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Quantum Corrections to the Equation of State for Nonanalytic Potentials

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A method used by Hemmer and Jancovici to calculate quantum corrections to the equation of state for a hard-sphere gas is extended to cover the case of a more general intermolecular potential. The basis of the method is an expansion of the partition function about its classical limit, the terms in the expansion being integrals over products of classical correlation functions and certain "modified" quantum Ursell functions. Conditions are discussed under which this series can be truncated to give the quantum corrections to a specified order in h (Planck's constant). A calculation of the first quantum correction is carried out for the square-well–plus–hard-core potential.

I. INTRODUCTION

The usual method of calculating quantum corrections to the classical equation of state uses the Wigner-Kirkwood (WK) expansion.[1] However, in cases where the intermolecular potential is a nonanalytic function of distance, this method fails,[2] and alternative procedures must be found. Up to now, most work has been on the second virial coefficient B.[3] For this case, the problem has essentially been solved, insofar as methods are available which allow the systematic calculation of the correction terms. At high temperatures, the direct part of B can be found from its expression as the inverse Laplace transform of the logarithmic derivative of the Jost function.[4–6] For the exchange part, one again uses Laplace-transform techniques, in combination with the Sommerfeld-Watson transform.[4,7]

In the case of higher virial coefficients, the only work appears to be that of Hemmer[8] and Jancovici[9] on the hard-sphere gas. The basis of their method is an expansion of the partition function about its classical limit, the terms in the expansion being integrals over products of classical correlation functions and quantum Ursell functions. The quantum corrections, as a series in powers of the thermal wavelength λ, can be found in a systematic way from this expansion.

In this paper, we show that the basic method of Hemmer and Jancovici can be extended to cover more general intermolecular potentials. The extension of the formalism is straightforward, but some consideration has to be given to the problem of how to truncate the resulting expansion to get all the quantum corrections to a given order in λ. The formalism, together with a discussion of this point, is given in Sec. II. Section III is a review of the hard-sphere case. In Sec. IV, we present a calculation for the square-well (with hard-core) potential. The first-order correction to the partition function is obtained in terms of the classical radial distribution function [Eqs. (17) and (33)], and an explicit expression is given for the first-order correction to the third virial coefficient [Eq. (42)].

It should be noted that in the following work we consider only the direct part of the virial coefficients—the effects of quantum statistics are completely neglected. If the potential is strongly repulsive at small distances (as is the case for all realistic potentials), it is expected that statistical effects will be negligible at temperatures where a series in powers of λ is useful. This has only been proved for the second virial coefficient,[10] but it seems clear that higher coefficients will exhibit a similar behavior, since the physical mechanism responsible for the rapid suppression of statistical effects with increasing temperature is present in all cases.[11]

II. EXPANSION OF PARTITION FUNCTION

Consider a system of N identical particles each of mass m in a container of volume Ω. Let the Hamiltonian be

$$H_N = H_N^0 + V_N \,, \tag{1}$$

where H_N^0 is the kinetic energy of the N particles, and V_N is the total potential energy. Let

$$W_N(1, \ldots, N) = \lambda^{3N} \langle \vec{r}_1, \ldots, \vec{r}_N | e^{-\beta H_N} | \vec{r}_1, \ldots, \vec{r}_N \rangle \,, \tag{2}$$

where $\beta = 1/kT$ and $\lambda = (2\pi\hbar^2\beta/m)^{1/2}$. The classical limit of W_N is

$$W_N^c(1, \ldots, N) = e^{-\beta V_N(\vec{r}_1, \cdots, \vec{r}_N)} \,. \tag{3}$$

We now define a "modified" W function $W_N^m(1, \ldots, N)$ by the relation

$$W_N = W_N^c \, W_N^m \,. \tag{4}$$

(If the pair potential has a hard core, both W_N and W_N^c will vanish for particle configurations in which hard cores overlap. In this case, W_N^m can be taken as zero also.) We note that since both W_N and W_N^c possess the "product property," W_N^m will possess it also. This means that when the particles split into two groups whose surfaces are separated by a distance that is large compared with the potential range and with the thermal wavelength λ, W_N^m can be expressed as a product of two terms, one referring to each group.

