

# Scaled Particle Theory: Solution to the Complete Set of Scaled Particle Theory Conditions: Applications to Surface Structure and Dilute Mixtures

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We present, so far as we know, the first solution to the *complete* set of conditions developed by scaled particle theory under the usual approximation that  $G(\lambda)$  can be expressed as a Laurent series for  $1/2 < \lambda < \infty$ . The theory leads to a fourth virial coefficient accurate to 0.6% and fair values for the first derivative of the radial distribution function  $g'(1)$ . The results are used to calculate both boundary tension and boundary adsorption in the hard sphere fluid, as well as the pressure of a dilute hard sphere mixture. It is probable that the nearly linear function we calculate deviates only slightly from the true  $G(\lambda)$  at fluid densities. Some discussion of this point is presented.

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**KEY WORDS :** Liquids ; rigid (hard) spheres ; radial distribution function ; fluid mixtures ; surface tension.

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## 1. INTRODUCTION

The Scaled Particle Theory (SPT) of Reiss, Frisch, and Lebowitz<sup>(1)</sup> (to be referred to as RFL) was one of the successful early attempts at determining the thermodynamic properties of the hard sphere fluid, but, as originally developed, did not provide enough of the structural information required for effective computation of the properties of real fluids. In this and subsequent papers, we will improve upon previous SPT results and, in addition, obtain structural information applicable to real fluids.

To expand these remarks, consider a fluid of unit-diameter hard spheres having a  $\lambda$ -cule at the origin. (A  $\lambda$ -cule is defined as a spherical cavity of radius  $\lambda$ , or, equivalently, a hard sphere of diameter  $2\lambda - 1$ . By a cavity we shall mean a region excluding hard sphere centers.) We define the generalized radial distribution function  $g(\lambda, r)$  proportional to the probability of finding a hard sphere at distance  $r$  from the center of the  $\lambda$ -cule. The domain of  $g(\lambda, r)$  is shown in Fig. 1. The ordinary radial distribution function (RDF) is given by  $g(r) \equiv g(1, r)$ , while the central function of SPT is  $G(\lambda) = g(\lambda, \lambda)$ . For  $\lambda \leq r \leq 1 - \lambda$ , we have the exact result<sup>(2)</sup>

$$g(\lambda, r) = [1 - 4\pi\lambda^3\rho/3]^{-1} \quad (1)$$

There are several relations between the thermodynamic properties of the

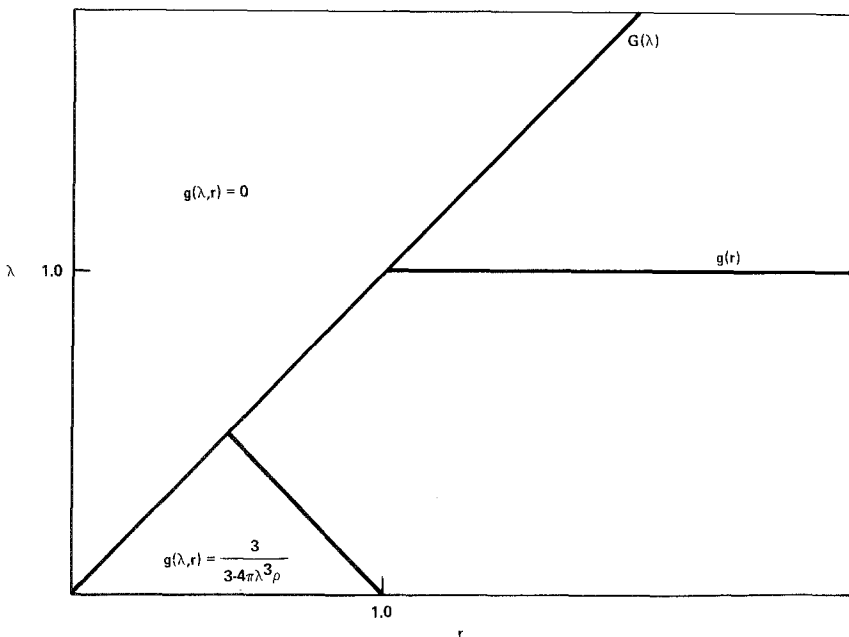


Fig. 1. Domain of the generalized radial distribution function  $g(\lambda, r)$ .

fluid and  $g(\lambda, r)$ . Of particular interest is the virial equation for hard spheres:

$$\beta p = \rho + (2\pi/3)\rho^2 g(1) = \rho + (2\pi/3)\rho^2 G(1) \quad (2)$$

and the compressibility equation of state:

$$\beta \partial p / \partial \rho = [1 + 4\pi\rho \int_0^\infty (g(r) - 1)r^2 dr]^{-1} \quad (3)$$

Because the SPT deals with  $\lambda \neq 1$ , we can hope to use it to gain information about the properties of hard sphere mixtures and the boundary surface structure of the hard sphere fluid, as well as the properties of homogeneous one-component liquids.

In Section 2, we review the basic outlines of SPT. Section 3 presents the complete solution of the SPT equations within the usual approximations, and compares the results with the known properties of the hard sphere fluid. In Section 4 we calculate properties of the hard sphere fluid near a boundary surface. In this and the following section, we make extensive use of the thermodynamics of curved boundary layers developed in the companion paper.<sup>(3)</sup> Section 5 deals with the theory of binary hard sphere mixtures and includes a new derivation of the "integral condition" along with some properties of dilute mixtures. The summary and conclusions appear in Section 6.

