

## Pressure-Consistent Integral Equation for Classical Fluids: Hard-Sphere Solutions\*

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An approximate integral equation for the pair correlation function of a classical fluid, proposed previously, has been solved numerically for the hard-sphere potential. The equation contains a parameter which is chosen so as to yield consistency between the virial and compressibility equations of state. The computed thermodynamic quantities are compared with those from the Percus-Yevick (PY) and hypernetted-chain (HNC) integral equations, and with the Ree-Hoover Padé  $P(3, 3)$  approximant. Further comparisons are made with a Monte Carlo solution at a density  $\rho\sigma^3=0.8$ . The pressure-consistent results are found to improve upon the PY and HNC equations.

## I. INTRODUCTION

In a previous paper,<sup>1</sup> we have proposed a simple generalization of the Percus-Yevick<sup>2</sup> (PY) and hypernetted-chain<sup>3</sup> (HNC) integral equations for the pair distribution function  $g(\mathbf{r})$  of a classical fluid. This equation is given by writing

$$C(\mathbf{r}) = g(\mathbf{r}) - g(\mathbf{r})e^{\beta u(\mathbf{r})} + \mu \{g(\mathbf{r})e^{\beta u(\mathbf{r})} - 1 - \ln[g(\mathbf{r})e^{\beta u(\mathbf{r})}]\} \quad (1)$$

for the direct correlation function  $C(\mathbf{r})$  in the Ornstein-Zernike equation

$$G(\mathbf{r}) \equiv g(\mathbf{r}) - 1 = C(\mathbf{r}) + \rho \int C(\mathbf{r}')G(|\mathbf{r} - \mathbf{r}'|)d\mathbf{r}', \quad (2)$$

where  $\beta=1/kT$ ,  $\rho$  is the number density, and  $u(\mathbf{r})$  is the two-body potential of the system. Although  $\mu$  in (1) can be defined in terms of infinite sets of doubly rooted graphs so as to make this equation exact, closure is achieved only by drastic approximations to this function. Thus,  $\mu=0$  and  $\mu=1$  lead to the PY and HNC equations, respectively. With the selection of  $\mu$  at our discretion, other approximations may be easily made and, in particular, may be more closely tailored to the potential function and thermodynamic constraints of the system being studied. In I, a simple, noniterative scheme resulting in a temperature-dependent  $\mu$  was used.<sup>4</sup> This and the above choices for  $\mu$ , however, lead to inconsistency between the equa-

tions of state as calculated from the virial theorem,<sup>5</sup>

$$\frac{\beta p}{\rho} = 1 - \frac{1}{6}\rho\beta \int_0^\infty r g(\mathbf{r}) u'(\mathbf{r}) 4\pi r^2 dr, \quad (3)$$

where the prime denotes differentiation, and from density fluctuations,<sup>6</sup>

$$\beta \left( \frac{\partial p}{\partial \rho} \right)_T = \left[ 1 + \rho \int_0^\infty G(\mathbf{r}) 4\pi r^2 dr \right]^{-1} = 1 - \rho \int_0^\infty C(\mathbf{r}) 4\pi r^2 dr. \quad (4)$$

The last equality follows from Eq. (2). Thus a natural criterion for the selection of  $\mu$  is to require a consistent equation of state from the two routes, resulting in a  $\mu$  varying with both temperature and density.<sup>7</sup> This is the choice made by Rowlinson,<sup>8</sup> who has also proposed Eq. (1). The coefficients of the first three terms in the density expansion of  $\mu$  have been obtained by Rowlinson.<sup>8</sup> A similar generalization of the HNC equation has been made by Hurst and others.<sup>9</sup>

A reliable test of this approach requires numerical solutions of (1) and (2) at densities beyond the range of the known virial expansions. These have been obtained for a fluid composed of hard spheres, with  $\mu$  adjusted to achieve a consistent equation of state. The results are presented in the next section.

## II. NUMERICAL PROCEDURE AND RESULTS

Defining

$$H(\mathbf{r}) \equiv g(\mathbf{r}) \exp[\beta u(\mathbf{r})] - 1, \quad (5)$$

\* Work performed under the auspices of the U.S. Atomic Energy Commission.

