assume the initial condition

$$f(t=0, v) = \delta(v - V_0) \tag{33}$$

and thus can write

$$f(t,v) = \frac{A(v,V_0)}{2\pi i} \int_C d\sigma \, \exp\left\{\sigma\left[t - \int_v^{V_0} dv'/b(v')\right]\right\} \tag{34}$$

$$= A(v,V_0)\delta\left[t - \int_v^{V_0} dv'/b(v')\right]. \tag{35}$$

$A(v,V_0)$ is some (normalizing) function of v.

This is just the form of the approximate distribution function (2). Furthermore, if we include terms of next-highest order, the second derivative of f appears in (29) but it is still possible to solve and invert the Laplace transform, by making use of the fact that the coefficient of $\partial^2 f/\partial v^2$ is small. The result is a distribution function of the kind (4), where the Gaussian shape arises from

use of saddle-point techniques in inverting the Laplace transform.

Finally, we remark that in the case where $\bar{w}_e > v$ on the average, we can put

$$b(v) = \frac{4\Gamma M N_e}{3\pi^{1/2} m_e \bar{w}_e^3}\left(v + \frac{3\pi^{1/2} m_e N_i \bar{w}_e^3}{4 m_i N_e v^2}\right) \tag{36}$$

$$\equiv \frac{1}{3\tau}\left(v + \frac{u^3}{v^2}\right) \tag{37}$$

and then the δ function in (35) can be replaced by

$$\delta\left(t + \tau \ln\frac{v^3 + u^3}{V_0^3 + u^3}\right). \tag{38}$$

This is exactly the result (16) in Butler and Buckingham's paper.

Perturbation Correction to the Radial Distribution Function*

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The effect on the radial distribution function $g(r)$ of adding a small, long-range interaction to a short-range potential is investigated. Two equations are obtained for the corrected g, corresponding to approximations similar to those used in obtaining the Percus-Yevick and convolution hypernetted chain integral equations. The equations relate the "short-range" g (assumed known) and the long-range perturbing potential to the g corresponding to the complete potential. These equations and equations previously obtained by Broyles, Sahlin, and Carley and Hemmer have been tested numerically for a model having a negative Gaussian-Mayer f function, for which near-exact solutions are available from the work of Helfand and Kornegay.

I. INTRODUCTION

THE thermodynamic behavior of a classical, one-component, monatomic fluid is completely characterized by the radial distribution function $g(r)$ when the potential energy of the system can be written as the sum of pair potentials. For an N-particle system in a volume V, $g(r)$ is defined as

$$g(r) = \frac{V^2 \int \cdots \int_V \exp{-\beta \sum_{i<j} \phi_{ij}} d\mathbf{r}_3 \cdots d\mathbf{r}_N}{\int \cdots \int_V \exp{-\beta \sum_{i<j} \phi_{ij}} d\mathbf{r}_1 \cdots d\mathbf{r}_N}, \tag{1}$$

when the limits $N \to \infty$, $V \to \infty$ are taken such that $\rho \equiv N/V$ remains constant; $\phi_{ij} \equiv \phi(|\mathbf{r}_i - \mathbf{r}_j|)$ is the pair potential and $\beta = 1/kT$.

This paper is concerned with the effect on $g(r)$, and hence on the thermodynamic quantities, of a small change in the potential $\phi(r)$. A solution to this problem could be used in a variety of applications. The need for a method to correct $g(r)$ arises, for example, in Monte Carlo calculations of the radial distribution function, where the long-range tail of a potential such as the Coulomb potential must necessarily be truncated at some finite distance. The effect of the neglected part of the potential must be found for a complete solution.[1] Furthermore, if the function $g(r)$ is known for some temperature T, $g(r)$ for some slightly different temperature T' may be easily found by considering $\beta'\phi(r)$, $\beta' = 1/kT'$, to be a perturbation of $\beta\phi(r)$ at T and applying the corresponding correction. This obviates

[1] D. D. Carley, Monte Carlo calculations for the Coulomb potential (to be published). The same problem arises from the Lennard-Jones 6–12 potential; W. W. Wood and F. R. Parker, J. Chem. Phys. **27**, 720 (1957).

the need for another long, iterative solution of the integral equations for $g(r)$. Finally, the effect of adding a long-range, attractive tail to a sharp barrier potential can be studied. A model with an exponential attractive potential added to a hard core has recently been investigated by Kac, Uhlenbeck, and Hemmer.[2] This model displayed a phase transition in the proper limit of the attractive potential, and its extension to three dimensions is of particular interest.