In the usual treatment of a quantum gas, W_N is expressed in terms of Ursell functions U_l.[12] In an analogous way, we express W_N^m in terms of "modified" Ursell functions U_l^m:

$$W_1^m(1)=U_1^m(1)=1, \tag{5}$$

$$W_2^m(1,2)=1+U_2^m(1,2), \tag{6}$$

$$W_3^m(1,2,3)=1+U_2^m(2,3)+U_2^m(3,1)+U_2^m(1,2)+U_3^m(1,2,3), \tag{7}$$

$$\vdots$$

$$W_N^m(1,\ldots,N)=1+\sum U_2^m(i,j)+\sum U_3^m(i,j,k)+\sum U_4^m(i,j,k,l)+\sum U_2^m(i,j)\,U_2^m(k,l)+\cdots\;. \tag{8}$$

Equation (8) is obtained by taking a partition of the N particles in groups, making the corresponding product of U_l^m functions, and summing over all possible partitions. These equations can be solved sucessively for U_1^m, $U_2^m, \ldots$:

$$U_2^m(1,2)=W_2^m(1,2)-1, \tag{9}$$

$$U_3^m(1,2,3)=W_3^m(1,2,3)-W_2^m(2,3)-W_2^m(3,1)-W_2^m(1,2)+2,\quad\text{etc.} \tag{10}$$

Since the W_l^m possess the "product property," it follows that U_l^m will possess the "cluster property." This means that U_l^m approaches zero for a configuration in which the l particles are separated into two or more groups sufficiently distant from each other.

We define

$$Q=\int W_N(1,\ldots,N)\,d^{3N}r, \tag{11}$$

$$Q^c=\int W_N^c(1,\ldots,N)\,d^{3N}r, \tag{12}$$

$$g_l(1,\ldots,l)=(\Omega^l/Q^c)\int W_N^c(1,\ldots,N)\,d^3r_{l+1}\cdots d^3r_N. \tag{13}$$

Note that g_l is a *classical* correlation function. Inserting the expansion (8) into (4), and integrating over the coordinates, gives

$$Q=Q^c\Big(1+\Omega^{-2}\sum\int g_2(i,j)\,U_2^m(i,j)\,d^6r+\Omega^{-3}\sum\int g_3(i,j,k)\,U_3^m(i,j,k)\,d^9r+\Omega^{-4}\sum\int g_4(i,j,k,l)\times[U_4^m(i,j,k,l)+U_2^m(i,j)\,U_2^m(k,l)]\,d^{12}r+\cdots\Big)\,. \tag{14}$$

Once Q has been calculated, the free energy F is given by

$$F=-kT\ln(Q/N!\,\lambda^{3N}) \tag{15}$$

and the pressure by

$$p=\frac{\rho^2}{N}\left(\frac{\partial F}{\partial\rho}\right)_T\,, \tag{16}$$

where

$$\rho=N/\Omega.$$

We wish to use (14) to calculate quantum corrections to Q at moderately high temperatures, where λ is small. In general, these corrections will take the form of a series in powers of λ. The expansion (14) will be useful only if it can be truncated in some well-defined way, to give the total correction to a specified order in λ. The λ contribution from a factor U_l^m depends on the potential, and we now consider various cases.

The simplest case is that of hard spheres, for which U_l^m is identical to the usual Ursell function U_l. The contribution from U_l to a term in (14) is determined by two factors. First, the correlation functions vanish for a particle configuration in which hard cores overlap, and second, U_l vanishes whenever the particles separate into two groups with a distance $\gg\lambda$ between surfaces. This means that the entire contribution comes from configurations in which the distance between centers of neighboring spheres is r, where $a<r\lesssim a+\lambda$ (a is the sphere diameter). It follows that the contribution from U_l to an integral in (14) is of order λ^{l-1}.

Turning now to more general potentials, we note first that, by their construction, the U_l^m vanish except for configurations in which the particle separations are such that quantum effects are present. For example, for a pure square-well potential $[v(r)=-\epsilon,\ r<b,\ v(r)=0,\ r>b]$, quantum effects are negligible unless neighboring particles are separated by a distance r, where $|r-b|\lesssim\lambda$. In this case, the contribution from U_l^m is of order λ^{l-1}. This result can be extended to a potential which is a finite chain of rectangular wells, with or without a hard core—again the contribution from U_l^m will be of order λ^{l-1}. [This phenomenon of the occurrence of quantum effects only at the potential boundaries is illustrated by Eq. (32), which gives U_2^m for a square-well-plus-hard-core potential.]

