Equation of State of the Hard-Disk Fluid from Approximate Integral Equations*

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The Percus–Yevick, hypernetted-chain, and "pressure-consistent' integral equations have been solved, using numerical Hankel transforms, for a fluid of two-dimensional hard cores. The thermodynamic quantities obtained from these solutions are presented and compared among themselves and with the results of other theories; a comparison of computed pair distribution functions g with a Monte Carlo g is also presented. The Percus–Yevick equation is found to give the best over-all results.

I. INTRODUCTION

The classical hard-disk fluid has been probed with a number of theoretical techniques, including Monte Carlo[1–3] (MC) and molecular dynamics[4,5] (MD) "computer experiments" and various approximate theories.[6–8] As yet, however, only the modified Yvon–Born–Green equation of Rice and Lekner[9] (RL) among the available integral equations has been solved for this model.[10,11] In this paper we present numerical solutions of the Percus–Yevick[12] (PY) and hypernetted-chain[13] (HNC) integral equations, as well as of a third equation[14] we will call "pressure-consistent" (PC), for a two-dimensional fluid of hard cores.

Let $g(r)$ be the pair distribution function of the fluid. We define the direct correlation function $C(r)$ by means of the Ornstein–Zernike equation,

$$\begin{aligned} G(r) &\equiv g(r)-1 \\ &= C(r)+\rho\int C(r')G(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}', \end{aligned} \tag{1}$$

where ρ is the particle number density. A second equation giving $C(r)$ in terms of $g(r)$ then specifies with (1) a particular integral equation for $g(r)$. The direct correlation functions for the three equations to be examined here may be written in the common form,

$$\begin{aligned} C(r) = G(r) - (1-\mu)\{g(r)\exp[\beta u(r)]-1\} \\ -\mu\ln\{g(r)\exp[\beta u(r)]\}. \end{aligned} \tag{2}$$

Here $u(r)$ is the pair potential and β is $(kT)^{-1}$. Setting the parameter μ equal to 0 then yields the PY equation, while for the HNC equation we put $\mu=1$. The third equation (PC) is obtained by selecting that value of μ in each case which will yield consistency between the virial equation of state,

$$\begin{aligned} \frac{\beta p_v}{\rho} &= 1-\tfrac{1}{4}\rho\beta\int_0^\infty ru'(r)g(r)2\pi r dr \\ &= 1+\tfrac{1}{2}\pi\rho\sigma^2 g(\sigma), \end{aligned} \tag{3}$$

and the compressibility equation of state,

$$\frac{\beta p_c}{\rho} = \rho^{-1}\int_0^\rho (\rho kTK)^{-1}d\rho. \tag{4}$$

In these expressions σ is the hard-disk diameter and the isothermal compressibility

$$K \equiv \rho^{-1}(\partial\rho/\partial p)_T \tag{5}$$

is given by

$$(\rho kTK)^{-1} = 1-\rho\int_0^\infty C(r)2\pi r dr. \tag{6}$$

II. NUMERICAL PROCEDURES

Much of the computational detail of solving the integral equations is carried over from the three-dimensional problems.[15] As in these cases, the method of solution is by iteration of Eq. (2) and the Fourier transform of Eq. (1). In two dimensions however the Fourier transform $h(k)$ of a circularly symmetric function $H(r)$

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TABLE I. Reduced pressures and compressibilities of hard disks calculated from the Percus–Yevick, hypernetted-chain, and "pressure-consistent" integral equations.[a]