<sup>1</sup> D. D. Carley and F. Lado, *Phys. Rev.* **137**, A42 (1965) (referred to here as I). We are concerned here only with Eq. (A) of this paper.

<sup>2</sup> J. K. Percus and G. J. Yevick, *Phys. Rev.* **110**, 1 (1958); J. K. Percus, *Phys. Rev. Letters* **8**, 462 (1962).

<sup>3</sup> J. M. J. Van Leeuwen, J. Groeneveld, and J. De Boer, *Physica* **25**, 792 (1959); E. Meeron, *J. Math. Phys.* **1**, 192 (1960); T. Morita, *Progr. Theoret. Phys. Kyoto* **23**, 385 (1960); M. S. Green, *J. Chem. Phys.* **33**, 1403 (1960); G. S. Rushbrooke, *Physica* **26**, 259 (1960); L. Verlet, *Nuovo Cimento* **18**, 77 (1960).

<sup>4</sup> The parameter  $m$  of I is related to  $\mu$  by  $\mu = 1 + m$ .

<sup>5</sup> J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 136.

<sup>6</sup> Reference 5, p. 128.

<sup>7</sup> F. Lado, thesis, University of Florida, 1964 (unpublished).

<sup>8</sup> J. S. Rowlinson, *Mol. Phys.* **9**, 217 (1965).

<sup>9</sup> C. Hurst, *Proc. Phys. Soc. (London)* **86**, 193 (1965); D. Henderson, *ibid.* **87**, 592 (1966); G. J. Throop and R. J. Bearman, *ibid.* **88**, 539 (1966).

Eqs. (1) and (2) may be conveniently written

$$H_{12} = \mu P_{12} + \rho \int (C_{13} + H_{13} - \mu P_{13}) C_{32} d\mathbf{r}_3, \quad (6)$$

with

$$P(\mathbf{r}) = H(\mathbf{r}) - \ln[1 + H(\mathbf{r})],$$

$$C(\mathbf{r}) = [1 + H(\mathbf{r})]f(\mathbf{r}) + \mu P(\mathbf{r}), \quad (7)$$

where  $f$  is the Mayer  $f$  function,  $f = \exp(-\beta u) - 1$ . Taking the Fourier transform of both sides of (6), we obtain

$$h(k) = \mu \phi(k) + \{\rho c^2(k) / [1 - \rho c(k)]\}, \quad (8)$$

where the transforms are defined as follows:

$$H(\mathbf{r}) = \frac{1}{2\pi^2 r} \int_0^\infty kh(k) \sin kr dk,$$

$$h(k) = \frac{4\pi}{k} \int_0^\infty rH(\mathbf{r}) \sin kr dr; \quad (9)$$

$\phi(k)$  and  $c(k)$  are similarly defined as the transforms of  $P(\mathbf{r})$  and  $C(\mathbf{r})$ .

The system of equations to be solved is the discrete counterpart of Eqs. (7) and (8). We choose a range  $(0, R)$  in  $\mathbf{r}$  and divide it into  $N = R/\Delta r$  intervals of equal size  $\Delta r$ , evaluating the functions at the points  $\mathbf{r}_j = j\Delta r$ . The same division is done in transform space, with the interval  $\Delta k$  determined by the condition

$$\Delta k \Delta r = \pi/N.$$

When the numerical quadratures of (9) are performed with the trapezoidal rule, this condition preserves the orthogonality of the sine functions.

The method of solution is by iteration and is similar to that applied to the PY and HNC equations.<sup>10</sup> Initial guesses are made for  $\mu$  and  $H_j = H(\mathbf{r}_j)$ ,  $j = 1, \dots, N$  (the zero point need not be computed). Equations (7) then give the corresponding  $P$  and  $C$  functions, whose transforms are computed and used in (8) to obtain a new value of  $H$  after an inverse transformation. This process is repeated until a self-consistent  $H$  for this guessed  $\mu$  has been found, whereupon the virial and compressibility equations of state are computed. (We use “ $v$ ” and “ $c$ ,” respectively, to label these quantities.) If these are not (approximately) equal, a new value of  $\mu$  is chosen according to the formula