## 2. OUTLINE OF SPT

Complete discussions of SPT are given in the original paper by Reiss *et al.*<sup>(1)</sup> as well as in a subsequent review by Reiss.<sup>(4)</sup> For completeness, a bare outline is presented here.

We have already defined the function  $G(\lambda)$  in terms of the generalized RDF  $g(\lambda, r)$ . It follows from the virial theorem<sup>(4)</sup> that  $\rho k T G(\lambda)$  is also the average normal stress at the boundary of a cavity of radius  $\lambda$ . For  $\lambda = \infty$ , this is the ordinary pressure, so that Eq. (1) gives immediately

$$p / \rho k T = G(\infty) = 1 + (2\pi/3)\rho G(1) \quad (4)$$

$G(\lambda)$  is equivalently<sup>(1,4)</sup> defined by

$$G(\lambda) = -(4\pi\rho\lambda^2)^{-1}(\partial/\partial\lambda) \ln p_0(\lambda) \quad (5)$$

where  $p_0(\lambda)$  is the probability that *exactly* zero hard spheres are contained in a spherical region of radius  $\lambda$ . This probability is given by

$$p_0(\lambda) = 1 + \sum_{m=1}^{\infty} (-1)^m F_m(\lambda) \quad (6)$$

where  $F_m(\lambda)$  is the average number of  $m$ -tuples of hard spheres contained in

the region. Each  $F_m$  is zero for  $\lambda < \lambda_m$ , the minimum radius capable of containing  $m$  hard spheres. In particular,

$$F_1 = (4\pi/3)\rho\lambda^3 \quad (7)$$

and

$$F_2 = (\rho^2/2) \int_{\Omega} d^3\mathbf{r}_1 \int_{\Omega} d^3\mathbf{r}_2 g(|\mathbf{r}_1 - \mathbf{r}_2|) \quad (8)$$

Since only  $F_1$  is nonzero for  $\lambda < 0.5$ , we have exactly

$$G(\lambda) = (1 - 4\pi\lambda^3\rho/3)^{-1} \quad (\lambda < 1/2) \quad (9)$$

$F_2$  connects  $G(\lambda)$  to the ordinary RDF, and leads to a discontinuity in the second derivative of  $G$  at  $\lambda = 0.5$ :

$$\Delta G''(\lambda) = -8\pi\rho G(1/2)G(1) \quad (10)$$

$F_3$  leads to a singularity in the fourth derivation of  $G$  at  $\lambda_3 = 1/\sqrt{3}$  of the form

$$\Delta G^{(4)}(\lambda_3 + \epsilon) = A\rho^2 g_3(1, 1, 1)\epsilon^{1/2} \quad (11)$$

where  $A$  is a positive constant and  $g_3(1, 1, 1)$  is the three-particle contact distribution function. Higher values of  $m$  lead to singularities in still higher derivatives. The usual approximation of SPT is to ignore all the high-order singularities and assume  $G(\lambda)$  is well approximated by a Laurent series for  $\infty > \lambda > 1/2$ .

For hard spheres of diameter  $a$ , define the dimensionless variables

$$x = \lambda/a, \quad y = \pi a^3 \rho/6, \quad \phi = \pi a^3 p/6kT \quad (12)$$

In terms of these variables, Eq. (4) becomes

$$G(\infty) = 1 + 4yG(1) \quad (13)$$

and at  $x = 1/2$  we have the three conditions

$$G(1/2) = (1 - y)^{-1} \quad (14)$$

$$G'(1/2) = 6y/(1 - y)^2 \quad (15)$$

$$G''(1/2) = \frac{24y}{1 - y} \left\{ \frac{1 + 2y}{(1 - y)^2} - 2G(1) \right\} \quad (16)$$

where the second derivative is understood to be the limit taken from above.

One of the earliest relations introduced by SPT is the "integral condition," which may be written

$$24y \int_{1/2}^1 G(x, y)x^2 dx = \int_0^y [\phi(v) - v] dv/v^2 + \ln(1 - y) + (\phi - y)/y \quad (17)$$

We shall derive this equation in Section 4. A final condition has more recently been added to SPT. We mentioned that it is customary to approximate  $G(\lambda)$  as a Laurent series,

$$G(\lambda) = \sum_{n=0}^N G_n(y)\lambda^{-n} \quad (18)$$

It was made plausible by Tully-Smith and Reiss<sup>(5)</sup> and proved by Stillinger and Cotter<sup>(6)</sup> that within this approximation

$$G_3(y) = 0 \quad (19)$$

[Note that the validity of condition (19), unlike the other conditions of SPT, depends on the validity of (18).]

In 1959, RFL found that Eq. (18), with  $N = 2$ , using the conditions (13)–(15), led to an excellent equation of state:

$$\phi_{\text{RFL}}(y) = (y - y^4)/(1 - y)^4 \quad (20)$$

Fortuitously, this result also satisfies Eqs. (19) and (17), but not (16). Since the latter condition comes from the function  $F_2(\lambda)$ , which connects  $g(r)$  to  $G(\lambda)$ , we cannot with confidence extract structural information from the 1959 result. Tully-Smith and Reiss,<sup>(5)</sup> Reiss and Casberg,<sup>(2)</sup> and Ahn and Frisch<sup>(7)</sup> have proposed approximations to  $G(\lambda)$  which satisfy Eq. (16) but not Eq. (17) and are thus not correct “on average.” We correct this flaw in the next section.