$\rho\sigma^2$	$(\beta p/\rho)-1$					$\rho K/\beta$		
	PY(V)	PY(C)	HNC(V)	HNC(C)	PC	PY	HNC	PC
0.05	0.0836	0.0836	0.0838	0.0836	0.0836	0.8528	0.8529	0.8528
0.10	0.179	0.179	0.180	0.178	0.179	0.7238	0.7249	0.7239
0.15	0.287	0.287	0.292	0.286	0.287	0.6113	0.6141	0.6116
0.20	0.410	0.412	0.423	0.407	0.412	0.5133	0.5189	0.5140
0.25	0.553	0.556	0.579	0.546	0.555	0.4285	0.4373	0.4295
0.30	0.717	0.725	0.766	0.705	0.722	0.3552	0.3675	0.3567
0.35	0.908	0.922	0.994	0.886	0.918	0.2922	0.3080	0.2943
0.40	1.13	1.16	1.27	1.10	1.15	0.2384	0.2571	0.2411
0.45	1.40	1.44	1.62	1.34	1.42	0.1927	0.2138	0.1958
0.50	1.71	1.77	2.05	1.62	1.75	0.1541	0.1768	0.1577
0.55	2.08	2.19	2.60	1.95	2.15	0.1217	0.1454	0.1256
0.60	2.54	2.70	3.30	2.34	2.63	0.0948	0.1186	0.0989
0.65	3.10	3.34	4.21	2.80	3.23	0.0728	0.0962	0.0770
0.70	3.79	4.16	5.40	3.36	3.99	0.0548	0.0772	0.0590
0.75	4.67	5.24	6.96	4.04	4.96	0.0404	0.0615	0.0445
0.80	5.80	6.68	9.06	4.87	6.23	0.0290	0.0484	0.0329
0.85	7.26	8.65	11.77	5.90	7.90	0.0203	0.0380	0.0239
0.90	9.26	11.47	···	···	10.20	0.0136	···	0.0166

[a] No solution was found for the HNC equation at $\rho\sigma^2=0.9$.

becomes a Hankel transform,

$$H(r)=(2\pi)^{-1}\int_0^\infty h(k)J_0(kr)kdk,$$

$$h(k)=2\pi\int_0^\infty H(r)J_0(kr)rdr, \qquad (7)$$

where $J_n(x)$ is the Bessel function of the first kind of order n. Let $\lambda_1, \lambda_2, \cdots, \lambda_N$ be the first N positive roots of $J_0(x)=0$. Then for the numerical calculation we replace Eqs. (7) with the finite series (see Appendix)

$$H(r_i)=\frac{1}{\pi R^2}\sum_{j=1}^{N-1}h(k_j)\frac{J_0(k_jr_i)}{J_1^2(k_jR)},$$

$$h(k_j)=\frac{4\pi}{K^2}\sum_{i=1}^{N-1}H(r_i)\frac{J_0(k_jr_i)}{J_1^2(Kr_i)}, \qquad (8)$$

where

$$r_i=\lambda_i/K,$$

$$k_i=\lambda_i/R, \qquad (9)$$

and $R\equiv r_N$, $K\equiv k_N$ are the computational limits of r and k. The roots λ_i and hence the points r_i and k_i are not equally spaced. Note that a choice of N and R is sufficient to determine all k_i and r_i, since $K=\lambda_N/R$.

With one exception to be noted below, solutions of the three integral equations were obtained for reduced densities $\rho\sigma^2$ up to 0.9 at intervals of 0.025. (The hard-disk phase transition indicated by MC[2] and MD[4] studies sets in at $\rho\sigma^2\approx0.88$; at close packing, $\rho\sigma^2=2/\sqrt{3}=1.155$.)

Convergence of the iterated solution was measured by the largest difference between successive iterates of H_j,[16]

$$D=\max_j|H_j^{\text{out}}-H_j^{\text{in}}|, \qquad (10)$$

which was required to be less than 10^{-5} in all cases. In the case of the PC equation, we required additionally that the relative difference between the excess reduced pressure from Eqs. (3) and (4) be less than 10^{-4}.

For efficiency in the transform calculations, a table of the N^2 values of $J_0(k_jr_i)$ was computed once for each solution and stored. Machine memory limitations then effectively restricted N to a maximum of 200. Up to $\rho\sigma^2=0.6$, a mean interval size $R/N=0.025\sigma$ was maintained, with R reaching up to 5σ. In the upper third of the density range studied, however, R was increased up to 8σ and R/N increased correspondingly to 0.040σ.

We estimate the error in the results presented to be less than 0.5% for reduced densities up to 0.6, and less than 2% for densities between 0.6 and 0.9.