Two recent papers have dealt with this problem. Broyles, Sahlin, and Carley[3] (BSC) employed a method of collective coordinate integration to evaluate the Fourier transform of Eq. (1). By explicit summation of diagrams, Hemmer[4] has obtained two asymptotic equations for the corrected $g(r)$, valid in the large r and small r regions. The equations derived in these papers, together with two equations for $g(r)$ obtained in the next section, have been tested on a model for which exact solutions are known from the work of Helfand and Kornegay.[5] The results are given in Sec. III. It is also shown that one of the equations derived in Sec. II reduces, in the large r region, to the BSC equation and Hemmer's first-order solution for the same region.

II. THEORY

The $3N$-dimensional integral of Eq. (1) can be made more tractable by the use of Mayer f functions, resulting in the well-known expansion of $G(r)$ in powers of the density[6,7]

$$G(r) \equiv g(r) - 1 = f(r) + [1 + f(r)]C(r), \qquad (2)$$

$$C(r) = \sum_{n=1}^{\infty} \rho^n \Sigma \frac{1}{\mu(n,\gamma)} \int \prod_{i,j} f_{ij} \prod_{j=3}^{n+2} d\mathbf{r}_j, \qquad (3)$$

where

$$f_{ij} = f(r_{ij}) = e^{-\beta\phi(r_{ij})} - 1, \qquad (4)$$

and a 1, 2 index has been suppressed on r. Each power of the density in Eq. (3) is associated with several integrals Σ. The integrals in the expansion of $C(r)$ can

FIG. 1. Diagram expansion of $C(r)$.

[2] M. Kac, G. E. Uhlenbeck, and P. C. Hemmer, J. Math. Phys. 4, 216 (1963).
[3] A. A. Broyles, H. L. Sahlin, and D. D. Carley, Phys. Rev. Letters 10, 319 (1963).
[4] P. C. Hemmer, J. Math. Phys. 5, 75 (1964).
[5] E. Helfand and R. L. Kornegay (to be published).
[6] J. de Boer and A. Michels, Physica 6, 409 (1939); J. E. Mayer and E. Montroll, J. Chem. Phys. 9, 2 (1941); J. de Boer, Physica 15, 680 (1949).
[7] Here and in the remainder of this section we have adopted, with some slight alterations, the notation of M. Klein and M. S. Green, J. Chem. Phys. 39, 1367 (1963).

FIG. 2. The series, parallel, and bridge sets.

be represented by diagrams with a one-to-one correspondence in the following manner: An f_{ij} in the integrand is drawn as a line connecting the points i and j, which are drawn as dots if they are variables of integration (field points) or circles if points 1 or 2 (fixed points); $\mu(n,\gamma)$ is a symmetry number for the generic (unlabeled points) diagrams dependent on the number of field points (n) and the diagram type (γ). The first few terms in the expansion of $C(r)$ in this shorthand notation are shown in Fig. 1, where the density and symmetry factors have been explicitly written. These diagrams can be classed into three groups according to their topological characteristics:

(a) A *series*, or nodal, diagram contains at least one field point (called a node) through which all paths connecting 1 and 2 must pass.

(b) A *parallel* diagram contains at least two paths between 1 and 2 which are connected only at 1 and 2.

(c) A *bridge* diagram is one which is neither series nor parallel.

The sum of all series, parallel, and bridge diagrams will be denoted by $S(r)$, $P(r)$, and $B(r)$, respectively. To the second power in density these sets are as shown in Fig. 2. Then we have

$$C(r) = S(r) + P(r) + B(r), \qquad (5)$$

and

$$G(r) = S(r) + P(r) + B(r) \\ + f(r)[1 + S(r) + P(r) + B(r)] \qquad (6)$$

or

$$g(r)e^{\beta\phi(r)} = 1 + S(r) + P(r) + B(r). \qquad (7)$$

We will denote the set of all non-nodal diagrams in the expansion of $G(r)$ by $T(r)$,

$$T(r) = P(r) + B(r) + f(r)[1 + S(r) + P(r) + B(r)], \qquad (8)$$

$$= g(r)f(r)e^{\beta\phi(r)} + P(r) + B(r), \qquad (9)$$

and thus

$$G(r) = S(r) + T(r). \qquad (10)$$

The set $S(r)$ is factorable in Fourier transform space and can be eliminated in the following way. Let $\mathbf{r}_3$ be the first node encountered along a path from 1 to 2 in a typical diagram of $S(r)$. Then the subdiagram between 1 and 3 must be of a non-nodal type, i.e., a member of