### 3. SOLUTION OF THE COMPLETE SET OF SPT EQUATIONS

In this section, we present the solution of Eqs. (13)–(19) with  $N = 5$ . By straightforward though tedious algebra, we eliminate from these equations  $G_1(y), \dots, G_5(y)$  to find that  $\phi = yG_0(y)$  satisfies the integral equation

$$\frac{5 - 2y}{1 - y} \phi + 24 \int_0^y \frac{\phi - y}{y^2} dy = \frac{77y - 100y^2 + 41y^3}{(1 - y)^3} - 24 \ln(1 - y) \quad (21)$$

The solution to Eq. (21) may be expanded in a virial series,

$$\phi = \sum_{m=1}^M B_m y^m \quad (22)$$

whose coefficients satisfy the relation

$$B_{n+1} = 1 + (n/12)(37a_n - 47a_{n-1} + 19a_{n-2} - \frac{5}{2}B_n - \frac{3}{2} \sum_{j=2}^{n-1} B_j), \quad n > 2 \quad (23)$$

with

$$\begin{aligned} a_1 &= 1; & a_n &= [(n+1)/(n-1)]a_{n-1} \\ B_1 &= 1; & B_2 &= 4; & B_3 &= 10 \end{aligned}$$

The virial series proves to be an asymptotic series, since for  $n > 24$ , Eq. (23) may be approximated by

$$B_{n+1} \approx -(5n/24)B_n \quad (24)$$

Equation (22) with  $M = 18$  is sufficient to achieve convergence beyond  $y \approx 0.49$ , at which the hard sphere fluid is known to undergo a phase transition to a close-packed solid. For still higher densities, Eq. (21) may be solved by transposing the integral to the right and solving by iteration. The results are compared to other theories in Fig. 2 and Tables I and II. The fourth virial coefficient is low by only 0.6%, and the fifth is substantially improved compared with RFL. The result follows closely the Padé approximant to seven virial coefficients beyond the close-packing limit  $y = 0.740$ .

Having determined  $\phi(y)$ , the coefficients  $G_n(y)$  are given by

$$yG_1(y) = \frac{(\phi - y)(4 - 3y)}{3y(1 - y)} - \frac{19\phi}{9} - \frac{58y - 35y^2 + 13y^3}{18(1 - y)^3} \quad (25)$$

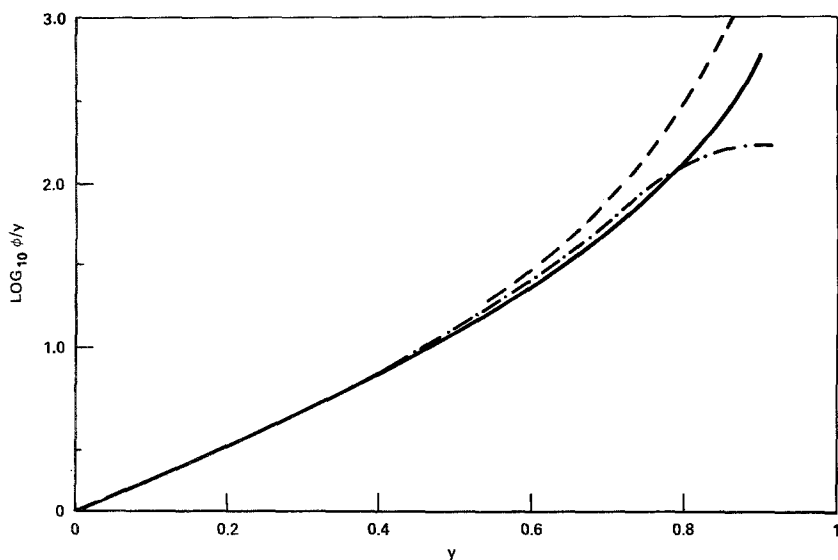


Fig. 2. Comparison of the equation of state from this work (solid line) with the "exact" (Padé approximant) equation of state (dot-dash line) and the 1959 RFL (or, equivalently, Percus-Yevick) result (dashed line). The ordinate is the common logarithm of the compressibility factor,  $p/\rho kT$ .

**Table I. Virial Coefficients Obtained in This Work (SPT) Compared with Those of Ref. 1, the "Exact" Results, and Those Given by the Carnahan-Stirling Formula (CS)**

$n$	$B_n$ [Eq. (22)]			
	SPT	RFL	Exact	CS
1	1	1	1	1
2	4	4	4	4
3	10	10	10	10
4	18.250	19	18.365	18
5	27.125	31	28.26	28
6	35.5	46	39.53	40
7	43.1	64	56.52	54
8	50.0	85		60
9	56.4	109		88
10	62.6			
11	68.6			
12	74.5			
13	80.5			
14	86.4			
15	92.4			
16	98.2			