III. DISCUSSION OF RESULTS

The computed values of the reduced pressure from Eqs. (3) and (4) are shown in Table I. (We were unable to obtain a converged solution to the HNC equation at $\rho\sigma^2=0.9$.) A graph of these data is given in Fig. 1 for the higher density values. Also shown in Fig. 1 are the results of some MC[2] (48-molecule system) and MD[5] (72-molecule system) calculations, the

[16] For the PY and PC equations, it is convenient to take $H=g\exp(\beta u)-1$; for the HNC equation the convenient choice is $H=\ln[g\exp(\beta u)]$.

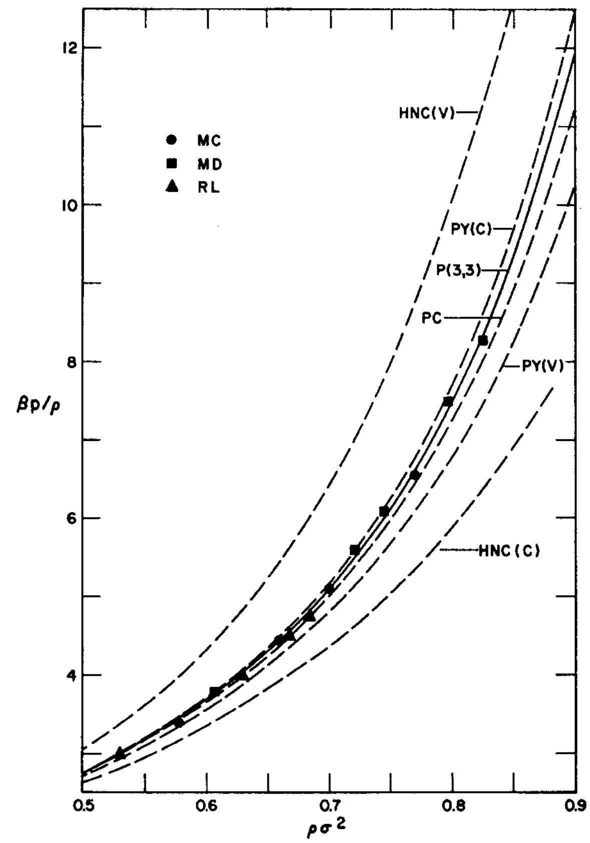

FIG. 1. Equation of state of a hard-disk fluid, calculated from the PY, HNC, and PC integral equations. Also shown for comparison are the Ree–Hoover $P(3, 3)$ approximant, MC and MD points, and results from the modified YBG equation of Rice and Lekner.

Ree–Hoover[7] (RH) Padé $P(3, 3)$ approximant, and four points[10] from the RL integral equation. Among the equations studied here we see that the PY equation with Eq. (4) and the PC equation give the best results, while the HNC curves are distinctly poorest. However, the RL points are slightly better than any others. This latter equation suffers unfortunately from having no solutions for reduced pressures above $\beta p/\rho=4.78$, well below the hard-disk phase transition. (An attempt to remedy this restriction resulted in much poorer values for the equation of state.[17]) Finally, among nonintegral equation results, we note that the scaled particle theory of Helfand, Frisch, and Lebowitz[6] (HFL) would lie in Fig. 1 below the PC curve until $\rho\sigma^2=0.792$, crossing over at this point to yield the best results at higher densities. Thus at $\rho\sigma^2=0.85$, for example, the percent deviations from the RH curve of the PY(C), HFL, and PC points are, respectively, 3.93%, -3.28%, and -5.10%.

The isothermal compressibility computed from Eq. (6) for the three integral equations is listed in Table I and compared graphically in Fig. 2 with the values of K obtained by differentiation of the RH $P(3, 3)$ approximant. Taking these latter points as approximately correct, we see that the PY equation gives a slightly better agreement than the PC equation. The value of μ needed in Eq. (2) to obtain a consistent equation of state is shown in Fig. 3 as a function of the reduced density.