$T(r)$. From 3 to 2 however there is no restriction on the subdiagram, either nodal or non-nodal being possible, hence some member of $G(r)$. Summing over all possible subdiagrams and integrating over $\mathbf{r}_3$ gives the set $S(r)$,

$$S(r)=\rho\int T(r_{13})G(r_{32})d\mathbf{r}_3, \tag{11}$$

so that we may write

$$G(r)=T(r)+\rho\int T(r_{13})G(r_{32})d\mathbf{r}_3. \tag{12}$$

This is the Ornstein-Zernicke integral equation[8] which gives $G(r)$ when the direct correlation function $T(r)$ is known. The Fourier transforms of $G(r)$ and $T(r)$ are thus seen to satisfy the relation

$$\tilde{G}(\mathbf{k})=\tilde{T}(\mathbf{k})/[1-\rho\tilde{T}(\mathbf{k})]. \tag{13}$$

Also, from Eqs. (10) and (11), we get that

$$\tilde{S}(\mathbf{k})=\rho\tilde{T}^2(\mathbf{k})/[1-\rho\tilde{T}(\mathbf{k})]. \tag{14}$$

The set $P(r)$ has the property that its members factor in direct space since there is no integration over points 1 and 2. An analysis of the diagrams of this set leads finally to the equation[9]

$$P(r)=g(r)e^{\beta\phi(r)}-1-\ln g(r)e^{\beta\phi(r)}, \tag{15}$$

which can be used to eliminate $P(r)$ in Eq. (7), yielding

$$g(r)e^{\beta\phi(r)}=e^{S(r)+B(r)}. \tag{16}$$

We note in passing that Eqs. (9), (12), and (15) result in the convolution-hypernetted chain (CHNC) integral equation[9] when the set $B(r)$ is neglected, while neglect of $P(r)+B(r)$ in Eq. (9) yields, with Eq. (12), the Percus-Yevick (PY) integral equation.[10-12]

We now assume that we have available a radial distribution function corresponding to the short range potential $\phi^{sr}(r)$:

$$g^{sr}(r)=\exp[-\beta\phi^{sr}(r)+S^{sr}(r)+B^{sr}(r)]. \tag{17}$$

We are interested in finding $g(r)$ for $\phi(r)=\phi^{sr}(r)+\phi^{lr}(r)$, where $\phi^{lr}(r)$ is a long-range potential assumed weak compared to $\phi^{sr}(r)$. Then

$$g(r)=\exp[-\beta\phi(r)+S(r)+B(r)], \tag{18}$$

$$=g^{sr}(r)\exp[-\beta\phi^{lr}(r)+\Delta S(r)], \tag{19}$$

where

$$\Delta S(r)\equiv S(r)-S^{sr}(r) \tag{20}$$

and $\Delta B(r)$, similarly defined, has been neglected.[13] This will be called the CHNC-type approximation. We have further from Eqs. (13) and (14) that

$$\Delta\tilde{S}(\mathbf{k})=\frac{\rho\tilde{T}^2(\mathbf{k})}{1-\rho\tilde{T}(\mathbf{k})}-\frac{\rho\tilde{T}^{sr2}(\mathbf{k})}{1-\rho\tilde{T}^{sr}(\mathbf{k})}, \tag{21}$$

$$=\frac{[1+\rho\tilde{G}^{sr}(\mathbf{k})]^2\Delta\tilde{T}(\mathbf{k})}{1-\rho[1+\rho\tilde{G}^{sr}(\mathbf{k})]\Delta\tilde{T}(\mathbf{k})}-\Delta\tilde{T}(\mathbf{k}), \tag{22}$$

where

$$\Delta T(r)\equiv T(r)-T^{sr}(r). \tag{23}$$

We now need to approximate $\Delta T(r)$. Since $\phi(r)$ has been written as the sum of long- and short-range terms, the Mayer f function for ϕ_{ij} may be written