**Table II. Some Results of the Present Theory (SPT) Contrasted with Other Theories**

$y$ :	0.1	0.2	0.3	0.4	0.45	0.5
Pressure $\phi$ :						
SPT	0.152	0.481	1.184	2.700	4.044	6.07
Padé	0.152	0.482	1.194	2.767	4.200	6.41
RFL	0.152	0.484	1.216	2.89	4.47	7.00
Expansion coefficients [Eq. (18)]:						
$G_1$	-0.230	-0.719	-1.72	-3.74	-5.45	-7.95
$G_2$	0.0115	0.0646	0.206	0.528	0.810	1.22
$G_4$	0.0015	0.0087	0.0310	0.0938	0.159	0.266
$G_5$	-0.0006	-0.0036	-0.0128	-0.0380	-0.0636	-0.106
Derivative of RDF, $g'(1)$ :						
SPT	-0.732	-2.299	-5.646	-13.0	-19.7	-30.0
MC <sup>8</sup>	-0.707	-2.395	-6.603	-17.8	-29.7	-50.5
Surface properties:						
$\sigma_\infty/y^2$	-2.30	-3.60	-5.7	-9.4	-12.1	-15.9
$\Gamma_\infty/y^2$	1.28	1.11	0.98	0.86	0.81	0.77
$\delta_\infty$	-0.05	-0.09	-0.12	-0.14	-0.15	-0.15

$$16yG_2(y) = \frac{8(\phi - y)}{y} - \frac{3y(2 - y)}{(1 - y)^2} - 26\phi - 22yG_1(y) \tag{26}$$

$$16G_4(y) = \frac{5 - 2y}{(1 - y)^2} - \frac{5\phi}{y} - 8G_1(y) - 12G_2(y) \tag{27}$$

$$4yG_5(y) = \frac{\phi - y}{y} - 4\phi[G_1(y) + G_2(y) + G_4(y)] \tag{28}$$

Despite being a fifth-order polynomial,  $G(x)$  proves to be an exceedingly dull function for all values of  $y$  (Fig. 3). A test of the accuracy of this function is the derivative of the RDF  $g'(1)$ . The RDF  $g(2x)$  is related to  $G(x)$  for  $1/2 < \lambda < 3^{-1/2}$  through  $F_2(x)$  by

$$\begin{aligned} & [96x/(1 - y)] \exp\left[24y \int_{1/2}^x x^2 G(x) dx\right] g(2x) \\ &= xG(x)[96G(x) + 72xG'(x) - 576x^3yG''(x)] \\ & \quad - [2G'(x)/x + G''(x)]/y \end{aligned} \tag{29}$$

and thus

$$g'(1) = \frac{1 + 16y + 10y^2}{2(1 - y)^3} + \frac{1 - 13y}{1 - y} G(1) - \frac{1 - y}{96y} G^{(3)}(1/2) \tag{30}$$

Equations (29) and (30) may be derived from Eq. (7.3) of Ref. 1 or Eq. (97) of Ref. 4. The derivative  $g'(1)$  depends on the third derivative  $G^{(3)}(1/2)$ , upon

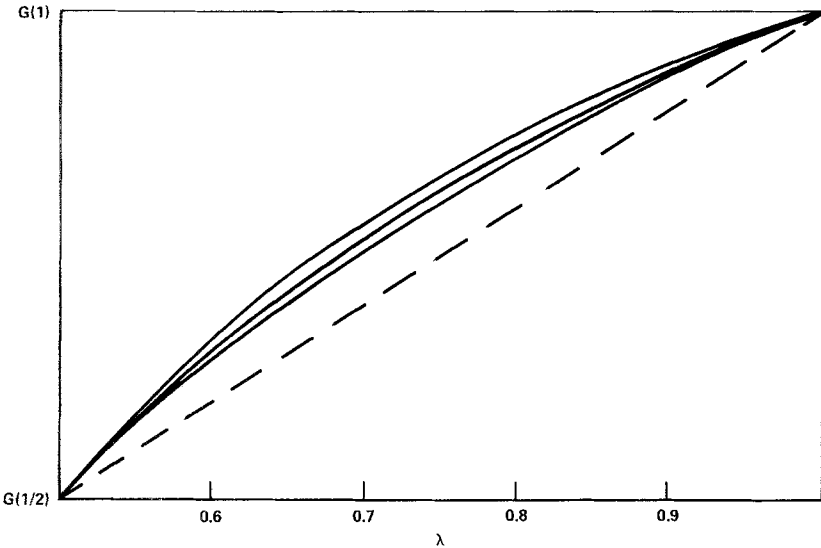


Fig. 3. The function  $G(\lambda)$  for  $y = 0.05$  (upper solid curve),  $0.25$  (middle solid curve), and  $0.40$  (lower solid curve). The dashed curve is a straight line. The ordinate is on a linear scale.



which no condition was placed. As seen in Table II, the agreement with Monte Carlo results<sup>(8)</sup> is excellent at low density, but deteriorates rapidly as the transition density is approached. Near  $y \approx 5$ , about one-fourth of the discrepancy is attributable to the error in the pressure  $\phi$ . The remainder would be corrected by roughly doubling  $G^{(3)}(1/2)$  from its value of  $\sim 1000$ . We would expect  $G^{(4)}(1/2)$  to be more negative than given by our theory in anticipation of the singularity at  $x = 1/\sqrt{3}$ . This suggests that the true  $G(x)$  oscillates about the function we have calculated with rather small amplitude.