In Fig. 4 we have a comparison of the radial distribution functions from the integral equations and from a recent Monte Carlo calculation,[18] all at a reduced density $\rho\sigma^2=0.794$. (The MC result is for a 192 molecule system at a constant pressure $\beta p/\rho_0=5$, where $\rho_0=2/\sqrt{3}\sigma^2$ is the close-packed density; $\rho\sigma^2=0.794$ is then the computed mean value of the fluctuating density.) As expected from its more accurate virial equation of state, the PC equation yields the best agreement with the MC points in the vicinity of the hard core. Beyond this first peak, however, the PY equation gives an equivalent or better representation of $g(r)$.

In general, we find then that the PY and PC equations are approximately equivalent in predicting the properties of the hard-disk fluid, while the HNC equation is distinctly poorest. Since the PY equation is somewhat easier to solve, it recommends itself as the

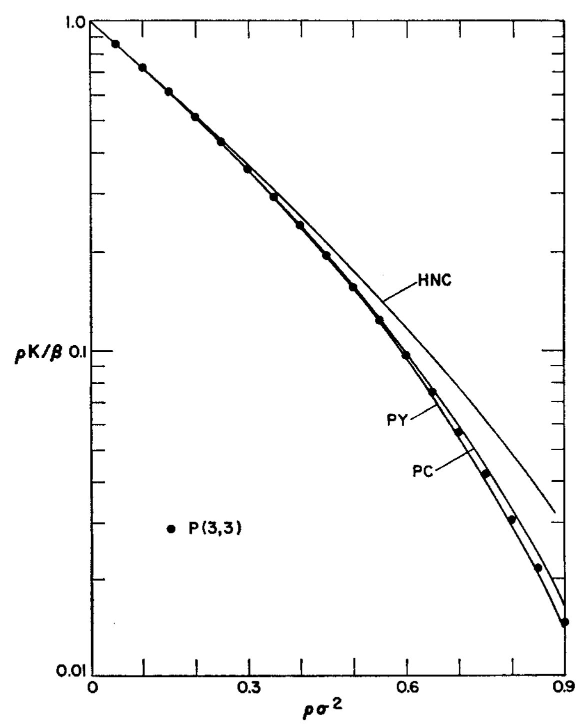

FIG. 2. Reduced isothermal compressibility of hard disks from the PY, HNC, and PC integral equations. The dots are from the derivative of the Ree–Hoover $P(3, 3)$ approximant.

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best available integral equation for the entire fluid region of the hard-disk system.

We note finally that the qualitative features of these hard-disk solutions are almost completely identical to those of the hard-sphere results,[16] where in particular the PC equation and the PY equation with the compressibility relation again provide the best results.

ACKNOWLEDGMENT

The author is grateful to Dr. W. W. Wood for providing a table of the Monte Carlo results of Ref. 18 used in Fig. 4, as well as for having initially suggested this problem.

APPENDIX

Since the orthogonality property of the Bessel functions is used in solving the integral equations (in applying the inverse transform to a transformed function), we seek to replace the integrations of Eqs. (7) with a numerical quadrature which will preserve, at least approximately, this property.

We begin by assuming that $H(r)$ effectively vanishes for $r>R$, which implies that the Fourier transform $h(k)$ need not be calculated for values of k more closely spaced than some finite minimum, about π/R. This leads to replacing Eqs. (7) with the well-known Fourier–Bessel expansion,[19]

$$H(r)=\frac{1}{\pi R^2}\sum_{j=1}^{\infty} h(k_j)\,\frac{J_0(k_jr)}{J_1^2(k_jR)}\,, \tag{A1}$$

$$h(k_j)=2\pi\int_0^R H(r)J_0(k_jr)rdr, \tag{A2}$$

where $k_j=\lambda_j/R$ and λ_j is the jth positive root of $J_0(x)=0$. If now we further assume that $H(r)$ is known only at a finite number of points N then it is not necessary to consider frequencies k larger than about $K=\lambda_N/R$. That is, the sum in (A1) is terminated at $j=N$ while the integral in (A2) is replaced with a sum over the N known points. The form of this latter sum may be determined by noting that the arguments above are symmetric, so that we could have begun with a function $h(k)$ defined on an interval $(0, K)$, expanded $h(k)$ in a Fourier–Bessel series, etc. We are thus led to consider the symmetric forms