The situation becomes less clear when we go beyond these simple potentials. Consider a potential which is analytic and sufficiently repulsive at the origin, so that the WK expansion exists. The quantum corrections to Q will then be given as a series in powers of λ^2. In Appendix A, we show that it is necessary to include contributions from both U_2^m and U_3^m in order to get the first-order-correction term. The order of the contribution from a general U_l^m does not seem to be obvious.

Finally, consider a potential which is analytic except at a finite number of points (e.g., a Sutherland potential). One might argue that the dominant quantum effects occur in the neighborhoods of these points, and that U_l^m will contribute to order λ^{l-1}, as in the rectangular-well case, but this conclusion is only tentative. However, it seems fairly certain that the first-order correction (of order λ) will come entirely from U_2^m, and since this is about all one would be able to calculate in practice, the method is applicable.

Let us now assume that the potential is such that the first-order correction is contained entirely in the U_2^m term. Then (14) gives

$$Q = Q^c [1 + N(N-1)c_2/\Omega + O(\lambda^2)], \tag{17}$$

where

$$c_2 = \frac{1}{2\Omega} \int g_2(1,2)\, U_2^m(1,2)\, d^6r. \tag{18}$$

For a spherically symmetric pair potential, this can be written

$$c_2 = 2\pi \int_0^\infty g(r)\, U_2^m(r)\, r^2 dr, \tag{19}$$

where $g(r)$ is the (classical) radial distribution function. The free energy is given by

$$\beta F/N = \beta F^c/N - \rho c_2 + O(\lambda^2) \tag{20}$$

and the pressure by

$$p = p^c - \frac{\rho^2}{\beta} \frac{\partial}{\partial \rho} (\rho c_2) + O(\lambda^2). \tag{21}$$

$U_2^m(r)$ can be found from the solution of the quantum-mechanical two-body problem. From (9), it can be written in the form

$$U_2^m(r) = 2^{3/2} e^{\beta v(r)} \lambda^3 G(\vec{r}, \vec{r}; \beta) - 1, \tag{22}$$

where $v(r)$ is the two-body potential and

$$G(\vec{r}, \vec{r}; \beta) \equiv \langle \vec{r} | e^{-\beta H_2^{\mathrm{rel}}} | \vec{r} \rangle, \tag{23}$$

where H_2^{rel} is the Hamiltonian for the relative motion of the two-particle system.

III. HARD SPHERES

This case has been considered in detail by Hemmer[8] and Jancovici,[9,13] and we include it only as the simplest illustration of the method. The Ursell function is

$$U_2^m(r) = -2^{-3/2} \lambda\, \delta(r - a+) + O(\lambda^2), \quad r > a \tag{24}$$

where a is the sphere diameter. Thus

$$c_2 = -2^{-1/2} \pi a^2 g(a+) \lambda + O(\lambda^2). \tag{25}$$

This value can be substituted in (20) and (21) to give the first-order corrections to F and p. Of course, the ρ differentiation in (21) cannot be performed explicitly, since $g(a+)$ is density dependent.

The equation of state for a classical gas in terms of the radial distribution function is[14]

$$\beta p^c = \rho - \tfrac{2}{3} \pi \beta \rho^2 \int_0^\infty g(r) \frac{dv}{dr}\, r^3 dr. \tag{26}$$

For the hard-sphere gas this becomes

$$\beta p^c = \rho + \tfrac{2}{3} \pi a^3 g(a+) \rho^2. \tag{27}$$

We can eliminate $g(a+)$ between (25) and (27) and substitute in (21) to give

$$p = p^c + \tfrac{3}{4}\sqrt{2} \left(\frac{\lambda}{a}\right) \rho^2 \frac{\partial}{\partial \rho} \left(\frac{p^c}{\rho}\right) + O(\lambda^2). \tag{28}$$

