction, we have for $\beta\Omega$.

$$\beta\Omega(a) = N \left\{ \zeta^{-1} \mathcal{Q}_{3/2}(a) + Q_{1x}(a) + \dots \right\}, \quad (93)$$

and noting that the temperature dependence of γ^2/ζ^2 is β^{-1} , we find that the internal energy is given by:

$$\beta E(a) = N \left\{ \frac{3}{2} \zeta^{-1} \mathcal{Q}_{3/2}(a) + Q_{1x}(a) + \dots \right\}. \quad (94)$$

Also, since Q_{1x} is $\propto(e^2)$ in the coupling constant, (7) gives the potential energy due to the exchange interaction as:

$$\beta U_x(a) = - N Q_{1x}. \quad (95)$$

These results, Eqs. (93), (94), and (95), are all expressed in terms of a which also depends on the magnitude of the exchange interaction, and is determined by:

$$\bar{N} = \frac{\partial}{\partial a} \left(\frac{\Omega}{kT} \right) = N \zeta^{-1} \mathcal{Q}_{1/2}(a) + \frac{\partial Q_{1x}}{\partial a} + \dots \quad (96)$$

The chemical potential is composed of several parts:

$$a = a_0 + (\delta a)_x + (\delta a)_{\text{ring}} + (\delta a)_{\text{non-ring}},$$

where $(\delta a)_{\text{ring}}$ is given by (81) and is $\propto(e^3)$ in the coupling constant. The non-ring portion is of higher order in e^2 . The exchange portion, $(\delta a)_x$, is $\propto(e^2)$ and hence may be treated independent of the ring contribution, at least to $\propto(e^2)$. Consequently, if $\mathcal{Q}_{1/2}(a_0 + (\delta a)_x)$ is expanded in Taylor series and the ring contribution is ignored, Eq. (96) gives:

$$\begin{aligned} (\delta a)_x &= - \frac{1}{N \theta_0^2} \frac{\partial Q_{1x}}{\partial a} + \dots \\ &= - \frac{\gamma^2 \theta_0^2}{(2\pi+1)} + \mathcal{O}(\gamma^4). \end{aligned} \quad (97)$$

By expanding $\mathcal{Q}_{3/2}(a_0 + (\delta a)_x)$ and using (97), we may write the pressure and energy as functions of a_0 to $\propto(e^2)$; the results are:

$$\begin{aligned} \frac{PV}{kT} &= N \left\{ \zeta^{-1} \mathcal{J}_{3/2}(a_0) - \frac{\gamma^2 \theta_0^2}{2(2s+1)} (1 - \eta_x(a_0)) + \alpha \gamma^4 \right\} \\ \frac{E}{kT} &= N \left\{ \frac{3}{2} \zeta^{-1} \mathcal{J}_{3/2}(a_0) - \frac{\gamma^2 \theta_0^2}{2(2s+1)} (1 - \frac{1}{2} \eta_x(a_0)) + \alpha \gamma^4 \right\} \end{aligned} \quad (98)$$

where

$$\begin{aligned} \eta_x(a_0) &= \frac{2 \int_0^{a_0} da' \mathcal{J}_{-1/2}^2(a')}{\mathcal{J}_{1/2}(a_0) \mathcal{J}_{-1/2}(a_0)} - 1 \\ &= \frac{a_0}{6\sqrt{2}} - \left(\frac{1}{3\sqrt{3}} - \frac{1}{6} \right) a_0^2 + \dots \end{aligned} \quad (99)$$

For the kinetic and potential energies separately, we find to $O(\epsilon^2)$:

$$\begin{aligned} \frac{U_x}{kT} &= - \frac{N \gamma^2 \theta_0^2}{2(2s+1)} (1 + \eta_x(a_0)) \\ \frac{T}{kT} &= N \left\{ \frac{3}{2} \zeta^{-1} \mathcal{J}_{3/2}(a_0) - \frac{\gamma^2 \theta_0^2}{2(2s+1)} (1 - 2\eta_x(a_0)) \right\} \end{aligned} \quad (100)$$

As given by (100), U_x and T satisfy the virial theorem, $PV = \frac{2}{3} T + \frac{1}{3} U_x$. In the near-classical limit, the main contribution to PV and E from the direct exchange interaction is of order of $\gamma^2 \theta_0^2$, a small quantity when compared with the ideal-gas kinetic energy. The $\eta_x(a_0)$ terms are small corrections to an already small quantity, since $a_0 \ll 1$ in the near-classical limit. Consequently, in this limit the increments to $\bar{U}$ and $\bar{T}$ due to the exchange interaction are nearly equal.

The formulae of (98) are valid for the entire temperature range. In the zero-temperature limit the internal-energy expression reduces to the well-known result for the exchange energy of an electron gas given by Mücke.¹⁷

¹⁷ W. Mücke, Z. Naturforsch. 5a, 192 (1950).