$$\mu^{(i+1)} = \mu^{(i)} - \Delta\phi^{(i)}(\mu^{(i)} - \mu^{(i-1)}) / \Delta\phi^{(i)} - \Delta\phi^{(i-1)},$$

$$\Delta\phi = \phi_c - \phi_v, \quad \phi \equiv \beta p / \rho. \quad (10)$$

<sup>10</sup> A. A. Broyles, S. U. Chung, and H. L. Sahlin, *J. Chem. Phys.* **37**, 2462 (1962); M. Klein and M. S. Green, *ibid.* **39**, 1367 (1963); G. J. Throop and R. J. Bearman, *Physica* **32**, 1298 (1966); and other references in these.

The superscripts label the successive iterations for  $\mu$ . With this new value of  $\mu$  the  $H$  iteration then begins afresh.

The solution thus has to satisfy two consistency requirements. For a given  $\mu$ , the consistency between successive iterates of  $H$  was measured by the root-mean-square difference

$$D_{\text{rms}} = [N^{-1} \sum_{j=1}^N r_j^2 (H_j^{\text{out}} - H_j^{\text{in}})^2]^{1/2} \quad (11)$$

as well as by the largest difference

$$D_{\text{max}} = \max_j |r_j(H_j^{\text{out}} - H_j^{\text{in}})|. \quad (12)$$

Consistency of the equation of state was measured by the relative difference (subtracting out the ideal-gas term)

$$D_\phi = (\phi_c - \phi_v) / (\phi_v - 1), \quad (13)$$

where the compressibility equation of state was evaluated by a Simpson’s rule integration of Eq. (4). Owing to this, the solutions had to be obtained stepwise in  $\rho$ , beginning at  $\rho = 0$ , in increments  $\Delta\rho$ .

Following Broyles,<sup>11</sup> we employed the successful techniques of mixing iterates of  $H$  and periodically introducing the “extrapolated”  $H$  to speed convergence.

### A. Hard-Sphere System

For hard spheres of diameter  $\sigma$  we write the Mayer  $f$  bond as

$$f(\mathbf{r}) = -1, \quad r < \sigma,$$

$$= -\frac{1}{2}, \quad r = \sigma,$$

$$= 0, \quad r > \sigma. \quad (14)$$

Numerical solutions were obtained in the range  $\rho\sigma^3 = 0.1-1.0$  at intervals  $\Delta(\rho\sigma^3) = 0.025$ . [Values of  $\beta(\partial p_c/\partial\rho)$  below 0.1 needed for the numerical integration of (4) were taken from the virial expansion for (6).] Below  $\rho\sigma^3 = 0.85$ , the range of  $R$  was at most  $R = 9.375\sigma$  with  $\Delta r = 0.0125\sigma$ . In this region, iteration was continued until the consistency measures defined above satisfied  $D_{\text{rms}} < 10^{-5}$ ,  $D_{\text{max}} < 10^{-4}$ , and  $D_\phi < 10^{-4}$ . At  $\rho\sigma^3 = 0.85$  and above, with increasing range and magnitude of the function  $H(\mathbf{r})$ , each of these consistency limits was increased by a factor of 10, while  $\Delta r$  was increased to  $0.02\sigma$  and the range extended to at most  $R = 14\sigma$ .

The computed excess equation of state for hard spheres is tabulated in Table I, along with the corresponding values from the Padé  $P(3,3)$  approximant of Ree and Hoover<sup>12</sup> (RH), the analytic PY solutions

<sup>11</sup> A. A. Broyles, *J. Chem. Phys.* **33**, 456 (1960).

<sup>12</sup> F. H. Ree and W. G. Hoover, *J. Chem. Phys.* **40**, 939 (1964).

TABLE I. The equation of state for hard spheres from the Ree-Hoover  $P(3, 3)$  approximant, Eq. (6) (pressure consistent), and the PY and HNC equations (virial and compressibility versions).