$$H(r_i)=\frac{1}{\pi R^2}\sum_{j=1}^{N} h(k_j)\,\frac{J_0(k_jr_i)}{J_1^2(k_jR)}\,, \tag{A3}$$

$$h(k_j)=\frac{4\pi}{K^2}\sum_{i=1}^{N} H(r_i)\,\frac{J_0(k_jr_i)}{J_1^2(Kr_i)}\,, \tag{A4}$$

with $r_i=\lambda_i/K$ and $k_i=\lambda_i/R$, as the discrete counterparts of Eqs. (7). (The upper limits in the sums may be replaced with $N-1$ since in each case the Nth term vanishes.)

Elimination of $h(k_j)$ in Eq. (A3) by means of (A4) yields

$$H(r_i)=\sum_{j=1}^{N} H(r_j)D_{ij}^{(N)}, \tag{A5}$$

where

$$D_{ij}^{(N)}=\frac{4}{\lambda_N^2J_1^2(\lambda_j)}\sum_{k=1}^{N-1}\frac{J_0(\lambda_i\lambda_k/\lambda_N)J_0(\lambda_j\lambda_k/\lambda_N)}{J_1^2(\lambda_k)}\,. \tag{A6}$$

Thus in order for the desired orthogonality property to be maintained, $D_{ij}^{(N)}$ must be shown to approximate

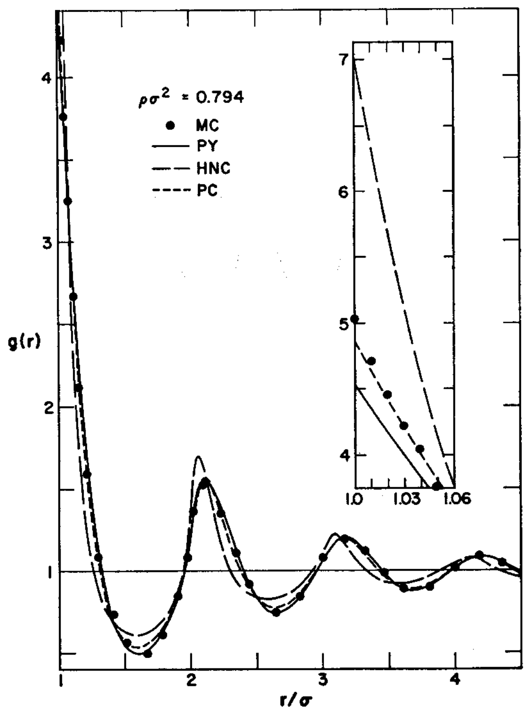

FIG. 4. Radial distribution function of hard disks at $\rho\sigma^2=0.794$, from solutions of the PY, HNC, and PC equations and from a Monte Carlo calculation of a 192-molecule constant-pressure system.

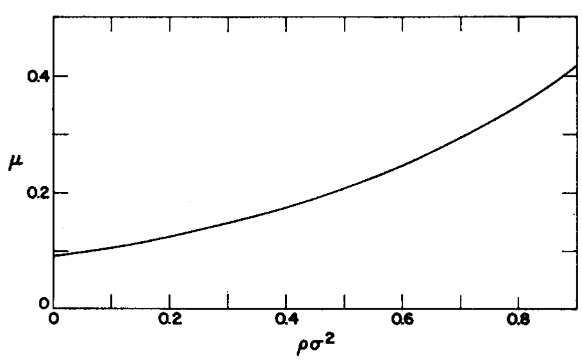

FIG. 3. Density dependence of the pressure-consistency parameter μ in the PC equation for hard disks.