$$f_{ij}=f_{ij}^{sr}+f_{ij}^{lr}+f_{ij}^{sr}f_{ij}^{lr}. \tag{24}$$

Each integrand of $T(r)$ then becomes a sum of integrands of mixed long- and short-range bonds. One of these will contain only short-range bonds f_{ij}^{sr}. Another will contain one long-range bond f_{ij}^{lr} or compound bond $f_{ij}^{sr}f_{ij}^{lr}$, and all remaining bonds of the short-range type, and so on, until no short-range bonds are present. The first group will sum to give $T^{sr}(r)$. The first term of the remainder is the single bond $f^{lr}(r)\approx-\beta\phi^{lr}(r)$, since the perturbing potential is assumed weak. We have thus to lowest order

$$(A)\quad \Delta T(r)=-\beta\phi^{lr}(r). \tag{25}$$

Higher approximations to $\Delta T(r)$ may easily be accommodated and are discussed in Sec. IV.

Insertion of the Fourier transform of Eq. (25) into Eq. (22) then gives, with Eq. (19), the final result,

$$g(r)=g^{sr}(r)e^{-H(r)}, \tag{26}$$

where the Fourier transform of $H(r)$ is

$$\tilde{H}(\mathbf{k})=\frac{[1+\rho\tilde{G}^{sr}(\mathbf{k})]^2\beta\tilde{\phi}^{lr}(\mathbf{k})}{1+\rho[1+\rho\tilde{G}^{sr}(\mathbf{k})]\beta\tilde{\phi}^{lr}(\mathbf{k})}. \tag{27}$$

In the large r limit where $g(r)$ and $g^{sr}(r)$ both approach 1, we may take the logarithm of both sides of Eq. (26) and replace $\ln g(r)$ by $g(r)-1$ and $\ln g^{sr}(r)$ by $g^{sr}(r)-1$ to obtain

$$G(r)=G^{sr}(r)-H(r), \tag{28}$$

which is the BSC equation.[3] This equation has been found to give satisfactory solutions for $g(r)$ at large r, but runs into difficulty at small r, often giving negative g's.[14] The derivation above indicates that the BSC

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[9] E. Meeron, J. Math. Phys. 1, 192 (1960); T. Morita, Progr. Theoret. Phys. (Kyoto) 20, 920 (1958); J. M. J. VanLeeuwen, J. Groeneveld, and J. de Boer, Physica 25, 792 (1959); M. S. Green, Hughes Aircraft Corporation Technical Report, 1959 (unpublished).

[10] J. K. Percus and G. J. Yevick, Phys. Rev. 110, 1 (1958); J. K. Percus, Phys. Rev. Letters 8, 462 (1962).

[11] A. A. Khan, Phys. Rev. 134, A367 (1964).

[12] George Stell, Physica 29, 517 (1963).

[13] The form of Eq. (19) was suggested by A. A. Khan (private communication).

[14] D. D. Carley, Phys. Rev. 131, 1406 (1963); H. L. Sahlin, thesis, University of Florida, 1963 (unpublished).

equation is not applicable at small r. If Eq. (28) is further approximated by assuming that the first term on the right is negligible, the resulting equation is equivalent to that obtained by Hemmer,[4] in first order, for the large r region.

We note in passing that in the limit $\phi^{sr}(r) \to 0$ so that $\phi^{lr}(r) \to \phi(r)$, Eqs. (26) and (27) give the Debye-Hückel[15] $g(r)$ when $\phi(r)$ is specified as the Coulomb potential.

An equation employing a PY-type approximation, where $\Delta P(r) + \Delta B(r)$ is neglected, is easily obtained from Eqs. (7), (22), and (25). The result is

$$g(r) = g^{sr}(r)e^{-\beta\phi^{lr}(r)} + e^{-\beta\phi(r)}[\beta\phi^{lr}(r) - H(r)]. \quad (29)$$

Equations (26) and (29), with $H(r)$ determined by Eq. (27), are the main results of this paper. In the next section a numerical test is made of these equations and the results compared to computations with the BSC and Hemmer equations.