$\rho\sigma^3$	$(\beta p/\rho) - 1$			
	RH	Eq. (6)	PY(V) PY(C)	HNC(V) HNC(C)
0.1	0.240	0.240	0.239	0.241
			0.240	0.239
0.2	0.554	0.553	0.550	0.566
			0.555	0.546
0.3	0.968	0.966	0.954	1.01
			0.973	0.938
0.4	1.52	1.51	1.48	1.64
			1.54	1.44
0.5	2.27	2.25	2.17	2.53
			2.31	2.08
0.6	3.29	3.24	3.09	3.81
			3.38	2.90
0.7	4.71	4.61	4.32	5.69
			4.90	3.98
0.8	6.73	6.51	6.00	8.49
			7.12	5.40
0.9	9.66	9.24	8.33	12.7
			10.5	7.31
1.0	14.0	13.2	11.6	19.5
			15.6	9.94

of Wertheim<sup>13</sup> and Thiele,<sup>14</sup> and numerical solutions of the HNC equation. (We have recomputed these HNC values. The results are in agreement with Levesque<sup>15</sup> and differ somewhat from those of Klein,<sup>16</sup> with differences ranging up to 10% in some cases.) Comparison with Monte Carlo<sup>17</sup> (MC) and molecular dynamics<sup>18</sup> (MD) computations indicates that the RH values may be taken as a reasonably "exact" hard-sphere equation of state in the fluid region. Thus in Fig. 1 we have plotted the results of the three approximate

<sup>13</sup> M. S. Wertheim, Phys. Rev. Letters **10**, 321 (1963); J. Math. Phys. **5**, 643 (1964).

<sup>14</sup> E. Thiele, J. Chem. Phys. **39**, 474 (1963).

<sup>15</sup> D. Levesque, Physica **32**, 1985 (1966).

<sup>16</sup> M. Klein, J. Chem. Phys. **39**, 1388 (1963).

<sup>17</sup> W. W. Wood, "Monte Carlo Study of Simple Liquid Models," in *The Physics of Simple Liquids*, H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke, Eds. (to be published).

<sup>18</sup> B. J. Alder and T. E. Wainwright, cited in Ref. 12.

integral equations in the form of deviations from the RH curve.

The most notable feature of the present solution, as well as that of the PY and HNC results, is the absence of the phase transition suggested by MC and MD calculations to begin at  $\rho\sigma^3 \approx 0.88$ . Despite this failure, Eq. (6) is seen to give improved agreement in the fluid region with the RH values.

The excess inverse compressibility,  $\beta(\partial p_e/\partial\rho) - 1$ , is listed in Table II for the same sources as Table I. (The RH values were obtained by differentiation of the Padé approximant.) The same quantities are plotted in Fig. 2 in the form of deviations from the RH curve. Again the improvement of the pressure-consistent equation over the PY and HNC equations is clear.

The present approximation shows comparable accuracy, referred to the RH values, with the computationally more difficult PY II equation of Verlet,<sup>19</sup> based on the examination of three hard-sphere calculations for this equation.<sup>20</sup>

We have also obtained, for purposes of comparison, a Monte Carlo<sup>21</sup> solution for hard spheres at the

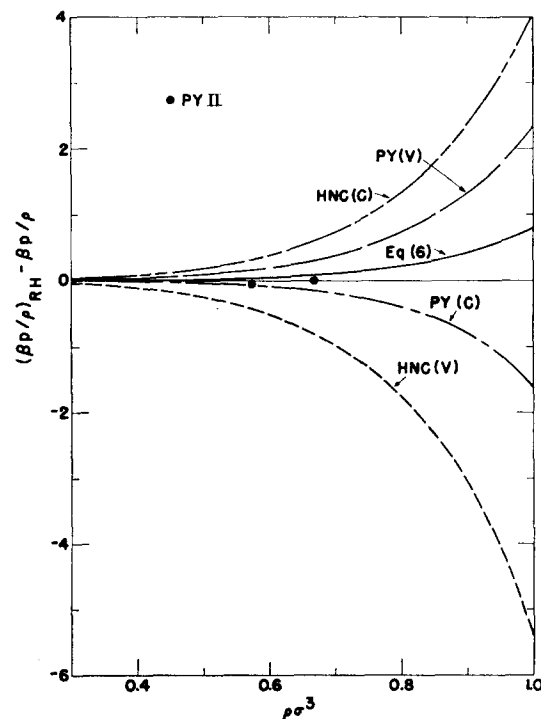


FIG. 1. The deviations from the Ree-Hoover  $P(3, 3)$  approximant of the hard-sphere equations of state computed from the HNC, PY, and pressure-consistent [Eq. (6)] equations. The solid points are from Verlet's PY II equation.