Expanding the pressure in a virial series,

$$\beta p = \rho + \sum_{n \geq 2} B_n \rho^n, \tag{29}$$

substituting in (28), and equating powers of ρ, gives the first-order correction to all the virial coefficients:

$$B_n = B_n^c [1 + (n-1)\, \tfrac{3}{4}\sqrt{2}\, (\lambda/a) + O(\lambda^2)]. \tag{30}$$

IV. SQUARE-WELL POTENTIAL WITH HARD CORE

The potential is

$$\begin{aligned} v(r) &= \infty, & r &< a \\ v(r) &= -\epsilon, & a &< r < b \\ v(r) &= 0, & r &> b. \end{aligned} \tag{31}$$

The function $\lambda^3 G(\vec{r}, \vec{r}; \beta)$, to first order in λ, is calculated in Appendix B. From (B10) and (22) we find,

$$\begin{aligned} U_2^m(r) &= -\sqrt{2}\, \lambda\, e^{-\beta\epsilon} L_\alpha^{-1} \left[\frac{1}{4\Gamma^2} \delta(r - a+) - \frac{1}{4\Gamma^2} \frac{\Gamma - \gamma}{\Gamma + \gamma} \right. \\ &\qquad \left. \times \delta(r - b-) + O\left(\frac{1}{\Gamma^3}\right) \right], \quad a < r < b \\ U_2^m(r) &= -\sqrt{2}\, \lambda\, L_\alpha^{-1} \left[\frac{1}{4\gamma^2} \frac{\Gamma - \gamma}{\Gamma + \gamma} \delta(r - b+) + O\left(\frac{1}{\gamma^3}\right) \right], \\ &\qquad r > b \end{aligned} \tag{32}$$

where L_α^{-1} is the inverse Laplace transform operator defined by (B5), $\alpha = \lambda^2/2\pi$, $\gamma = p^{1/2}$, and $\Gamma^2 = \gamma^2 - m\epsilon/\hbar^2$. Substituting in (19), doing the r integration and then the inverse transform, gives

$$c_2 = -2^{1/2}\pi [e^{\beta\epsilon} a^2 y(a) + \theta(\beta\epsilon)\, b^2 y(b)] \lambda + O(\lambda^2), \tag{33}$$

where

$$\theta(x) \equiv 1 + e^x - 2e^{x/2} I_0(\tfrac{1}{2}x). \tag{34}$$

I_0 is the modified Bessel function of the first kind and order zero. We have also introduced $y(r)$, which is related to the radial distribution function $g(r)$ by

$$y(r) = g(r)\, e^{\beta v(r)}. \tag{35}$$

Equations (33), (20), and (21) give the first-order corrections to F and p.

From (26), the classical equation of state is

$$\beta p^c = \rho + \tfrac{2}{3}\pi\,[e^{\beta\epsilon}\,a^3 y(a) + (1 - e^{\beta\epsilon})\,b^3 y(b)]\,\rho^2. \qquad (36)$$

Comparison of (33) and (36) shows that it is not possible to eliminate the distribution function in favor of the pressure, as in the hard-sphere case. However, for a pure square well with no hard core, this elimination is possible, since the $y(a)$ terms vanish from (33) and (36). For the potential

$$\begin{aligned} v(r) &= -\epsilon, \quad r < b \\ v(r) &= 0, \quad\;\; r > b \end{aligned} \qquad (37)$$

we find

$$B_n = B_n^c \left[1 + (n-1)\,\tfrac{3}{4}\sqrt{2}\,\frac{\theta(\beta\epsilon)}{1 - e^{\beta\epsilon}}\left(\frac{\lambda}{\beta}\right) + O(\lambda^2)\right]. \qquad (38)$$

This equation applies only to the direct part of the virial coefficients, since statistical effects have been completely neglected in its derivation. Since the potential does not have a hard core this may not be a good approximation to the total virial coefficient.