#### 4. SURFACE PROPERTIES

Knowledge of  $G(\lambda)$ , together with the thermodynamics presented in the companion paper,<sup>(3)</sup> enables the calculation of superficial quantities near a boundary surface. Such a surface may be provided not only by container walls, but also by a solute molecule or colloidal particle. In this section and the next, we refer to formulas from the companion paper<sup>(3)</sup> as Eq. (I.xx), etc., and use, in addition to Eq. (12), dimensionless variables

$$\sigma(x, y) = \pi a^2 \gamma_s / 3kT, \quad u(x, y) = a_s / a \quad (31)$$

where  $a$  is the hard sphere diameter and  $\gamma_s$  is the surface tension at the Gibbs surface of tension  $a_s$  near a boundary of radius  $\lambda = ax$  in a fluid of reduced density  $y$ . As before, we take  $a = 1$  and use  $\lambda$  and  $x$  interchangeably.

In terms of these variables, the "cycle equation" (I.19) becomes

$$(\partial/\partial r)(\sigma u^2) + 2x^3(\partial/\partial r)(\sigma/u) = 0 \quad (32)$$

With the identification of  $\rho kTG(\lambda)$  with the average normal surface stress, the definition of the surface of tension (I.10) may be written

$$\sigma/u = yG(x) - \phi(y) = y \sum_{n=1}^N G_n(y)x^{-n} \quad (33)$$

where the second equality assumes the validity of the Laurent expansion, Eq. (18). The exact equation (9) and the boundary condition

$$\sigma u^2|_{x=0} = 0 \quad (34)$$

allow us to use Eqs. (32) and (33) to find

$$\sigma u^2 = \begin{cases} \frac{-2x^3y}{1-8x^3y} - \frac{1}{4} \ln(1-8x^3y), & x \leq 1/2 \\ \sigma u^2(1/2) + 2y \sum_{n=1}^N [n/(3-n)](\lambda^{3-n} - 2^{n-3})G_n(y) & x \geq 1/2 \end{cases} \quad (35)$$

Equations (33) and (35) make possible the separate computation of surface

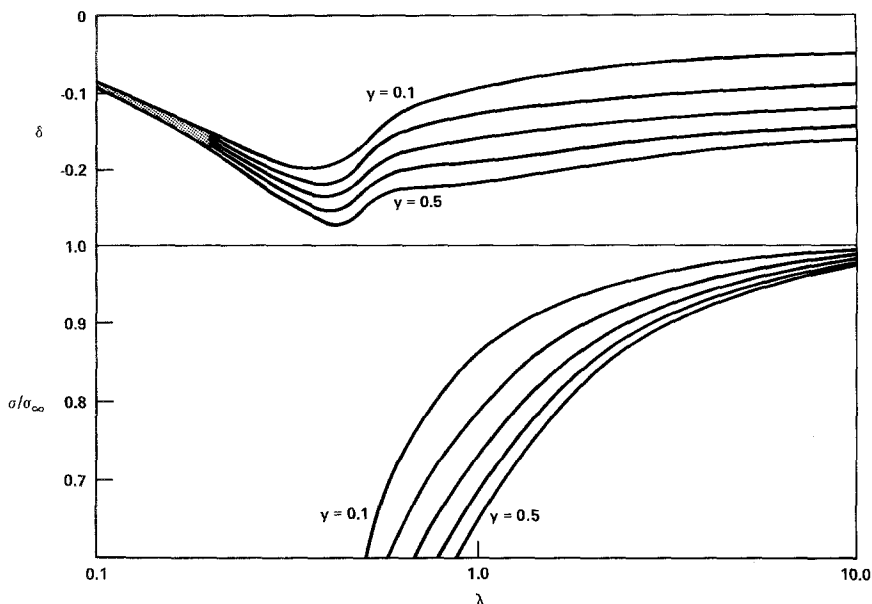


Fig. 4. The parameter  $\delta = u - x$  locating the Gibbs surface of tension, and the surface tension ratio  $\sigma/\sigma_\infty$  vs. boundary radius  $x$  for densities  $\gamma = 0.1, 0.2, 0.3, 0.4, 0.5$ .

tension  $\sigma(x, y)$  and the radius of the surface of tension  $u(x, y)$ . Results are shown in Fig. 4, where we have defined  $\delta = u - x$ . For the hard sphere fluid, we note that  $-1/2 < \delta \leq 0$ .

Denoting the planar limit of the superficial quantities by the subscript  $\infty$ , the following relations may be derived from Eqs. (33) and (35):

$$\sigma_\infty(y) = yG_1(y) \quad (36)$$

$$\delta_\infty(y) = G_2(y)/G_1(y) \quad (37)$$

$$\sigma(x, y) \simeq \sigma_\infty(y)(1 + 2\delta_\infty/x), \quad x \gg 1 \quad (38)$$

Using Eq. (25), we may find the surface tension virial series

$$\sigma_\infty(y) = (3/2)y^2\{1 + 4\frac{2}{9}y + 9\frac{5}{9}y^2 + 15.6y^3 + 21.1y^4 + \dots\} \quad (39)$$

which may be compared with Bellemans' exact result<sup>(9)</sup>

$$\sigma_\infty(y) = (3/2)y^2\{1 + [4\frac{9}{35}y + \dots]\} \quad (40)$$

Finally, we may calculate the adsorption per unit area at the boundary, defined as (I.13),

$$A\Gamma = N - \rho V \quad (41)$$

where  $V$  is the total volume outside the boundary and  $\rho$  is the homogeneous density. The quantity  $N$  excludes adsorbed molecules at the distant outer surface. The planar limit of the Gibbs adsorption isotherm (I.16) is

$$\Gamma_{\infty} = -(\partial\gamma/\partial\mu)_{T,\tau=\infty} = -\frac{1}{2}y(\partial\phi/\partial y)^{-1} \partial\sigma_{\infty}/\partial y \quad (42)$$

where the last equality is derived using the Gibbs–Duhem relation.  $\Gamma_{\infty}$  may be calculated from Eq. (25). We give some results in Table II.