To obtain the low-temperature limit, we note that the chemical potential at $T = 0$ is $\mu_0 = p_{0F}^2 / 2m$, where p_{0F} is the usual Fermi momentum; hence near $T = 0$, we have $a_0 = \beta \mu_0 \approx (p_{0F} / p)^2$. The asymptotic forms of the various $\mathcal{J}_\nu$ functions are:

$$\begin{aligned} \mathcal{J}_{1/2}(a_0) &= \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^2 dx}{1 + e^{ax^2}} \\ &\xrightarrow{T \rightarrow 0} \frac{2}{\sqrt{\pi}} \int_0^{a_0^{1/2}} x^2 dx = \frac{2 a_0^{3/2}}{3\sqrt{\pi}} \\ \mathcal{J}_{3/2}(a_0) &= -\frac{4 a_0^{5/2}}{15\sqrt{\pi}}, \quad \mathcal{J}_{-1/2}(a_0) = \frac{a_0^{1/2}}{\sqrt{\pi}}. \end{aligned} \quad (101)$$

Hence, near $T = 0$,

$$\theta_0^2 \approx \frac{3}{2 a_0} = \frac{3}{2} \left(\frac{p}{p_{0F}} \right)^2. \quad (102)$$

Using the definition of $\eta_\lambda(a_0)$ and (101), we find:

$$\lim_{T \rightarrow 0} \eta_\lambda(a_0) = \frac{1}{2}. \quad (103)$$

Also, using the definitions of γ^2 and ζ and (101), we find near $T = 0$:

$$\begin{aligned} \frac{\gamma^2 \theta_0^2}{2s+1} &= \frac{1}{kT} \frac{e^2 p_{0F}}{m} \\ \zeta &= \frac{4}{3\sqrt{\pi}} \left(\frac{p_{0F}}{p} \right)^2. \end{aligned} \quad (104)$$

When these various results are used in (98), the zero-temperature limit of the pressure and energy of a Fermi gas is given by the following:

$$\begin{aligned}
 PV &= N \left\{ \frac{2}{5} \left(\frac{p_{0F}^2}{2m} \right) - \frac{e^2 p_{0F}}{4\pi\hbar} + \dots \right\}, \\
 E &= N \left\{ \frac{3}{5} \left(\frac{p_{0F}^2}{2m} \right) - \frac{3e^2 p_{0F}}{4\pi\hbar} + \dots \right\}.
 \end{aligned}
 \quad (105)$$

The second term of the energy expression is the zero-temperature exchange energy derived by Macke from first-order perturbation theory. The exchange energy and pressure have a density dependence of $\rho^{-1/3}$ in the $T=0$ limit, and of ρ in the high-temperature limit. Between these two limits there is no simple dependence on density.

For each direct interaction in the ring diagrams, an exchange interaction is also possible and will give rise to exchange correlation energy and pressure. For a cluster of two particles interacting twice, once directly and once with exchange, the contribution to the pressure and energy is finite at all temperatures, since the term $1/q^2$ for a direct interaction is replaced by $1/(q+p_1-p_2)^2$ for an exchange interaction. This contribution was calculated numerically by Gell-Mann and Brueckner for the zero-temperature electron gas (their $\epsilon_b^{(2)}$) and found to contribute only in the constant term of their result for the correlation energy. In the high-temperature case this exchange contribution is of order $\Delta\gamma$, and hence smaller than the sum of the direct-interaction ring terms by a factor of γ . The ring diagrams with three or more particles and one exchange interaction are divergent, but the divergence is of lower order than the corresponding direct-interaction terms. Since the exchange correlation energy and pressure are small in comparison with the Debye-Hückel term in the near-classical limit (i. e., for high temperature and low density so that $\gamma \ll 1$), the detailed treatment of exchange interactions in the ring terms will be reserved for a later paper in connection with the more complete evaluation of the direct ring interactions, Eq. (69).

V. APPLICATION TO A MULTICOMPONENT GAS

We consider now a real, fully ionized gas composed of N_e electrons and N_i ions of charge z_i , mass M_i , and spin s_i . Electrical neutrality requires $N_e = z_i N_i$. We may assume either Fermi or Bose statistics for the ions by using $f^*(p_i) f^*(p_i')$ or $b^*(p_i) b^*(p_i')$ in the expressions for the Q_n 's. Since only the ring diagrams will be used, no account is taken of the sequence of bound states possible for the electron-ion system. The grand partition function is:

$$\exp\left(\frac{\Omega(a_e, a_i)}{kT}\right) = \sum_{N_e, N_i} \text{Tr} \exp(a_e N_e + a_i N_i - \beta H_{N_e N_i})$$

$$= Z_0(a_e) Z_0(a_i) \exp\left(Q_1 + \sum_{n=2} Q_n\right), \quad (106)$$

where $a_e = \beta \mu_e$ and $a_i = \beta \mu_i$ are the chemical potentials of the electrons and ions, respectively. The Q_n 's now refer to all possible clusters of n_e electrons and n_i ions so that $n_e + n_i = n$. The chemical potentials, a_{e0} and a_{i0} , of the noninteracting particles are defined by:

$$\zeta_e = \frac{(2\pi\hbar)^3 \rho_e}{(2s_e + 1) v^{3/2} \bar{p}_e^3} = \mathcal{J}_{1/2}(a_{e0})$$

$$\zeta_i = \frac{(2\pi\hbar)^3 \rho_i}{(2s_i + 1) v^{3/2} \bar{p}_i^3} = \begin{cases} \mathcal{J}_{1/2}(a_{i0}) & \text{F. D.} \\ \mathcal{J}_{1/2}(a_{i0}) & \text{B. E.} \end{cases} \quad (107)$$

where

$$\rho_e = N_e/V, \quad \rho_i = N_i/V$$

$$\bar{p}_e = (2mkT)^{1/2}, \quad \bar{p}_i = (2M_i kT)^{1/2}.$$

The pressure of the component gas in the ring-diagram approximation is given by:

$$\frac{\Omega(a_e, a_i)}{kT} = N_e \zeta_e^{-1} J_{3/2}(a_e) + N_i \zeta_i^{-1} \left\{ \begin{array}{l} J_{3/2}(a_i) \\ J_{3/2}(a_i) \end{array} \right\} + Q_1 + \sum_{n=2} Q_n, \quad (108)$$

and the two chemical potentials are determined by normalizing to N_e and N_i according to:

$$N_e = \frac{\partial}{\partial a_e} \left(\frac{\Omega(a_e, a_i)}{kT} \right)_{\beta},$$

$$N_i = \frac{\partial}{\partial a_i} \left(\frac{\Omega(a_e, a_i)}{kT} \right)_{\beta}. \quad (109)$$