In the case where the hard core is present, one can obtain explicit expressions for the first few virial coefficients by making use of the density expansion of the radial distribution function.[15] We write

$$y(r) = y_0(r) + \rho\, y_1(r) + \rho^2 y_2(r) + \cdots , \qquad (39)$$

which leads to

$$\begin{aligned} B_n = B_n^c + (n-1)\,2^{-1/2}\pi\,[e^{\beta\epsilon}\,a^2 y_{n-2}(a) \\ + \theta(\beta\epsilon)\,b^2 y_{n-2}(b)]\lambda + O(\lambda^2). \end{aligned} \qquad (40)$$

Since $y_0(r) = 1$, we get for the second virial coefficient

$$B = B^c + 2^{-1/2}\pi\,[e^{\beta\epsilon} a^2 + \theta(\beta\epsilon)\, b^2]\lambda + O(\lambda^2), \qquad (41)$$

which agrees with previous calculations.[4,5,16–18] $y_1(r)$ has been calculated by Kirkwood,[19] so the first-order quantum correction to the third virial coefficient can be obtained. It is rather lengthy to write down, and we give the result only for the special case where $b = 2a$:

$$\begin{aligned} C = C^c + \tfrac{3}{16}\sqrt{2}\,(\tfrac{2}{3}\pi a^3)^2\,[e^{\beta\epsilon}(5 - 22\Delta + 54\Delta^2) \\ + 4\,\theta(\beta\epsilon)\,(-13\Delta + 27\Delta^2)]\,(\lambda/a) + O(\lambda^2), \end{aligned} \qquad (42)$$

where

$$\Delta \equiv e^{\beta\epsilon} - 1.$$

APPENDIX A: WK EXPANSION

We show that if the WK expansion applies, the first quantum correction (of order λ^2) to the partition function, as given by (14), comes from the U_2^m and U_3^m terms.

The WK expansion to first order is[20]

$$W_N = W_N^c\left(1 + \lambda^2 \sum_{j=1}^{n} w_2^{(j)} + O(\lambda^4)\right), \qquad (\text{A1})$$

where

$$w_2^{(j)} = -\frac{\beta}{24\pi}\,[\nabla_j^2 V_N - \tfrac{1}{2}\beta(\nabla_j V_N)^2] . \qquad (\text{A2})$$

The usual WK expansion of Q can readily be obtained directly from (A1). However, we wish to investigate its relation to our present formalism. We assume V_N can be written as a sum of pair potentials:

$$V_N = \sum_{i<j} v_{ij} . \qquad (\text{A3})$$

Applying (A1) to (9) and (10) gives

$$\begin{aligned} U_2^m(1,2) = -2\lambda^2 \frac{\beta}{24\pi} \\ \times [\nabla_{12}{}^2 v_{12} - \tfrac{1}{2}\beta\,(\nabla_{12} v_{12})^2] + O(\lambda^4), \end{aligned} \qquad (\text{A4})$$

$$\begin{aligned} U_3^m(1,2,3) = \lambda^2\beta\frac{\beta}{24\pi}\,(\nabla_{12} v_{12}\cdot\nabla_{23} v_{23} + \nabla_{23} v_{23}\cdot\nabla_{31} v_{31} \\ + \nabla_{31} v_{31}\cdot\nabla_{12} v_{12}) + O(\lambda^4) . \end{aligned} \qquad (\text{A5})$$

It follows from the cluster property that U_l^m for $l > 3$ does not contribute to order λ^2.

Rather than substituting directly in (14), we go back to (8). Multiplying by W_N^c and integrating over the coordinates gives

$$\begin{aligned} Q = Q^c[1 + \tfrac{1}{2}N(N-1)\,\langle U_2^m(1,2)\rangle_c \\ + \tfrac{1}{6}N(N-1)(N-2)\,\langle U_3^m(1,2,3)\rangle_c + \cdots], \end{aligned} \qquad (\text{A6})$$

where

$$\langle f\rangle_c = (Q^c)^{-1}\int W_N^c\, f(\vec{r}_1, \ldots, \vec{r}_N)\, d^{3N}r . \qquad (\text{A7})$$

Using (A4) and (A5),

$$\begin{aligned} Q = Q^c\Big(1 - N(N-1)\,\lambda^2\frac{\beta}{24\pi}\,\{\langle\nabla_{12}{}^2 v_{12}\rangle_c \\ - \tfrac{1}{2}\beta\,[\langle(\nabla_{12} v_{12})^2\rangle_c + (N-2) \\ \times\langle\nabla_{12} v_{12}\cdot\nabla_{23} v_{23}\rangle_c]\} + O(\lambda^4)\Big) \end{aligned} \qquad (\text{A8})$$