[19] G. N. Watson, *A Treatise on the Theory of Bessel Functions* (Cambridge University Press, Cambridge, England, 1966), 2nd ed., Chap. 18.

the Kronecker delta δ_{ij}. If N is large, we may use the asymptotic forms[20]

$$J_1(x) \sim (2/\pi x)^{1/2}\cos(x-\tfrac{3}{4}\pi),$$
$$\lambda_k \sim (k-\tfrac{1}{4})\pi, \tag{A7}$$

in the summand of (A6) with noticeable error only in the first few terms of the sum, which then becomes

$$\begin{aligned}\tfrac{1}{2}\pi\sum_{k=1}^{N-1}\lambda_k J_0\left(\frac{\lambda_i\lambda_k}{\lambda_N}\right)J_0\left(\frac{\lambda_j\lambda_k}{\lambda_N}\right) &= \tfrac{1}{2}\lambda_N^2\sum_{k=1}^{N-1}x_k J_0(\lambda_i x_k)J_0(\lambda_j x_k)\,\Delta x \\ &\approx \tfrac{1}{2}\lambda_N^2\int_0^1 xJ_0(\lambda_i x)J_0(\lambda_j x)\,dx \\ &= \tfrac{1}{4}\lambda_N^2 J_1^2(\lambda_j)\delta_{ij},\end{aligned} \tag{A8}$$

[20] Ref. 19, pp. 199, 505.

where we put $x_k=\lambda_k/\lambda_N$ and $\Delta x=x_{k+1}-x_k \sim \pi/\lambda_N$. With this result in (A6) we get

$$D_{ij}^{(N)} \approx \delta_{ij}, \tag{A9}$$

as desired.[21]

For small values of N it was found by numerical calculation that Eq. (A9) still holds. Thus for $N=5$ the differences between $D_{ij}^{(N)}$ and δ_{ij} were less than 4×10^{-6} for all i, j,

$$|D_{ij}^{(5)}-\delta_{ij}| < 4\times10^{-6}.$$

For $N=20$ the differences were on the order of the error in the computed Bessel functions, about 10^{-8}.

[21] Further discussion on the quantity $D_{ij}^{(N)}$ may be found in Ref. 19, pp. 582 ff and in A. Gray, G. B. Mathews, and T. M. MacRobert, *A Treatise on Bessel Functions* (MacMillan and Co., London, 1952), 2nd ed., pp. 94 ff.

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Refractive Index of Gaseous and Liquid Hydrogen*

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The refractive index of gaseous and liquid hydrogen has been measured by an interferometric method at temperatures between 15° and 298.15°K and at pressures up to 230 atm. The measurements have been analyzed in terms of the density and temperature dependence of the Lorentz–Lorenz function,

$$\text{L–L} \equiv [(n_\lambda^2-1)/(n_\lambda^2+2)]\rho^{-1},$$

where n_λ is the refractive index at $\lambda=5462$ Å and ρ is the fluid density in grams per cubic centimeter. The precision and reproducibility of L–L is better than 0.05% in most cases. L–L for gaseous parahydrogen first increases with increasing density to a maximum and then decreases to values below the low-density limit. L–L is also slightly temperature dependent; the low-density limit increases with increasing temperature; the maximum on the L–L isotherms decreases with increasing temperature. L–L for saturated liquid parahydrogen decreases with increasing density by about 0.1% at temperatures between 15° and 32°K. The difference in L–L for normal and parahydrogen is consistent with previous theoretical and experimental estimates of the molecular-polarizability difference.

I. INTRODUCTION

The Lorentz theory of the dielectric constant[1] predicts that the Lorentz–Lorenz function,

$$[(n_\lambda^2-1)/(n_\lambda^2+2)]\rho^{-1}=4\pi N_0\alpha/3M, \tag{1}$$

should be nearly independent of temperature and density for a nonpolar fluid. It is well known, however, that L–L is weakly temperatures and density dependent for many fluids.[2–4] More sophisticated theories[5–8] have been able to interpret some of the details of the dielectric and refractive-index behavior of compressed fluids, but quantitative agreement between theory and experiment is still not very satisfactory. It appears that more precise measurements of refractive indices and densities throughout a wide range of temperatures would be useful to provide a satisfactory test. Analysis of previous refractive-index measurements[9] on gaseous and liquid hydrogen has shown no significant dependence of L–L on either temperature or density. Recent dielectric measure-

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