## 5. APPLICATION TO BINARY HARD SPHERE MIXTURES

Scaled particle theory was applied to fluid mixtures by Lebowitz *et al.*<sup>(10)</sup> The treatment which follows is less ambitious but more rigorous, as it deals only with those properties of a solution that follow from the structure of the pure solvent.

The compressibility of a fluid mixture may be expressed, in terms of the direct correlation function, as<sup>(11,12)</sup>

$$\beta \partial p/\partial\rho_j = 1 - \sum_i \rho_i \int C_{ij}(\mathbf{r}) d^3\mathbf{r} = 1 - \sum_i \rho_i C_{ij}(0) \quad (43)$$

For our purpose, it will be more convenient to write Eq. (43) in terms of the  $k = 0$  Fourier component of the pair correlation function:

$$H_{ij} = \int d^3\mathbf{r} [g_{ij}(\mathbf{r}) - 1] \quad (44)$$

so that it becomes, for a binary mixture,

$$\beta \partial p/\partial\rho_B [(1 + H_{AA}\rho_A)(1 + H_{BB}\rho_B) - H_{AB}^2\rho_A\rho_B] = 1 + \rho_A(H_{AA} - H_{BA}) \quad (45)$$

For the case of hard spheres, we may write

$$H_{ij} = -(4\pi/3)\rho_j\lambda_{ij}^3 + 4\pi\lambda_{ij}^2\Gamma_{ij} \quad (46)$$

where  $\lambda_{ij}$  is the sum of the radii of particles  $i$  and  $j$ , and  $\Gamma_{ij}$  is the number of  $j$ -particles “adsorbed” per unit area of a boundary with radius  $\lambda_{ij}$  [see Eq. (13) of accompanying paper<sup>(3)</sup>]. We further specialize to a dilute solution of  $B$  molecules in a solvent of  $A$  molecules ( $\Gamma_{AB} = \Gamma_{BB} = \rho_B = 0$ ) and set  $\rho_A = 6y/\pi$ ,  $\rho_B = 6z/\pi$ ,  $\lambda_{AA} = 1$ ,  $\lambda_{AB} = \lambda_{BA} = \lambda$ , and  $p = (6\phi/\pi)kT$ . Equation (45) now becomes

$$\begin{aligned} \frac{\partial\phi}{\partial z} &= \frac{1 - 8y(1 - \lambda^3) + 4\pi(\Gamma_{AA} - \lambda^2\Gamma_{BA})}{1 - 8y + 4\pi\Gamma_{AA}} \\ &= 1 + \frac{\partial\phi}{\partial y} (8y\lambda^3 - 4\pi\lambda^2\Gamma_{BA}) \end{aligned} \quad (47)$$

To express  $\Gamma_{BA}$  in terms of  $G(\lambda)$ , we make use of the thermodynamics of curved surfaces. Referring all superficial quantities to the boundary surface  $\lambda$ , we have

$$\Gamma_{BA} = -\partial\gamma_{BA}/\partial\mu_A = -\rho_A \partial\gamma_{BA}/\partial p$$

where  $\gamma_{BA}$  is the surface tension and we have used the Gibbs–Duhem relation. Transforming to dimensionless variables ( $\gamma_{BA} = 3\sigma_\lambda/\pi kT$ ) gives

$$\Gamma_{BA} = -(3y/\pi)(\partial\phi/\partial y)^{-1} \partial\sigma_\lambda/\partial y \quad (48)$$

Using Eq. (I.12) to relate  $\sigma_\lambda$  to the surface tension  $\sigma$  at the Gibbs surface of tension  $u$ , we obtain

$$\begin{aligned} \lambda^2\Gamma_{BA} &= -3y/\pi(\partial\phi/\partial y)^{-1}(\partial/\partial y)\{\sigma u^2 + 2\lambda^3(\sigma/u)\} \\ (\partial/\partial\lambda)(\lambda^2\Gamma_{BA}) &= -3y/\pi(\partial\phi/\partial y)^{-1}(\partial/\partial y) \\ &\quad \times \{6\lambda^2(\sigma/u) + (\partial/\partial\lambda)(\sigma u^2) + 2\lambda^3(\partial/\partial\lambda)(\sigma/u)\} \end{aligned} \quad (49)$$

The last two terms cancel via the “cycle equation” (I.19).

Using Eq. (33), Eq. (46) becomes

$$\left. \frac{\partial}{\partial\lambda} \frac{\partial\phi}{\partial z} \right|_{z=0} = 24\lambda^2 y \frac{\partial}{\partial y} [yG(\lambda, y)] \quad (50)$$

Equation (50) is an important relation between the function  $G(\lambda)$  and the properties of hard sphere mixtures. The “integral condition” [Eq. (17)] may be derived from Eq. (50) by noting that

$$\int_0^1 \frac{\partial}{\partial\lambda} \frac{\partial\phi}{\partial z} \Big|_{z=0}^{a\lambda} = \frac{\partial\phi}{\partial y} \quad \text{and} \quad \int_0^y \frac{\partial\phi}{\partial y} dy = \phi(y)$$

Carrying out this operation leads, with the use of Eq. (9), to Eq. (17).