III. THE GAUSSIAN MODEL

For a proper test of Eqs. (26) and (29) we need an exact solution of $g^{sr}(r)$, so that no additional approximations are introduced, as well as of the final $g(r)$ to permit a comparison of results. Such solutions are available, and can be used for this purpose, for a model with a Mayer f function approximated by a negative Gaussian. Helfand and Kornegay[5] have explicitly evaluated the coefficients $g_n(r)$ in

$$g(r) = e^{-\beta\phi(r)}\left[1 + \sum_{n=1}^{\infty} \rho^n g_n(r)\right] \quad (30)$$

up to $n = 5$ for this Gaussian model. At small values of density the $g(r)$ obtained in this way is essentially exact, the criterion being that $\rho^5 g_5(r)$ be small.
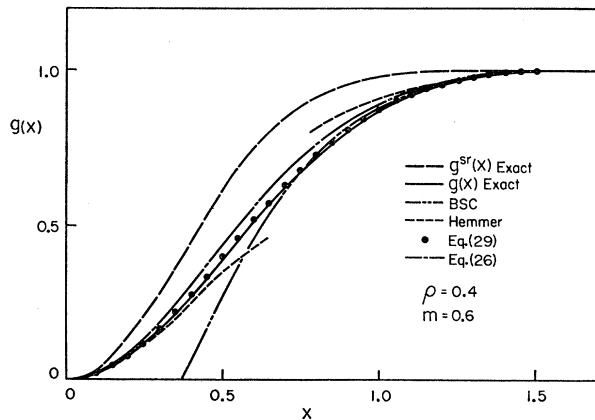
FIG. 3. Comparison of the computed g's for the Gaussian model with the exact solution of Helfand and Kornegay for a density of 0.4. The parameter of perturbation m is 0.6.

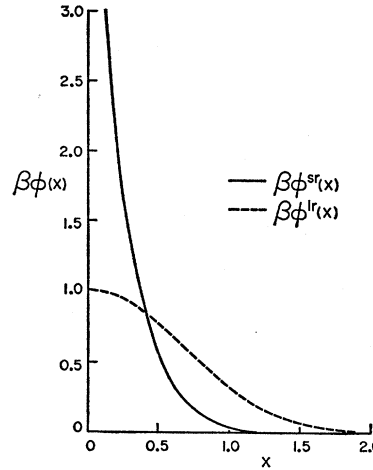[15] P. Debye and E. Hückel, Z. Physik 24, 185 (1923).

FIG. 4. The corresponding short-range potential and perturbing long-range potential for the g's of Fig. 3.

The Mayer f function is given by

$$f(r) = -e^{-(r/a)^2}, \quad (31)$$

and the unit of distance is selected so as to make the second virial coefficient of the pressure identical with that of a gas of hard spheres of diameter d. The reduced units are then

$$x = r/d, \quad \rho = Nd^3/V,$$

where

$$d = (\tfrac{3}{4})^{1/3}\pi^{1/6}a = 1.100a. \quad (32)$$

The potential corresponding to a solution $g(x)$ is

$$\beta\phi(x) = -\ln(1 - e^{-1.21x^2}). \quad (33)$$

We can obtain a $g(x)$ for a slightly different potential in the following way. Perform a coordinate transformation $x' = x/m$, where $0 < m \leq 1$. Then the function $\bar{\phi}(x) = \phi(x/m)$ will be of the same form as $\phi(x)$ but go to zero sooner. We will call $\phi(x/m)$ the short-range potential, $\phi^{sr}(x)$. The corresponding $g^{sr}(x)$ is obtained by replacing x by x/m and ρ by ρm^3 in the right-hand side of Eq. (30).

With $\phi^{lr}(x)$ given by

$$\phi^{lr}(x) = \phi(x) - \phi^{sr}(x), \quad (34)$$

and the $g^{sr}(x)$ obtained above, Eqs. (26) and (29) have been used to compute $g(x)$. This $g(x)$ was then compared with the known $g(x)$ from Eq. (30). The same input data were used to compute $g(x)$ from the BSC equation, Eq. (28), and the two first-order asymptotic forms of $g(x)$ obtained by Hemmer, Eqs. (35) and (41) of Ref. 4. (The application of Hemmer's equations to the Gaussian model should be qualified by the fact that a "hard" barrier short-range potential was assumed in their derivation, a condition not quite satisfied here.)