<sup>19</sup> L. Verlet, Physica **31**, 959 (1965).

<sup>20</sup> L. Verlet and D. Levesque, "On the Theory of Classical Fluids VI," April 1966, Laboratoire de Physique Theorique et Hautes Energies, Orsay, France (preprint).

<sup>21</sup> N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953); W. W. Wood and F. R. Parker, *ibid.* **27**, 720 (1957).

density  $\rho\sigma^3=0.8$ . The MC system was composed of 108 molecules in a cubical volume, replicated into an infinite system by periodic boundary conditions. The results presented represent slightly more than 50 000 moves per molecule in the basic random walk of the system. The pair correlation function  $g(r)$  defined by this system is shown in Fig. 3, as are the  $g$ 's which satisfy Eq. (6) and the PY and HNC equations; intertwining and crossing each other at several places, they are seen to be in reasonably good agreement with one another. The most noticeable outlier is the HNC solution. In the vicinity of the hard core, the differences become greater, resulting in accentuated differences in the equation of state. Here Eq. (6) is seen to give the best agreement with Monte Carlo. The value of the MC  $g$

TABLE II. The inverse compressibility for hard spheres from the Ree-Hoover  $P(3, 3)$  approximant, Eq. (6) (pressure consistent), and the PY and HNC equations.

$\rho\sigma^3$	$\beta(\partial p_c/\partial\rho) - 1$			
	RH	Eq. (6)	PY(C)	HNC(C)
0.1	0.513	0.513	0.513	0.509
0.2	1.27	1.27	1.28	1.24
0.3	2.40	2.38	2.42	2.26
0.4	4.08	4.03	4.15	3.69
0.5	6.60	6.49	6.82	5.69
0.6	10.4	10.2	11.0	8.52
0.7	16.3	15.8	17.7	12.6
0.8	25.2	24.6	28.6	18.5
0.9	38.8	38.6	47.3	27.3
1.0	58.0	61.9	80.4	41.2

at contact, estimated by least-squares fitting, yields  $\beta p/\rho - 1 = 6.748 \pm 0.014$ . This compares well with the RH value of 6.73 used as the standard in Fig. 1.

Differences appear more clearly in the direction correlation functions  $C(r)$  shown in Fig. 4, corresponding to the  $g$ 's of Fig. 3. The Monte Carlo  $C$  shown is not a direct result of the MC calculation. However, a relation recently derived by Baxter<sup>22</sup> from the Ornstein-Zernike equation connects the values of  $g$  and  $C$  within the region where  $C$  is nonvanishing, the range  $(0, R_c)$  say, obviating the need to know  $g$  for separations greater than  $R_c$ . We have used this relation to obtain  $C$  from the MC  $g$  between 0 and  $R_c$ . Here a word of caution is in order. Since  $C$  does not vanish identically as in the case of the PY equation, there is some ambiguity with regard to the proper value of  $R_c$  to be used. The points shown result from taking  $R_c = 1.125\sigma$  and indistinguishable values, on the scale plotted, follow from the choice  $R_c = 1.225\sigma$ . However, significant differences appear with  $R_c = 1.5\sigma$ , and with  $R_c = 2.5\sigma$

<sup>22</sup> R. J. Baxter, Phys. Rev. **154**, 170 (1967), Eqs. (38) and (39).