Let us now use Eq. (50) to determine the effect of a small concentration of B-type solute molecules with relative volume  $\sigma_B^3$  on the pressure of the hard sphere fluid. (The diameter of a B-type particle  $\sigma_B$  is not to be confused with the surface tension  $\sigma$  or  $\sigma_\lambda$ . We take  $\sigma_A = 1$ .) We define the number densities and mole fractions

$$\rho_A + \rho_B = \rho, \quad x_A = \rho_A/\rho, \quad x_B = \rho_B/\rho \quad (51)$$

and the packing fraction

$$\eta = \pi/6(\rho_A + \sigma_B^3\rho_B) \quad (52)$$

The derivatives of interest are

$$\left( \frac{\partial \ln p}{\partial X_B} \right)_\rho = y/\phi \left( \frac{\partial\phi}{\partial z} - \frac{\partial\phi}{\partial y} \right) \quad (53)$$

and

$$\left(\frac{\partial \ln p}{\partial x_B}\right)_\eta = y/\phi \left(\frac{\partial \phi}{\partial z} - \sigma_B^3 \frac{\partial \phi}{\partial y}\right) \quad (54)$$

Here we understand the derivatives to be taken at  $x_A = 1$ . The results are shown in Figs. 5–8. It is of interest to notice that the relation

$$\left(\frac{\partial \ln p}{\partial x_B}\right)_\eta \simeq 1 - \sigma_B^3 \quad (55)$$

holds accurately over a wide range of density and particle size. This relation can be derived using Eqs. (13), (52), and (54), expanding  $G(\lambda)$  about  $\lambda = 1$ . It follows that for constant  $x_B$  and  $\eta$ , the pressure is an extremum for  $\sigma_B = \sigma_A$ .

## 6. DISCUSSION AND CONCLUSIONS

We have presented a solution for the properties of the hard sphere fluid within the approximations of SPT, using *all* of the exact conditions offered by SPT. The theory gives an excellent fourth virial coefficient, an improved equation of state, and fairly good values for the derivative of the radial distribution function  $g'(1)$ .

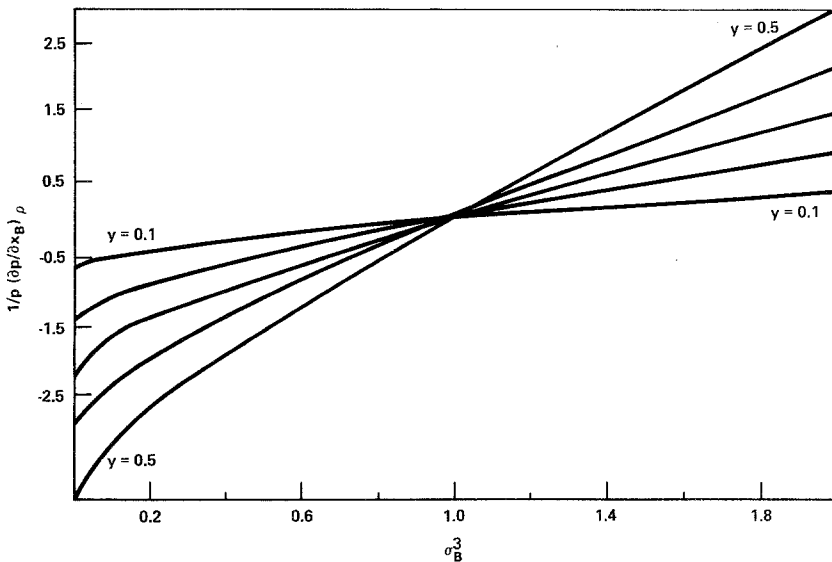


Fig. 5. Logarithmic derivative of pressure with respect to solute mole fraction at constant number density as a function of solute molecular volume for densities  $\gamma = 0.1, 0.2, 0.3, 0.4, 0.5$ .

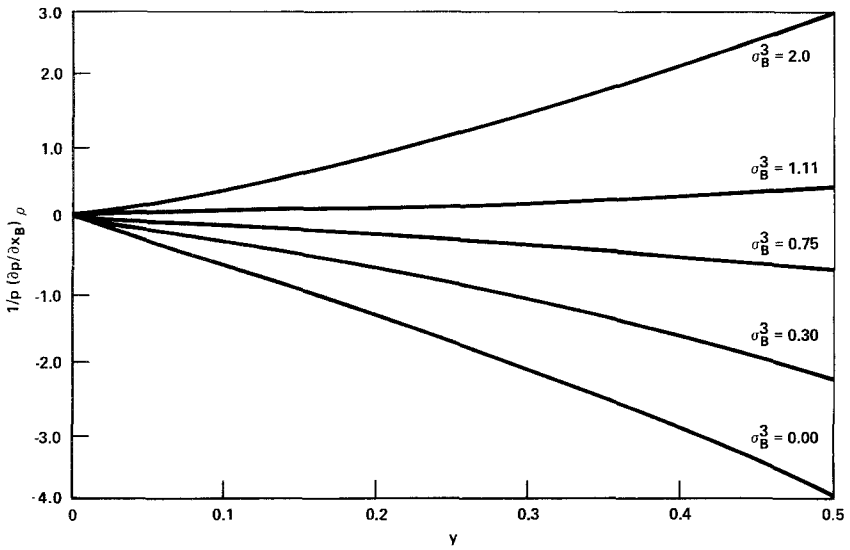


Fig. 6. Logarithmic derivative of pressure with respect to solute mole fraction at constant number density as a function of density for various solute molecular volumes.