Equations (109) reduce to (107) for no interaction, $e^2 = 0$.

The treatment of the ring diagrams will be illustrated for the case $n = 2$. In the place of one diagram for two electrons, Fig. 2a, we now have the three diagrams of Fig. 5 which show the electron-electron, electron-ion, and ion-ion interactions. If $U(r)$ is taken equal to e^2/r , the interaction potential between electron and ion is given by $-z_i U(r)$, and for an ion-ion pair it by $z_i^2 U(r)$. The contribution from the three diagrams of Fig. 5 is:

$$Q_2 = Q_{2ee} + Q_{2ei} + Q_{2ii},$$

where Q_{2ee} is given by (34) and Q_{2ei} is:

$$Q_{2ei} = z_i^2 (2s_e + 1) (2s_i + 1) \left(\frac{V}{(2\pi\hbar)^3} \right)^3 \int d\mathbf{q} u(\mathbf{q})^2$$

$$\int d\mathbf{p}_e \tilde{f}(\mathbf{p}_e) \tilde{f}^*(\mathbf{p}_e^*) \int d\mathbf{p}_i \left\{ \begin{array}{l} \tilde{f}(\mathbf{p}_i) \tilde{f}^*(\mathbf{p}_i^*) \\ b^-(\mathbf{p}_i) b^+(\mathbf{p}_i^*) \end{array} \right\} R_2(\beta, D_{ei}), \quad (110)$$

where $R_2(\beta, D_{ei})$ is given by (33) with

Fig. 5. The diagrams for electron-electron, electron-ion, and ion-ion interactions. The heavy lines indicate ions.

$$D_{ei} = \Delta_e + \Delta_i = (p_e'^2 - p_e^2)/2m + (p_i'^2 - p_i^2)/2m.$$

The combinatorial factor of $1/2$ in (34) does not occur in Q_{2ei} , since the two particles are not identical. Each of the three diagrams of Fig. 5 may be analysed as in Sec. II. For example, for Fig. 5b we have:

$$\begin{aligned} R_2(\beta, D_{ei}) &= \int_0^\beta d\beta_2 \int_0^{\beta_2} dt_1 e^{-D_{ei} t_1} \\ &= \int_0^\beta d\beta_2 \int_0^{\beta_2} d\beta_1 e^{-(\beta_2 - \beta_1)\Delta_e - (\beta_2 - \beta_1)\Delta_i}, \end{aligned} \quad (113)$$

from which we obtain:

$$Q_{2ei} = \frac{V}{(2\pi\hbar)^3} \int d\mathbf{q} z_1^2 u(q)^2 \frac{1}{2} \int_0^\beta \int_0^\beta d\beta_1 d\beta_2 G_e(\beta_2 - \beta_1) G_i(\beta_2 - \beta_1), \quad (112)$$

where $G_i(\tau)$ is the ion propagator appropriate to either Fermi or Bose statistics:

$$G_i(q, \tau) = \frac{(2s_i + 1)V}{(2\pi\hbar)^3} \int d\mathbf{p}_i \begin{Bmatrix} f^-(p_i) f^+(p_i) \\ b^-(p_i) b^+(p_i) \end{Bmatrix} e^{-\tau\Delta_i}. \quad (113)$$

The eigenvalues of the integral equation (55), for $G_i(\tau)$ used as the kernel, are:

$$\begin{aligned} \lambda_{ik}(q) &= \int_0^\beta d\tau e^{-2\pi i k T/\beta} G_i(q, \tau) \\ &= V \rho_i \beta \mathcal{L}(q/\bar{p}_i, 2\pi k), \end{aligned} \quad (114)$$

with $\mathcal{L}(q/\bar{p}_i, 2\pi k)$ given by (63). By using the expansion of the electron and ion propagators (55) in terms of the eigenvalues and eigenfunctions, we find that (112) becomes:

$$Q_{2ei} = \frac{V}{(2\pi\hbar)^3} \int d\mathbf{q} z_1^2 u(q)^2 \frac{1}{2} \sum_k \lambda_{ek} \lambda_{ik}. \quad (115)$$

Similarly, the ion-ion interaction gives:

$$Q_{2ii} = \frac{1}{2} \cdot \frac{V}{(2\pi\hbar)^3} \int d\mathbf{q} z_i^4 u(\mathbf{q})^2 \frac{1}{2} \int_0^\beta \int d\beta_1 d\beta_2 G_1^2(|\beta_2 - \beta_1|) \\ = \frac{1}{2} \cdot \frac{V}{(2\pi\hbar)^3} \int d\mathbf{q} z_i^4 u(\mathbf{q})^2 \frac{1}{2} \sum_{\mathbf{k}} \lambda_{ik}^2. \quad (116)$$

