

the behavior of  $g(1.0)$  from Eq. (6) as a function of  $r_c$ . Also shown for comparison are  $g^{\text{CHNC}}(1.0)$ ,  $g^{\text{PY}}(1.0)$ , and  $g^{\text{DH}}(1.0)$ . The labels CHNC and PY on the lowest curves in Fig. 2 indicate the results obtained with Eq. (6) when  $g^{\text{SR}}$  is calculated with the CHNC and PY equations, respectively.

Any errors in  $g$  from Eq. (6) might be expected to vary with  $r_c$ . When these errors are negligible,  $g$  will be independent of  $r_c$ . For this reason, we believe that the flat region of  $g$  in Fig. 2 (where the CHNC and PY equations are producing almost the same  $g^{\text{SR}}$ ) may be very close to the exact value of  $g$ . This value compares much more favorably with  $g^{\text{PY}}$  than with  $g^{\text{CHNC}}$  (with  $r_c = \infty$ ).

In conclusion then, we are lead to believe that

the PY equation is superior to the CHNC equation for long-range potentials as well as short-range at the temperatures and densities we have investigated. In addition, the procedure described here may provide a means of determining a nearly exact  $g$  in cases where it shows a region independent of  $r_c$ .

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<sup>1</sup>J. K. Percus, Phys. Rev. Letters 8, 462 (1962).

<sup>2</sup>A. A. Broyles, S. U. Chung, and H. L. Sahlin, J. Chem. Phys. 37, 2462 (1962).

<sup>3</sup>D. Pines and D. Bohm, Phys. Rev. 85, 338 (1952).

<sup>4</sup>A. A. Broyles, Z. Physik 151, 187 (1958).

## EXACT SOLUTION OF THE PERCUS-YEVICK INTEGRAL EQUATION FOR HARD SPHERES\*

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An increasing body of numerical computations has given strong evidence for the adequacy, over an extensive range of parameters, of various approximate integral equations for the radial distribution function of a classical fluid. The simplest, and on the basis of comparisons thus far made, the most satisfactory of these, is due to Percus and Yevick (PY).<sup>1</sup> Despite its simplicity, this equation until now has not been solved rigorously in any special situation, so that its basic properties have not been ascertained. It is the purpose of this Letter to obtain in closed form the pair distribution and equation of state of the PY equation for the prototype of interacting hard spheres.

The PY equation<sup>1</sup> for hard spheres is given by

$$\begin{aligned} \tau(\vec{r}) = 1 + n \int_{|\vec{r}'| < R} \tau(\vec{r}') d\vec{r}' \\ - n \int_{\substack{|\vec{r}'| < R, \\ |\vec{r} - \vec{r}'| > R}} \tau(\vec{r}') \tau(\vec{r} - \vec{r}') d\vec{r}', \end{aligned} \quad (1)$$

where  $R$  is the hard-sphere diameter,  $n$  is the particle density. The function  $\tau(\vec{r})$  of PY<sup>1</sup> is related to the pair distribution function  $g(\vec{r})$  and the direct correlation function  $C(\vec{r})$  of Ornstein and Zernike<sup>2</sup> by

$$\begin{aligned} g(\vec{r}) &= 0 & (r < R), \\ g(\vec{r}) &= \tau(\vec{r}) & (r > R), \\ C(\vec{r}) &= -\tau(\vec{r}) & (r < R), \\ C(\vec{r}) &= 0 & (r > R). \end{aligned} \quad (2)$$

If we take the one-side Laplace transform of (1), defining

$$F(t) = R^{-2} \int_0^R r \tau(r) \exp(-sr) dr,$$

$$G(t) = R^{-2} \int_R^\infty r \tau(r) \exp(-sr) dr,$$

$$K = R^{-3} \int_0^R \tau(r) r^2 dr,$$

$$\eta = \frac{1}{8} n R^3, \quad sR = t,$$

we obtain

$$\begin{aligned} t[F(t) + G(t)] = t^{-1} [1 + 24 \eta K \\ - 12 \eta [F(-t) - F(t)] G(t)], \end{aligned} \quad (3)$$

where the real part of  $s$  must be greater than zero.