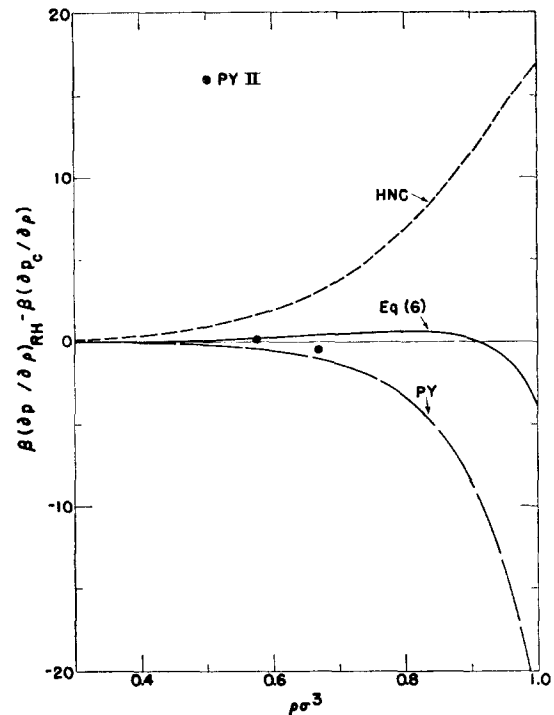


FIG. 2. The deviations from the derivative of the Ree-Hoover  $P(3, 3)$  approximant of the hard-sphere inverse compressibilities computed from the HNC, PY, and pressure-consistent [Eq. (6)] equations. The solid points are from Verlet's PY II equation.

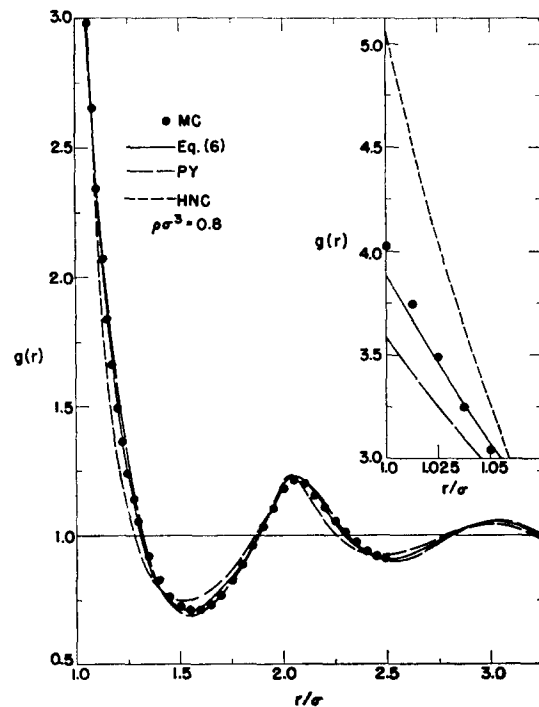


FIG. 3. The pair correlation function  $g(r)$  for hard spheres at a density  $\rho\sigma^3=0.8$ , obtained by Monte Carlo methods and from the HNC, PY, and pressure-consistent [Eq. (6)] equations.

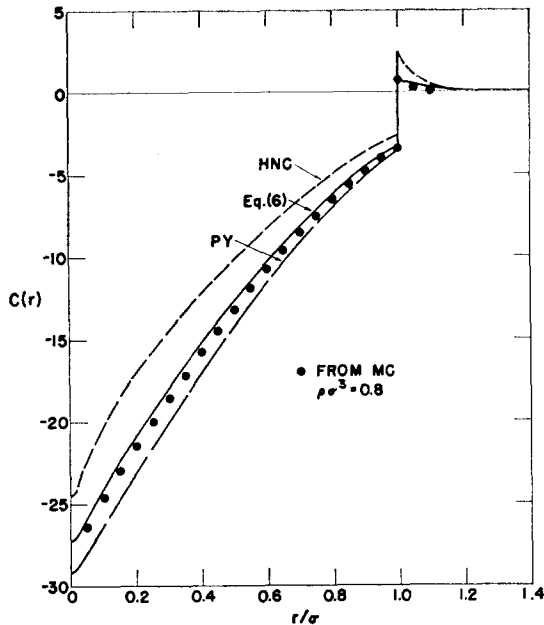


FIG. 4. The direct correlation function  $C(r)$  corresponding to the  $g$ 's of Fig. 3. The MC  $C(r)$  was computed using Baxter's equation (see text).