Addition of the three contributions gives:

$$Q_2 = \frac{1}{2} \cdot \frac{V}{(2\pi\hbar)^3} \int d\mathbf{q} u(\mathbf{q})^2 \frac{1}{2} \sum_{\mathbf{k}} \left(\lambda_{ek} + z_i^2 \lambda_{ik} \right)^2. \quad (117)$$

For an n -particle cluster composed of n_e electrons and n_i ions arranged in a particular order on a ring, one must add the contributions from diagrams of all time orderings as was done in (54). The result ana-

logous to (57) is $(-1)^n / 2n \sum_{\mathbf{k}} z_i^{2n_i} \lambda_{ek}^{n_e} \lambda_{ik}^{n_i}$, and this must be multiplied

by $n! / n_e! n_i!$, the number of ways in which n_e electrons and n_i ions may be placed on a ring. Finally, when these terms of the binomial expansion are summed for all values of n_e and n_i so that $n_e + n_i = n$, the generalization of Q_n to a two-component gas is:

$$Q_n = \frac{V}{(2\pi\hbar)^3} \int d\mathbf{q} u(\mathbf{q})^n \frac{(-1)^n}{2n} \sum_{\mathbf{k}} \left(\lambda_{ek} + z_i^2 \lambda_{ik} \right)^n. \quad (118)$$

The further generalization to a several-component gas obviously requires $\left(\sum_i z_i^2 \lambda_{ik} \right)^n$ in (118) where the summation is over every ionic species.

The ring-integral contribution to the pressure is:

$$(\Omega/kT)_{\text{ring}} = \frac{1}{2} \cdot \frac{V}{(2\pi\hbar)^3} \int d\mathbf{q} \sum_{\mathbf{k}=-\infty}^{\infty} \left[x_{\mathbf{k}}(\mathbf{q}) - \ln(1 + x_{\mathbf{k}}(\mathbf{q})) \right], \quad (119)$$

where

$$x_{\mathbf{k}}(\mathbf{q}) = u(\mathbf{q}) \sum_i z_i^2 \lambda_{ik} = (4\pi e^2 \beta \rho \hbar^2) q^{-2} \sum_i z_i^2 f_i \mathcal{L}(q/\bar{p}_i, 2\pi\hbar)$$

with $\rho = \sum_i \rho_i$ and $f_i = \rho_i/\rho$.

Expression (119) is the ring-diagram contribution for a mixture of fermions and bosons for the entire temperature range. It will, of course, fail to be a valid approximation to the pressure as the temperature is reduced to the point where a significant number of electron and ion pairs are in hydrogenic-like bound states. We obtain near-classical-limit result from (119) as in Sec. III, by approximating $\mathcal{L}(q/\bar{p}_i, 2\pi k)$ with its leading term, $\theta_i^2(a_i)$, and neglecting all higher powers of q^2 . The generalization of (74) to the multicomponent system, including the ideal gas terms and the direct-exchange term for electrons, is:

$$\frac{\Omega}{kT} = \sum_i N_i \zeta_i^{-1} \mathcal{J}_{3/2}(a_i) + \frac{N_e}{2(2s_e+1)} \left(\frac{4\pi e^2 \rho_e \hbar^2}{\bar{p}_e^2} \right) \zeta_e^{-2} \int_0^\infty da' \mathcal{J}_{1/2}^2(a') + \frac{2}{3} N \Lambda \phi^{3/2}, \quad (120)$$

where

$$\begin{aligned} N &= \sum_i N_i \\ \Lambda &= \sqrt{\pi} e^3 \rho^{3/2} \rho^{1/2} \\ \phi &= \sum_i z_i^2 f_i \theta_i^2(a_i). \end{aligned} \quad (121)$$

The ring contribution in (119) in this limit is:

$$\left(\frac{\Omega}{kT} \right)_{\text{ring}} = \frac{V}{12\pi\lambda^3} = \frac{N}{12\pi\rho\lambda^3}, \quad (122)$$

and, similarly, the potential energy due to the correlations of the ring interactions is, with use of (7), given by:

$$\frac{U}{kT} = - \frac{V}{8\pi\lambda^3}, \quad (123)$$

where λ is the screening length generalized to include the effects of quantum statistics:

$$\lambda^{-2} = 4\pi e^2 \beta \sum_i z_i^2 \theta_i^2 \rho_i. \quad (124)$$

This form of the screening length also comes into the Debye-Hückel theory when modified with Fermi and Bose statistics in place of Boltzmann statistics.¹⁸ The effective ionic charge in (124) is $z_i e \theta_i$, and, hence, less than the true charge $z_i e$ for Fermi statistics and greater for Bose statistics.