It is easily shown, by integration by parts, that

$$\langle\nabla_1{}^2 V_N\rangle_c = \beta\langle(\nabla_1 V_N)^2\rangle_c . \qquad (\text{A9})$$

Inserting (A3) gives

$$\langle\nabla_{12}{}^2 v_{12}\rangle_c = \beta[\langle(\nabla_{12} v_{12})^2\rangle_c + (N-2)\,\langle\nabla_{12} v_{12}\cdot\nabla_{23} v_{23}\rangle_c] . \qquad (\text{A10})$$

From (A8) and (A10),

$$Q = Q^c[1 + \lambda^2 N(N-1)q/\Omega + O(\lambda^4)] , \qquad (\text{A11})$$

where

$$\begin{aligned} q &= -\tfrac{1}{2}\Omega\frac{\beta}{24\pi}\,\langle\nabla_{12}{}^2 v_{12}\rangle_c \\ &= -\frac{\beta}{48\pi}\int g(r)\,\nabla^2 v\, d^3r , \end{aligned} \qquad (\text{A12})$$

which is the usual result.[21]

APPENDIX B: $G(\vec{r}, \vec{r}; \beta)$ FOR SQUARE-WELL POTENTIAL

We wish to calculate $\lambda^3 G(\vec{r}, \vec{r};\, \beta)$ correct to first order in λ for the square-well potential (31).[22] We assume $\lambda \ll a$ and $\lambda \ll (b-a)$. To first order in λ, the curvature in the potential boundaries can be neglected.[16,23] This enables us to write

$$G(\vec{r}, \vec{r};\, \beta) \approx \tfrac{1}{2}\lambda^{-2} G_1(r, r;\, \beta)\,, \tag{B1}$$

where G_1 is the one-dimensional function defined by

$$G_1(x', x;\, \beta) = \langle x' \,|e^{-\beta H_{\rm OD}}|\, x\rangle\,, \tag{B2}$$

where

$$H_{\rm OD} = -\frac{\hbar^2}{m}\frac{d^2}{dx^2} + v(x)\,. \tag{B3}$$

Here, $v(x)$ is the one-dimensional potential

$$\begin{aligned} v(x) &= \infty, & x&<a\\ v(x) &= -\epsilon, & a&<x<b\\ v(x) &= 0, & x&>b. \end{aligned} \tag{B4}$$

To calculate G_1, we use the fact that its Laplace transform is the Green's function of the negative-energy Schrödinger equation.[24] This Green's function can be constructed, in the usual way, from two linearly independent solutions of the Schrödinger equation. If we use the symbol

$$L_\alpha^{-1} \equiv \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} dp\, e^{\alpha p} \tag{B5}$$

for the inverse Laplace transform, and let $\gamma = p^{1/2}$, $\alpha = \lambda^2/2\pi$, then the relation is

$$G_1(x', x;\, \beta) = -L_\alpha^{-1}\bar{G}_1(x', x;\, \gamma)\,, \tag{B6}$$

where

$$\bar{G}_1(x', x;\, \gamma) = [W(u_1, u_2)]^{-1} u_1(x_<) u_2(x_>). \tag{B7}$$

u_1, u_2 are solutions of

$$\left(-\frac{d^2}{dx^2} + \frac{m\,v(x)}{\hbar^2} + \gamma^2\right) u(x) = 0\,, \quad \mathrm{Re}\,\gamma > 0 \tag{B8}$$

and $W(u_1, u_2) = u_1 u_2' - u_1' u_2$ is their Wronskian.

The calculation for the square-well potential is straightforward. The result is (we need only diagonal elements)

$$\begin{aligned} &\bar{G}_1(x, x;\, \gamma) = 0\,, \quad x<a\\ &\bar{G}_1(x, x;\, \gamma) \approx -\frac{1}{2\Gamma}\left(1 - e^{-2\Gamma(x-a)} + \frac{\Gamma-\gamma}{\Gamma+\gamma}e^{-2\Gamma(b-x)}\right), \\ &\qquad\qquad a<x<b\\ &\bar{G}_1(x, x;\, \gamma) \approx -\frac{1}{2\gamma}\left(1 - \frac{\Gamma-\gamma}{\Gamma+\gamma}e^{-2\gamma(x-b)}\right), \quad x>b, \end{aligned} \tag{B9}$$

where $\Gamma^2 = \gamma^2 - m\epsilon/\hbar^2$. In deriving this, we have neglected terms such as $\exp[-2\Gamma(b-a)]$ which give exponentially small contributions to $G_1(x, x;\, \beta)$.