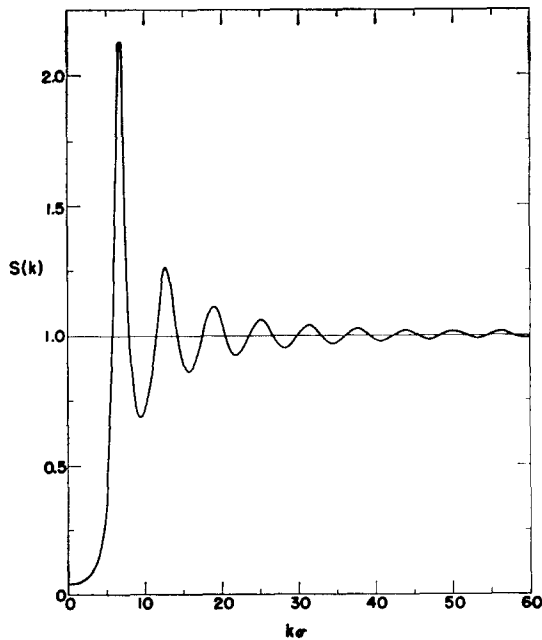


FIG. 5. The liquid structure factor

$$S(k) = 1 + \rho \int G(r) \exp(i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r}$$

for hard spheres at  $\rho\sigma^3 = 0.8$  from the pressure-consistent [Eq. (6)] equation.

the resulting  $C$  is qualitatively wrong. This behavior was verified with the integral equation  $g$ 's, where the correct  $C$  was known. Consequently, while the values of the Monte Carlo  $C$  presented are believed to be essentially correct, no claim of accuracy is made and they are shown for purposes of qualitative comparison.

Finally, we show in Fig. 5, for the same density, the liquid structure factor,

$$S(k) = 1 + \rho \int G(r) \exp(i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r},$$

obtained from Eq. (6). The other integral equations lead to essentially the same curve and are not plotted.

The first three terms in the virial expansion of  $\mu$  were evaluated by Rowlinson<sup>9</sup> and are, for hard spheres,

$$\mu = 0.1656 + 0.2716 (\rho\sigma^3) + 0.1242 (\rho\sigma^3)^2 + \dots \quad (15)$$

The general dependence of  $\mu$  on  $\rho\sigma^3$ , as found by itera-

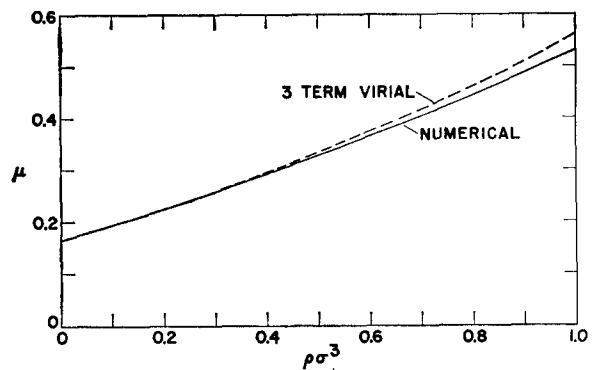


FIG. 6. Variation with density of the pressure-consistency parameter  $\mu$  for hard spheres.

tion, is shown in Fig. 6. (The value of  $\mu$  used previously in I was 0.2708.)

Variation of  $\mu$  between 0 and 1 produces corresponding changes in  $\beta p_v/\rho$  and  $\beta(\partial p_c/\partial \rho)$  between their values for the PY and HNC equations. This is shown in Fig. 7 for a density  $\rho\sigma^3 = 0.7$ . As  $\mu$  is increased,  $p_v$  increases and  $\partial p_c/\partial \rho$  (and hence  $p_c$ ) decreases. The particular value of  $p_c$  depends of course on previous solutions at lower densities. The value of  $\mu$  needed for continued pressure consistency at this density was found to be 0.404.

### B. Errors

The initial source of errors in these calculations is the introduction of a finite range and interval in the evaluation of the integrals. The effect of the former was studied by automatically augmenting the range of the solutions by an average 50% upon arriving at a

final converged solution. The new solutions then obtained yielded values of the computed excess thermodynamic quantities differing from the previous ones by less than 0.01% in all cases. We conclude that errors due to the finite range are of no significance in the results quoted.