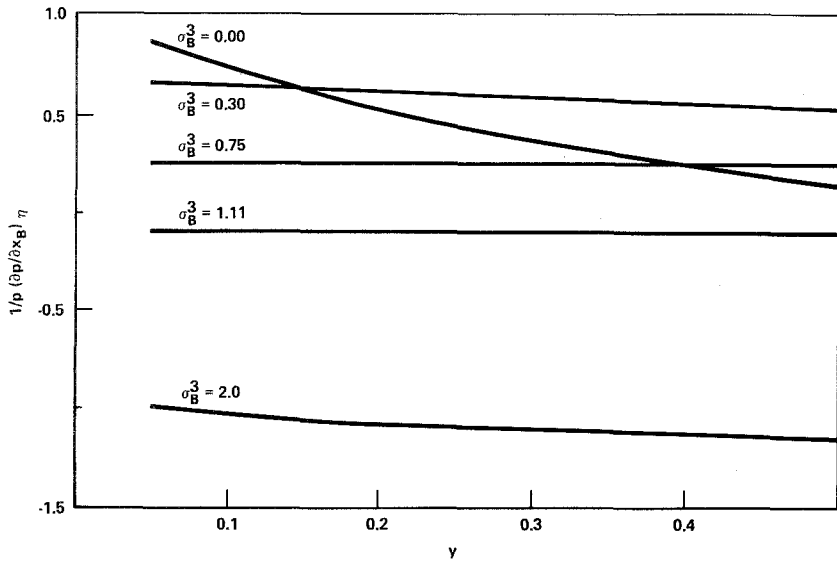


Fig. 7. Logarithmic derivative of pressure with respect to solute mole fraction at constant packing fraction vs. density for various solute molecular volumes.

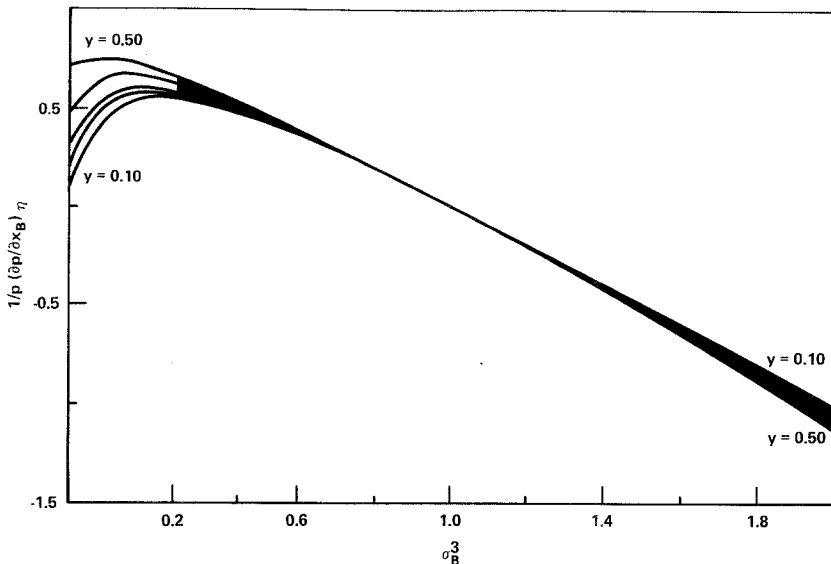


Fig. 8. Logarithmic derivative of pressure with respect to solute mole fraction at constant packing fraction vs. solute molecular volume for densities  $\gamma = 0.1, 0.2, 0.3, 0.4, 0.5$ .

*Form of  $G(\lambda)$ .* Cotter and Stillinger,<sup>(13)</sup> by considering  $G(\lambda)$  for nearly close-packed hard disks, have suggested that  $G(\lambda)$  should be nonmonotonic for sufficiently dense systems. The solution to the Reiss-Casberg equation,<sup>(2)</sup> which may be obtained with some confidence for  $\gamma \leq 0.3$ , also suggests such behavior. In our theory, however, the mathematics seems to contrive to make  $G(\lambda)$  the dullest function possible. Consideration of the known errors in our theory suggests that the true  $G(\lambda)$  shows only small deviations from the SPT curve (Fig. 3). It is difficult to measure  $G(\lambda)$  computationally, although its integral has been measured<sup>(14)</sup> and shows only such deviations from SPT as may be attributed to errors in the pressure  $\phi(\gamma)$ .

*Hard Sphere Mixtures.* We have shown that the pressure derivatives upon adding a hard sphere solute to a hard sphere solvent can be obtained from SPT without further approximation, and we have presented such results. Also obtainable are the surface tension and adsorption about a solute molecule. Unfortunately, the derivative  $(\partial/\partial r)g(\lambda, r)$  involves the quantity

$$\int d^2\mathbf{r}_2 n_2(\mathbf{r}_1, \mathbf{r}_2)$$

where  $n_2(\mathbf{r}_1, \mathbf{r}_2)$  is the two-particle density function in the presence of a  $\lambda$ -cule on whose surface  $r_1, r_2$  are constrained to lie. This quantity is not directly obtainable from SPT.

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