In order to obtain formulae for the pressure and internal energy of the multicomponent gas in terms of density (i. e., through a_{i0}) instead of the activities, it is necessary to find the dependence on the coupling constant for each a_i . As before, in Sec. III, we assume for each species that a_i is the sum of a_{i0} and δa_i , and find δa_i by using (109), which gives:

$$N_i = N_i \zeta_i^{-1} \mathcal{J}_{1/2}(a_i) + N \Lambda \phi^{1/2} \frac{\partial \phi}{\partial a_i}, \quad (125)$$

where

$$\frac{\partial \phi}{\partial a_i} = z_i^2 \zeta_i^{-1} \mathcal{J}_{-3/2}(a_i).$$

By expanding $\mathcal{J}_{1/2}(a_{i0} + \delta a_i)$ (or $\mathcal{J}_{1/2}(a_{i0} + \delta a_i)$, for Bose statistics) and solving for δa_i in (125), we find:

$$\delta a_i = - \Lambda \phi^{1/2} z_i^2 \left(\frac{\mathcal{J}_{-3/2}(a_{i0})}{\mathcal{J}_{-1/2}(a_{i0})} \right), \quad (126)$$

which reduces to (81) for a one-component gas. The expansion of the ideal-gas terms in (120) give

$$\begin{aligned} & \sum_i N_i \zeta_i^{-1} \left[\mathcal{J}_{3/2}(a_{i0} + \delta a_i) - \mathcal{J}_{3/2}(a_{i0}) \right] \\ & = N \sum_i \zeta_i \delta a_i = - N \Lambda \phi^{3/2} + N \Lambda \phi^{1/2} \sum_i z_i^2 \zeta_i \eta(a_{i0}), \end{aligned} \quad (127)$$

¹⁸ R. E. Kidder and H. E. DeWitt (to be published).

where $\eta(a_{io})$ is given by (85) and (86) for Fermi and Bose statistics, respectively. The final result for the pressure to order e^3 is given by:

$$PV/kT = \sum_i N_i \zeta_i^{-1} \mathcal{Q}_{3/2}(a_{io}) - N_e \frac{1}{4} \gamma_e^2 \theta_{eo}^2 (1 - \eta_e(a_{eo})) \\ - \frac{1}{3} N \Lambda \Phi^{3/2} + N \Lambda \Phi^{1/2} \sum_i z_i^2 f_i \eta(a_{io}), \quad (128)$$

and, similarly, the internal energy is given by:

$$E/kT = \frac{3}{2} \sum_i N_i \zeta_i^{-1} \mathcal{Q}_{3/2}(a_{io}) - N_e \frac{1}{2} \gamma_e^2 \theta_{eo}^2 (1 - \eta_e(a_{eo})) \\ - N \Lambda \Phi^{3/2} + \frac{3}{2} N \Lambda \Phi^{1/2} \sum_i z_i^2 f_i \theta_{io}^2 \eta(a_{io}). \quad (129)$$

The ionic exchange terms have not been included, since they are smaller than the electron exchange term by a factor of m/M_i . These expressions (128) and (129) are valid only in the near-classical limit, i.e., for temperatures and densities such that no degeneracy parameter differs too much from 1. At lower temperatures, (119) must be evaluated more completely, and the contributions from bound states should be included. Also, exchange correlation terms which give a contribution of order $\Lambda \gamma$ become important. Because of the actual smallness of the electronic-to-ionic mass ratio, m/M_i , even if the electrons are slightly degenerate ($0.9 < \theta_{eo}^2 < 1$), the ions will be almost completely nondegenerate. The ideal-gas term for each ion is $\zeta_i^{-1} \mathcal{Q}_{3/2}(a_{io}) \approx 1$ and $\theta_{io}^2 \approx 1$, so that the $\eta(a_{io})$ terms are negligible. Thus, the statistics modifications embodied in (128) and (129) are, in practice, important only for electrons, the ions being nearly classical. Within the limits of validity, however, these expressions are easy to use to obtain numerical results for the pressure and energy of a slightly degenerate gas. The dimensionless parameters ζ , γ_e^2 , and Λ are given in terms of temperature, density, and fundamental constants. The value of a_{eo} may be

read from the McDougall and Stoner tables, using $\zeta_e = \mathcal{J}_{1/2}(a_{eo})$. Those authors have also tabulated values of $\mathcal{J}_{-1/2}(a_{eo})$ and $\mathcal{J}_{-3/2}(a_{eo})$ needed to calculate θ_{eo}^2 and $\eta(a_{eo})$. Only the $\eta_x(a_{eo})$ needed for the direct-exchange term is not available in numerical tables; the series expansion (99), however, gives it with sufficient accuracy in the near-classical limit.

VI. DISCUSSION

In Sec. II, a formal expression valid for the entire temperature range was derived for the contribution of the direct-interaction ring diagrams to the equation of state of a one-component quantum gas. From this formal expression, explicit formulae suitable for numerical computation of pressure and internal energy in the near-classical limit were obtained by an appropriate mathematical approximation, i.e., neglect of terms of $O(q)^2$. The limits of validity of these near-classical-limit expressions, (87) for a one-component gas and (128) and (129) for a multicomponent gas, will now be considered. These formulae represent an incomplete evaluation of (69), resulting in (1) the neglect of quantum-mechanical diffraction effects, (2) the neglect of the exchange interactions in the ring diagrams, and (3) the neglect of the innumerable non-ring interactions.