The numerical results are somewhat more sensitive to the size of the interval  $\Delta\tau$ . To examine the consequences of varying  $\Delta\tau$ , numerical solutions were obtained at  $\rho\sigma^3=0.7$  for the PY equation with  $\Delta\tau/\sigma=0.1, 0.05, 0.025,$  and  $0.0125$ . All other numerical parameters were held fixed. By comparison with the known exact values, it was found that the errors in the computed excess equation of state using the above intervals were 2.96%, 0.79%, 0.20%, and 0.04%, respectively. The corresponding errors in the excess inverse compressibility were 4.82%, 1.29%, 0.33%, and 0.06%. With the interval used in the reported solution, 0.0125, the errors are seen to be small, though they are likely to increase somewhat with increasing  $\rho$  as the iterated function  $H$  becomes more sharply varying in  $\tau$ .

The final source of error is the possibility of incomplete convergence of the iterated function  $H$ , in particular at higher densities where the convergence rate is low. This error is more difficult to control or estimate. Besides the previously mentioned convergence criteria

$D_{\text{rms}}$  and  $D_{\text{max}}$ , another measure of the convergence is the rms difference between a computed  $H$  and its "extrapolated" value,<sup>11</sup> defined as in Eq. (11). This number, which is not very stable from iteration to iteration, showed an upward trend from orders of  $10^{-7}$ – $10^{-8}$  at the lowest densities to  $10^{-2}$ – $10^{-3}$  at the highest, suggesting a steadily worsening convergence. We believe that incomplete convergence is the most significant source of error in the upper third of the density region studied.

In order to obtain a reliable over-all estimate of the computational errors, we have solved the hard-sphere PY equation numerically over the same density range with the same numerical parameters used in solving Eq. (6). The results so obtained can then be compared to the exact solutions.<sup>13,14</sup> These comparisons show errors in the excess thermodynamic quantities everywhere less than 0.75% with the exception of  $\beta(\partial p_c/\partial\rho)-1$  at  $\rho\sigma^3=1.0$  where the error was 1.11%. For  $\rho\sigma^3=0.7$  and below, the errors were less than 0.1%. We conclude that the results displayed in Tables I and II are correct to about 1.0% or less in the upper third of the density range studied and to about 0.1% or less in the lower two-thirds.

### III. CONCLUSIONS

The introduction of a temperature- and density-dependent parameter,  $\mu$ , selected so as to make the virial and compressibility equations of state consistent with each other, has been shown to lead to improvements over the PY and HNC equations for hard spheres. Limited comparisons with Verlet's PY II equation indicate comparable accuracy with that approximation, which is computationally more difficult.

One of the advantages of Eq. (6) is that the approximation made is not fixed *a priori*, but rather depends on the particular potential function and thermodynamic conditions of the problem being studied. This gives some hope that, with  $\mu$  chosen so as to achieve pressure consistency, for example, it may be applied under a wide variety of such conditions.

### ACKNOWLEDGMENT

The author is indebted to Dr. W. W. Wood for several helpful discussions, as well as for guidance in the Monte Carlo method.

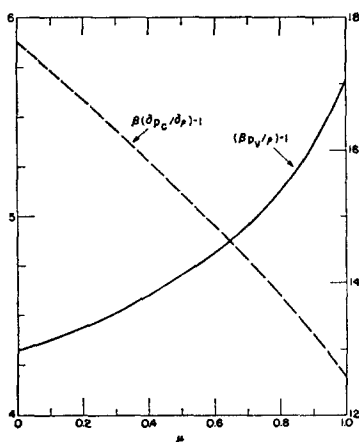


FIG. 7. Variation with  $\mu$  of the computed excess quantities  $(\beta p_v/\rho)-1$  and  $\beta(\partial p_c/\partial\rho)-1$  for hard spheres at a density  $\rho\sigma^3=0.7$ . The values at  $\mu=0$  and  $\mu=1$  are those for the PY and HNC equations, respectively. The scale for  $(\beta p_v/\rho)-1$  is on the left, for  $\beta(\partial p_c/\partial\rho)-1$  on the right.