On expanding the PY equation in powers of the density, one finds that in second order  $C(r)$  retains the functional form obtained in first order, namely, a cubic polynomial with quadratic term absent. This suggests trying a solution of the form

$$-C(x) = \alpha + \beta x + \gamma x^2 + \delta x^3, \quad (4)$$

where  $x = (r/R)$ , computing  $F(t)$  and  $F(-t)$  and solving Eq. (3) for  $G(t)$ . One can show directly from (1) that  $\tau^{(n)}(r)$ , with the superscript denoting differentiation, is continuous at  $r = R$  for  $n = 0, 1, 2$ , and that  $\tau(0) = 1 + 24 \eta K$ . The values of

$\tau_{>}(n)(R)$  can be expressed in terms of  $G(t)$  by noting that for  $t$  large

$$G(t) = e^{-t} \sum_{n=0}^{\infty} \sigma_{>}^{(n)}(1) t^{-n-1} + O(e^{-2t}),$$

where  $\sigma(x) = x\tau(x)$ . Solving the four simultaneous algebraic equations, we obtain two solutions:

$$\begin{aligned} \alpha &= (1+2\eta)^2/(1-\eta)^4, \\ \beta &= -6\eta(1+\frac{1}{2}\eta)^2/(1-\eta)^4, \\ \gamma &= 0, \\ \delta &= \eta(1+2\eta)^2/2(1-\eta)^4, \end{aligned} \quad (5)$$

and  $\alpha = \gamma = \delta = 0$ ,  $\beta = -(6\eta)^{-1}$ . The second set must be discarded, since it implies a negative  $g(r)$  at  $r=R$ . We have shown that the first solution indeed satisfies all conditions on  $\tau(r)$  arising from the discontinuities of higher derivatives of  $\tau(r)$  at  $r=R$ ; the details will be given elsewhere.

Thus the direct correlation function is

$$C(x) = -(1-\eta)^{-4}[(1+2\eta)^2 - 6\eta(1+\frac{1}{2}\eta)^2 x + \eta(1+2\eta)^2 \frac{1}{2} x^3], \quad (6)$$

and the equation of state calculated from this by Eq. (71) of PY<sup>1</sup> is

$$\beta P n = (1-\eta)^{-3}(1+\eta+\eta^2), \quad (7)$$

where  $P$  is the pressure and  $\beta = (1/kT)$ . Equation (7) is identical with the result of Reiss, Frisch, and Lebowitz.<sup>3</sup> It follows that the PY equation does not show a phase transition, and that near close packing it has the form of the free-volume theory with the packing density too large by a factor  $3\sqrt{2}/\pi$ .

Inserting the result of Eq. (5) into

$$G(t) = \frac{1+24\eta K - t^2 F(t)}{t^2 + 12\eta t[F(-t) - F(t)]}, \quad (8)$$

we find that a factor of  $[L(-t) + S(-t)\exp(-t)]$  appearing in both the numerator and denominator of (8) cancels, and we obtain for  $g(x)$

$$xg(x) = (2\pi i)^{-1} \int_{\delta-i\infty}^{\delta+i\infty} \frac{tL(t)e^{tx} dt}{12\eta[L(t) + S(t)e^t]}, \quad (9)$$

where  $S(t) = (1-\eta)^2 t^3 + 6\eta(1-\eta)t^2 + 18\eta^2 t - 12\eta(1+2\eta)$  and  $L(t) = 12\eta[(1+\frac{1}{2}\eta)t + (1+2\eta)]$ .

We have shown that the denominator of Eq. (9) has no zeros in the right-half plane (RHP). This has two consequences. For  $x < 1$  we can close the contour by a large semicircle in the RHP, obtaining  $g(r) = 0$  for  $r < R$ , as required. For  $x > 1$ , we

close the contour by a large semicircle in the left-half plane (LHP). The residue of the pole at  $t=0$  contributes 1 to  $g(x)$ . The other poles occur in pairs  $t_i, t_i^*$ . Among them there exists a pair which is closest to the  $y$  axis and which determines the asymptotic behavior for large  $x$  of  $g(x) - 1$ . In the limit of  $\eta$  going to 1, however, all poles approach points on the  $y$  axis given by  $\frac{1}{2}y = \tan(\frac{1}{2}y)$  and the oscillation frequency of  $g(x) - 1$  increases without limit with increasing  $x$ .

In order to obtain  $g(x)$  in closed form for given  $x$ , it is necessary to expand the denominator of Eq. (9) in powers of  $L(t)/S(t)$ . We must find a contour on which  $|S(t)| > |L(t)e^{-t}|$  is satisfied. We can accomplish this by replacing the segment of the  $y$  axis from  $-iP$  to  $iP$  by a semicircle  $|t| = P$  in the RHP, with  $P$  sufficiently large. We can show that  $P$  must be greater than the real positive root of  $S(t)$ . Therefore we will get contributions from all three roots of  $S(t)$ . Writing

$$g(x) = \sum_{n=1}^{\infty} g_n(x),$$

we have

$$g_n(x) = (24\pi\eta x i)^{-1} \int e^{t(x-n)} [L(t)/S(t)]^n dt,$$

so that  $g_n(x) = 0$  for  $x < n$ , and for  $x > n$ ,  $g(x)$  is equal to the sum of the residues of  $(12\eta x)^{-1} \times e^{t(x-n)} [L(t)/S(t)]^n t$  at the roots  $t_0, t_1, t_2$  of  $S(t)$ . Thus, in the  $m$ th shell  $m < x < m+1$ ,  $xg(x)$  has the form

$$\sum_{l=0}^2 P_{lm}(x) \exp(t_l x),$$

where  $P_{lm}(x)$  is a polynomial of order  $m-1$  in  $x$ . For the  $t_l$ , we obtain

$$t_l = 2\eta(1-\eta)^{-1}[-1+x_+^l + x_-^l], \quad (10)$$

where  $l=0, 1, 2$  and  $j = \exp(\frac{2}{3}\pi i)$ . Here  $x_{\pm} = [f + (f^2 + \frac{1}{3})^{1/2}]^{1/3}$  and  $f = (3+3\eta-\eta^2)/4\eta^2$ .