To estimate the validity of the near-classical-limit formulae, we first note that three lengths are sufficient to completely describe the one-component quantum gas. These lengths are the average interparticle separation $l = \rho^{-1/3}$, the classical Debye screening length $\lambda_D = (4\pi e^2 \beta \rho)^{-1/2}$, and the thermal de Broglie wavelength $\lambda_{th} = \hbar(\beta/2m)^{1/2}$. From the ratios of these lengths, two independent dimensionless parameters are possible. For expressing the results of the theory, it was found convenient to use three quantities ζ , Λ , and γ , which, in terms of the fundamental lengths, are given by:

$$\begin{aligned}
 \Lambda &= \frac{1}{8\pi} \left(\frac{f}{\lambda_D} \right)^3 \\
 \gamma &= \kappa_{th}/\lambda_D \\
 \zeta &= 4\pi^{3/2} (\kappa_{th}/\lambda_D)^3 \quad (\text{using } \kappa = 1/2) \\
 &= \frac{\pi^{1/2}}{2} \frac{\gamma^3}{\Lambda} \quad (130)
 \end{aligned}$$

The ideal-gas term, $\zeta^{-1} \mathcal{G}_{3/2}(\alpha_0)$, is a function of ζ only, and this term goes to 1 in the classical limit, $\zeta \ll 1$. The sum of the ring-diagram contribution in the classical limit reduces to the Debye-Hückel term which is $O(\Lambda)$. If all interactions are taken into account, it is expected that in the classical limit defined by $\hbar \rightarrow 0$, the thermodynamic functions of a one-component gas may be completely expressed in terms of the one classical parameter Λ . Considerable work has already been done on the problems of classifying and summing non-ring diagrams for classical gases, particularly by McMillan and Mayer,¹⁹ Haga,²⁰ Meeron,²¹ and Friedman.²² Their results indicate that the next contribution to the pressure beyond the Debye-Hückel term is of order Λ^2 in Λ for $\Lambda \ll 1$. Consequently, in the near-classical region where some deviations due to quantum statistics may be seen (the θ_0^3 factor), the sufficient smallness of Λ may be used as a criterion for obtaining accurate results with only the ring diagrams. It should be noted that $\Lambda = 1$ is a critical value for the mathematics of the classical electron gas. The results of Berlin and Montroll indicate that the correlations became so pronounced that a phase change occurs with the gas being forced into a lattice.²³

¹⁹ W.G. McMillan and J. E. Mayer, J. Chem. Phys. 10, 629 (1945).

²⁰ E. Haga, J. Phys. Soc. Japan 8, 714 (1953).

²¹ E. Meeron, Physics of Fluids 1, 139 (1958).

²² H. L. Friedman, Molecular Physics 2, 23, 190 (1959).

²³ T.H. Berlin and E. W. Montroll, J. Chem. Phys. 20, 75 (1952).

At high temperature, the complete evaluation of the ring-diagram contribution in (69) may be expected to yield $\Lambda f(\gamma, \zeta)$. Because of the mathematical approximation of dropping $O(q^2)$ terms, we obtained only $f(\gamma, \zeta) = \theta_0^3$. In a later paper it will be shown that a complete evaluation of (69) yields an expansion of $f(\gamma, \zeta)$ in powers of γ . The higher powers of γ beyond the first, or near-classical, term are due to the wave nature of the particles, and may be called "diffraction terms." In addition, the calculation of contributions from exchange interactions in the ring diagrams will yield terms of order $\Lambda\gamma$, $\Lambda\gamma^2$, $\Lambda\gamma^3$, etc. Thus the Debye-Hückel term, $\Lambda\theta^3$, is sufficiently accurate only if γ is small. Noting that κ_{th} is proportional to $\rho^{1/2}$, f is equal to $\rho^{-1/3}$, and λ_D is proportional to $\rho^{-1/2}\beta^{-1/2}$, we see that the high-temperature and low-density limit for which the near-classical-limit formulae are rigorously accurate requires:

$$\kappa_{th} \ll f \ll \lambda_D.$$

The conditions for the validity of (87) may be taken as $\Lambda < a$ and $\gamma < b$, where a and b are appropriate upper limits. If we take $a \sim b \sim 0.3$, then using (130) we have $\zeta_{max} \approx b^3/a \approx 0.08$, for which $\theta_{0min}^2 \approx 0.9$. Thus, the near-classical-limit formulae apply only to a slightly degenerate gas, $0.9 < \theta_0^2 < 1$.

For a multicomponent gas, say ionized hydrogen, it is not possible to express the thermodynamic functions in terms of only the one classical parameter Λ . Because of the series of bound states possible for electron-proton pairs, the calculation of the partition function must be performed quantum mechanically, and the contributions from bound states will appear in the non-ring terms. The considerations of previous paragraph, however, apply to the ring terms in the near-classical-limit. The recent results of Friedman indicate that the leading non-ring contribution, which for a one-component gas is $O(\Lambda^2 \ln \Lambda)$, is $O[\Lambda^2 \ln(\Lambda/\gamma)]$ for a two component

gas and hence infinite as $h \rightarrow 0$.

The near-classical-limit formulae, (128) and (129), are applicable to a gas such as hydrogen when the temperature is high enough to insure nearly complete ionization. This requirement determines the ratio N/γ , since:

$$N/\gamma = \frac{e^2 m^{1/2}}{h (kT)^{1/2}} = \left(\frac{\text{Rydberg}}{kT} \right)^{1/2}.$$

If we take $(kT)_{\min} = \text{Ryd.}$, then the maximum density is determined from:

$$\gamma_{\max} = \frac{h(2\pi e^2 \rho/m)^{1/2}}{\text{Ryd.}} = \left(8\pi a_0^3 \rho \right)^{1/2},$$

where a_0 is the Bohr radius. Hence, with $\gamma_{\max} = h = 0.3$ we find $\rho_{\max} = h^2/8\pi a_0^3 \sim 0.3 \times 10^{25} \text{ cm}^{-3}$. The exchange correlation and diffraction effects involving powers of γ are thus appreciable only for high densities, but will be significant for astrophysical applications.