Equation (B9) can be further simplified by using the δ-function expansions of the exponentials.[25] We need keep only the first term, and the result is

$$\begin{aligned} &\bar{G}_1(x, x;\, \gamma) = 0,\quad x<a\\ &\bar{G}_1(x, x;\, \gamma) = -\frac{1}{2\Gamma} + \frac{1}{4\Gamma^2}\delta(x-a+) - \frac{1}{4\Gamma^2}\frac{\Gamma-\gamma}{\Gamma+\gamma}\\ &\qquad\times\delta(x-b-) + O\!\left(\frac{1}{\Gamma^3}\right), \quad a<x<b\\ &\bar{G}_1(x, x;\, \gamma) = -\frac{1}{2\gamma} + \frac{1}{4\gamma^2}\frac{\Gamma-\gamma}{\Gamma+\gamma}\delta(x-b+) + O\!\left(\frac{1}{\gamma^3}\right),\\ &\qquad\qquad x>b\,. \end{aligned} \tag{B10}$$

One could now perform the inverse Laplace transforms, and obtain $G(\vec{r}, \vec{r};\, \beta)$ explicitly. However, in our application, it is easier to leave the inverse transform until after the coordinate integrations.

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Low-Frequency Electric Microfield Distributions in a Plasma Containing Multiply Charged Ions[*,†]

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A theory for calculating low-frequency component electric microfield distributions for a plasma containing more than a single ion species is developed. Calculations at a charged point are made for a plasma containing N^+ singly charged ions and N^{++} doubly charged ions together with a charge neutralizing number of electrons, $N_e(N_e=N^+ + 2N^{++})$. Three different ion ratios ($R\equiv N^{++}/N^+$) are treated: $R=0.0,\ 1.0,\ \infty$. It is shown that the calculations allow for all ion-ion correlations to a high degree of accuracy. Numerical results are shown both graphically and in tabulated form.

I. INTRODUCTION

In recent years considerable effort has been devoted to the problem of spectral line broadening in plasmas.[1–3] In relation to this problem various theories of the static electric microfield distributions have been formulated.[4,5] However, all of these theories and subsequent calculations have only been concerned with plasmas containing a single positive-ion species. The purpose of this paper is to extend the theory developed by one of us to treat plasmas containing more than a single species of positive ion. Calculations for a plasma containing two positive-ion components have been made; the procedure for extending the calculations to situations with more than two species is indicated.

In this paper, calculations are made for a plasma that contains N^+ singly charged ions and N^{++} doubly charged ions $(N=N^+ + N^{++})$ together with a charge neutralizing number of electrons $N_e(N_e=N^+ + 2N^{++})$. It is assumed that ions interact with each other through an effective potential which includes electron-ion shielding. This model is the two-component analog of the single-component low-frequency model previously developed.[4,5] Since helium plasmas may have both singly and doubly charged species present, the model proposed here is appropriate for discussing the effect of a helium plasma on a radiating He$^+$ ion (He$^+\equiv$He II) or He atom. As in the papers dealing with singly charged perturbing ions, the calculation of the electric-microfield distribution at a neutral point (e.g., at a He atom) is just a special case of the charged-point development obtained by setting the charge at the origin equal to zero.

To make the mathematical development more general, we make the assumption that it is valid to consider a two-temperature plasma, one temperature for the ions, T_i and one for the electrons T_e. This procedure implies that while the ions may be considered to be in equilibrium with each other, and the electrons with each other, that the ions are not necessarily in equilibrium with the electrons. In the event that a true equilibrium situation prevails, $T_e=T_i$.

All numerical results presented here assume an equilibrium situation. The actual distribution functions are expressed in reduced field units which are a function of electron density only. The calculational programs that we have developed are quite general; they allow for the possibility of a two-temperature plasma, for the possibility that there may be any number of charged-ion perturber species (i.e., singly, doubly, etc.), and for the possibility that the radiator may have any degree of ionization.

Section II of this paper deals with the formal calculations. The asymptotic expressions for the microfield distribution function are presented in