In the first shell  $1 < x < 2$ , for example, we obtain

$$xg(x) = (1-\eta)^{-2} \sum_{l=0}^2 A_l \exp t_l(x-1),$$

where

$$A_l = \frac{1}{3} \sum_{m=0}^2 H_m^j{}^{ml}$$

and

$$H_0 = 1 + \frac{1}{2}\eta,$$

$$H_1 = -(4\eta)^{-1}(f^2 + \frac{1}{8})^{-1/2}[x_-^2(1 - 3\eta - 4\eta^2) + x_+(1 - \frac{5}{2}\eta^2)],$$

$$H_2 = (4\eta)^{-1}(f^2 + \frac{1}{8})^{-1/2}[x_+^2(1 - 3\eta - 4\eta^2) + x_-(1 - \frac{5}{2}\eta^2)].$$

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<sup>1</sup>J. K. Percus and G. J. Yevick, Phys. Rev. **110**, 1 (1957).

<sup>2</sup>Ornstein and Zernike, Koninkl. Ned. Akad. Wetenschap., Proc., Ser. B **17**, 793 (1914).

<sup>3</sup>H. Reiss, H. L. Frisch, and J. L. Lebowitz, J. Chem. Phys. **31**, 369 (1959). See also E. Helfand, H. L. Frisch, and J. L. Lebowitz, J. Chem. Phys. **34**, 1037 (1961), and preceding papers cited there.

### COOPERATIVE OSCILLATIONS IN A HIGH-TEMPERATURE PLASMA FORMED BY NEUTRAL ATOM INJECTION\*

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A method of creating a magnetically confined hot plasma for study utilizes energetic particle injection. This method, as it is being employed in the Livermore ALICE experiment,<sup>1-3</sup> and in a similar experiment<sup>4</sup> in the United Kingdom, involves the passage of beams of energetic neutral atoms diametrically through a highly evacuated region within which steady confining magnetic fields of mirror geometry are maintained. Ionization of a portion of the neutral beam, by collision with residual gas atoms and by Lorentz force breakup,<sup>5,4</sup> leads to the buildup of a plasma of high mean kinetic energy (20 keV in the ALICE experiment). While the plasma densities thus far achieved in our experiments have been modest (of order  $10^8$  ions/cm<sup>3</sup>), unusual cooperative effects have already been seen.

This Letter reports the observation of new modes of stable oscillation of a low-density plasma confined between magnetic mirrors. The oscillations are of low frequency, ranging between 5 and 50 kc/sec. Two "branches" are observed: One branch is close to the calculated frequency of precession ( $\nu_B$ ) of 20-keV ions in the midplane magnetic field gradient and is roughly independent of plasma density; the other branch varies roughly linearly with plasma density. Discontinuous "jumps" between these two branches are also occasionally seen, supporting the picture that we are observing cooperative modes of stable plasma oscillations. Although the frequencies and

observed characteristics of the oscillations are not compatible with any of the usual modes of plasma oscillation, we believe that they can possibly be explained in terms of "finite-orbit" stabilization effects of the general type proposed by Rosenbluth, Kroll, and Rostoker (RKR).<sup>6</sup> One of us (R. F. P.) has extended their theory to the low-density regime, finding oscillation frequencies which seem to agree reasonably well with the observations.

The oscillations were detected on three electrostatic probes disposed around the periphery of the plasma. One of these also serves to limit the radius of the plasma to 12 cm. The following summarizes the observations:

(1) The signals are of two types, as characterized by frequency vs plasma density. Figure 1 presents observations made at a midplane magnetic field  $B_0 = 12.5$  kG. The plotted points, each representing several runs, are averages of readings made during beam injections at various levels; errors shown are standard deviations of the mean. The dashed curves are data taken after beam turn-off and represent individual runs. Signals of Type 1 lie at or near the calculated value of  $\nu_B$  (22 kc/sec) for all densities. During the plasma density decay (after beam turn-off) signals of this type remain nearly constant in frequency. Curve 1 of Fig. 1 shows a typical individual decay of this type. Signals of Type 2 taken during beam injection exhibit frequencies which