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APPENDIX A. EXPANSION OF $R_n(\beta)$

The complex integral $R_n(\beta)$ occurring in the Q_n expression, (36), may be reduced to a sum of the $R_2(\beta)$ functions by expanding the product in the integrand in partial fractions:

$$\prod_{i=1}^{n-1} \frac{1}{(w-D_i)} = \sum_{i=1}^{n-1} \frac{a_i}{(w-D_i)}$$

$$a_i = \prod_{j \neq i} \frac{1}{(D_i - D_j)} \quad (A.1)$$

Consequently, (37) becomes:

$$R_n(\beta) = \sum_{i=1}^{n-1} a_i R_2(\beta, D_i)$$

$$= \sum_{i=1}^{n-1} \frac{a_i}{D_i^2} \left(e^{-\beta D_i} - 1 + \beta D_i \right)$$

$$= \sum_{i=1}^{n-1} a_i \left(\frac{\beta^2 D_i^2}{2!} - \frac{\beta^3 D_i^3}{3!} + \frac{\beta^4 D_i^4}{4!} - \dots \right)$$

$$= \sum_{r=2}^{\infty} \frac{(-1)^r \beta^r b_{nr}}{r!}, \quad (A.2)$$

where

$$b_{nr} = \sum_{i=1}^{n-1} a_i D_i^{r-2}. \quad (A.3)$$

The expansion coefficient may easily be found for all r with the help of the Vandermonde determinant which, $n-1$ factors, $D_1 \dots D_{n-1}$, is:

$$\Delta_{n-1} = \begin{vmatrix} 1 & 1 & \dots & 1 \\ D_1 & D_2 & \dots & D_{n-1} \\ D_1^2 & D_2^2 & \dots & D_{n-1}^2 \\ \vdots & \vdots & \ddots & \vdots \\ D_1^{n-2} & D_2^{n-2} & \dots & D_{n-1}^{n-2} \end{vmatrix} = \prod_{i < j}^{n-1} (D_i - D_j) \quad (A.4)$$

The minors of D_{n-1} , when expanded about the bottom row, are also Vandermonde determinants:

$$\mathcal{D}_{n-1} = \sum_{i=1}^{n-1} (-1)^{n-1+i} \mathcal{D}_{n-2}(D_i) D_i^{n-2}, \quad (\text{A. 5})$$

where $\mathcal{D}_{n-2}(D_i)$ is the Vandermonde determinant of $n-2$ factors with D_i excluded. The partial-fraction coefficient in (A. 1) is:

$$a_1 = -\frac{\mathcal{D}_{n-2}(D_1)}{\mathcal{D}_{n-1}},$$

so that (A. 3) becomes:

$$b_{nr} = \mathcal{D}_{n-1}^{-1} \begin{vmatrix} 1 & 1 & \dots & 1 \\ D_1 & D_2 & \dots & D_{n-1} \\ D_1^2 & D_2^2 & \dots & D_{n-1}^2 \\ \vdots & \vdots & \ddots & \vdots \\ D_1^{n-3} & D_2^{n-3} & \dots & D_{n-1}^{n-3} \\ D_1^{r-2} & D_2^{r-2} & \dots & D_{n-1}^{r-2} \end{vmatrix}. \quad (\text{A. 6})$$

The numerator of (A. 6) vanishes when the bottom row is identical with any other row; hence

$$\begin{aligned} b_{nr} &= 0 & r < n \\ b_{nn} &= \mathcal{D}_{n-1} / \mathcal{D}_{n-1} = 1, \end{aligned} \quad (\text{A. 7})$$

and the expansion of $R_n(\beta)$ must begin with $O(\beta^n)$. If we define

$$Q_{n-1}(x) = \prod_{i=1}^{n-1} (x - D_i),$$

then it can be shown that:²⁴

²⁴ W. L. Ferrar, Algebra (Oxford University Press, 1941), pp. 22, 24.

$$\frac{1}{Q_{n-1}(x)} = \mathcal{L}_{n-1}^{-1} \begin{vmatrix} 1 & \dots & 1 \\ D_1 & & D_{n-1} \\ \vdots & & \vdots \\ D_1^{n-3} & & D_n^{n-3} \\ (x - D_1)^{-1} & \dots & (x - D_{n-1})^{-1} \end{vmatrix}. \quad (\text{A.8})$$

By putting $x = 1/y$ and expanding both sides of (A.8) in powers of y , one finds that the coefficients y^{n-2+p} on the right-hand side are the b_{nr} of (A.6) with $r = n-2+p$. The coefficients of y^{n-2+p} on the left-hand side are ${}_{n-1}H_p$, the sum of homogeneous products of $D_1, D_2, \dots, D_{n-1}$ of order p . Hence:

$$b_{n, n-2+p} = {}_{n-1}H_p. \quad (\text{A.9})$$

or

$$\begin{aligned} b_{n, n+1} &= \sum_i^{n-1} D_i \\ b_{n, n+2} &= \sum_i^{n-1} D_i^2 + \sum_{i < j} D_i D_j. \end{aligned}$$

In the zero-temperature limit, $\beta \rightarrow 0$, $R_n(\beta)$ is linear in β , and (A.2) becomes:

$$\begin{aligned} R_n(\beta) &= \beta \sum_i^{n-1} \frac{a_i}{D_i} + \sum_i^{n-1} \frac{a_i}{D_i^2} \left(e^{-\beta D_i} - 1 \right) \\ &\approx \beta b_{n-1, -1} \quad \text{for } \beta \text{ large}. \end{aligned} \quad (\text{A.10})$$