Calculations were made for densities of 0.1, 0.2, 0.3, and 0.4, for which the truncated series for $g(x)$ yields an essentially exact solution. For each value of density, four values of the parameter m were taken, $m = 0.9$, 0.8, 0.7, and 0.6, representing successively larger

perturbations. The results for $\rho = 0.4$, $m = 0.6$ are shown in Fig. 3. We see that, as expected, $g(x)$ computed from the BSC equation compares favorably with the exact $g(x)$ in the large x region, but becomes far too small as it approaches the origin. Hemmer's two asymptotic equations yield good agreement in the small and large x limits but allow no means of interpolation for intermediate values of x. Of the two equations obtained in this paper, that corresponding to the PY-type approximation gives a better result for $g(x)$, although an additional infinite set of diagrams has been neglected in its derivation. As with the PY integral equation, this is explained on the basis of cancellations between the sets $P(r)$ and $B(r)$.[11] The potentials for the g's of Fig. 3 are shown in Fig. 4. The results of other cases for Eqs. (26) and (29) are given in Fig. 5 in the form of rms deviation from the exact $g(x)$, where the rms is defined by

$$\text{rms} = \{N^{-1} \sum_{j=1}^{N} [g^{\text{ex}}(j\Delta) - g^{\text{comp}}(j\Delta)]^2\}^{1/2}. \quad (35)$$

Here N is the number of points taken in the numerical solutions and Δ the interval. The superscripts on $g(x)$
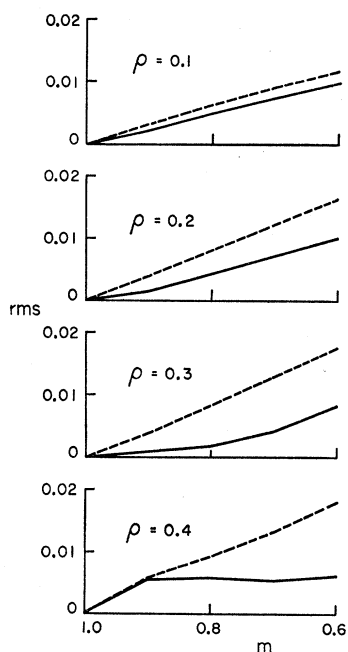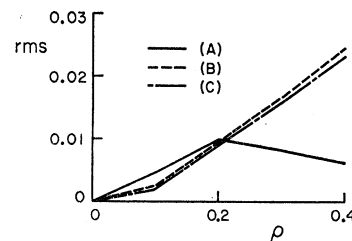
FIG. 5. The rms deviations from the exact Gaussian model $g(x)$ for g computed from Eq. (26) (dashed line) and Eq. (29) (solid line). Decreasing m corresponds to increasing perturbation of the potential.

FIG. 6. Density dependence of the rms deviations from the exact Gaussian model $g(x)$ for g's computed by neglecting $\Delta B(x) + \Delta P(x)$ and approximating $\Delta T(x)$ by (A), (B), and (C). The value of m is 0.6.

refer to the exact and computed g's. We note from Fig. 5 that the rms values obtained for Eqs. (26) and (29) are relatively insensitive to changes in density.

IV. HIGHER APPROXIMATIONS

More terms may easily be included in the evaluation of $\Delta T(r)$. Thus in the diagram expansion of $T(r)$ with short- and long-range bonds, we may retain beyond $T^{sr}(r)$ both the single bond $f^{lr}(r)$ and the smaller compound bond $f^{sr}(r)f^{lr}(r)$ to give

$$\text{(B)} \quad \Delta T(r) = e^{-\beta\phi sr(r)} f^{lr}(r). \quad (36)$$

Beyond this all diagrams with a direct bond between 1 and 2, either $f_{12}{}^{sr}$ or $f_{12}{}^{lr}f_{12}{}^{sr}$, may be summed to yield

$$\text{(C)} \quad \Delta T(r) = g^{sr}(r) f^{lr}(r). \quad (37)$$

At small densities these higher approximations do indeed lead to successively more accurate g's than does (A), Eq. (25), but at the price of worse answers at larger densities. This is seen for the Gaussian model in Fig. 6, where the rms values for the equations resulting from the PY-type approximation and approximations (A), (B), and (C), are shown as functions of the density for $m = 0.6$.

ACKNOWLEDGMENTS