The coefficient $b_{n-1, -1}$ is given by the right-hand side of (A.8) with $x = 0$, and hence from the left-hand side we find:

$$b_{n-1, -1} = (-1)^n \prod_i^{n-1} \frac{1}{D_i}. \quad (\text{A.11})$$

APPENDIX B. EVALUATION OF THE DIRECT EXCHANGE INTEGRAL

The contribution to $\beta\Omega$ from the simple exchange interaction depends on the integral defined by (91). Since this integral is typical of the types of integrals encountered, some of the steps in its evaluation will be given here. In (91) one set of angular integration, say over y_1 , may be done immediately to give 4π , and the integration of the azimuthal angle of y_2 gives 2π , so that (91) becomes:

$$\begin{aligned} \mathcal{J}_x(a) &= 8\pi^2 \int_0^\infty \frac{dy_1 y_1^2 \tilde{f}(y_1)}{r^{3/2}} \int_0^\infty \frac{dy_2 y_2^2 \tilde{f}(y_2)}{r^{3/2}} \int_0^\pi \frac{d(\cos \theta)}{r_1^2 + r_2^2 - 2y_1 y_2 \cos \theta} \\ &= \frac{8}{\pi} \int_0^\infty dy_1 y_1 \tilde{f}(y_1) \int_0^\infty dy_2 y_2 \tilde{f}(y_2) \log \left| \frac{y_1 + y_2}{y_1 - y_2} \right| \quad (B.1) \end{aligned}$$

By expanding $\tilde{f}(y_1) \tilde{f}(y_2)$ in powers of e^a we have:

$$\mathcal{J}_x(a) = \sum_{r_1=1, r_2=1}^{\infty} (-1)^{r_1+r_2} e^{(r_1+r_2)a} \mathcal{J}_{xr_1 r_2} \quad (B.2)$$

$$\mathcal{J}_{xr_1 r_2} = \frac{8}{\pi} \int_0^\infty dy_1 y_1 e^{-r_1 y_1^2} \int_0^\infty dy_2 y_2 e^{-r_2 y_2^2} \log \left| \frac{y_1 + y_2}{y_1 - y_2} \right| \quad (B.3)$$

After the variables are changed to $v^2 = r_2 y_2^2$, the y_2 integration gives:

$$\begin{aligned} \int_0^\infty dy_2 y_2 e^{-r_2 y_2^2} \log \left| \frac{y_1 + y_2}{y_1 - y_2} \right| &= \frac{1}{r_2} \int_0^\infty dv v e^{-v^2} \log \left| \frac{\sqrt{r_2} y_1 + v}{\sqrt{r_2} y_1 - v} \right| \\ &= \frac{\sqrt{\pi}}{2} e^{-r_2 y_1^2} \operatorname{Erfi}(\sqrt{r_2} y_1), \end{aligned}$$

where $\operatorname{Erfi}(a)$ is the imaginary error function, $\int_0^\infty dt e^{t^2}$. Consequently,

$\mathcal{J}_{xr_1 r_2}$ becomes:

$$\begin{aligned} \mathcal{I}_{x r_1 r_2} &= \frac{8}{\sqrt{\pi r_2}} \int_0^\infty dy_1 y_1 e^{-(r_1+r_2)y_1^2} \int_0^{\sqrt{r_2} y_1} dt e^{t^2} \\ &= \frac{4}{\sqrt{\pi r_2}} \int_0^\infty dy_1 y_1 e^{-(r_1+r_2)y_1^2} \int_0^{y_1} du e^{r_2 u^2} . \end{aligned} \quad (\text{B. 4})$$

The remaining integrations may be performed most conveniently by changing the order of the integration with the help of the Dirichlet inversion formula:²⁵

$$\begin{aligned} \mathcal{I}_{x r_1 r_2} &= \frac{8}{(\pi r_2)^{1/2}} \int_0^\infty du e^{r_2 u^2} \int_u^\infty dy_1 y_1 e^{-(r_1+r_2)y_1^2} \\ &= \frac{8}{(\pi r_2)^{1/2}} \int_0^\infty du e^{r_2 u^2} \frac{e^{-(r_1+r_2)u^2}}{2(r_1+r_2)} \\ &= \frac{2}{(r_1+r_2)(r_1 r_2)^{1/2}} . \end{aligned} \quad (\text{B. 5})$$

Hence:

$$\mathcal{I}_x(a) = 2 \sum_{r_1=1, r_2=1} \frac{(-1)^{r_1+r_2} e^{-(r_1+r_2)a}}{(r_1+r_2)(r_1 r_2)^{1/2}} . \quad (\text{B. 6})$$

We may express the double summation as an integral by noting that the series expansion of $\mathcal{I}_{-1/2}^2(a')$ is:

$$\mathcal{I}_{-1/2}^2(a') = \sum_{r_1=1, r_2=1} \frac{(-1)^{r_1+r_2} e^{-(r_1+r_2)a'}}{(r_1 r_2)^{1/2}} .$$

Hence, (B. 6) is:

$$\mathcal{I}_x(a) = \int_{-\infty}^a da' \mathcal{I}_{-1/2}^2(a') . \quad (\text{B. 7})$$

²⁵ E. T. Whittaker and G. N. Watson, Modern Analysis (Cambridge University Press, 1952), fourth edition, p. 77.