ABSTRACT

New theoretical results for the three-particle equilibrium probability distribution function $g_3(123)$ for classical hard-sphere fluids are given on the basis of the Percus-Yevick approximation applied to the inhomogeneous pair distribution function in the presence of a third particle, $g_2(12/3)$. In particular, comprehensive results are given for three spheres in rolling contact and partial results are given for two spheres in contact with a third particle in arbitrary position. When compared with available simulation data, our results are found to be accurate, and the inhomogeneous Percus-Yevick approach appears to be the first quantitatively successful one for the three-particle configurations considered here.

I. INTRODUCTION

The three-particle equilibrium probability distribution function $g_3(123)$ plays an important role in fluid-state statistical mechanics, but for decades it has proven to be a difficult function to adequately approximate. Here we give some new results for the g_3 of a classical hard-sphere fluid, based on an approximation scheme the first author has recently developed and implemented [1]. We describe the results in terms of a theoretical framework developed some time ago by the second author [2]. Our quantitative results are seen to be highly accurate when compared with existing simulation data; our theoretical approach appears to be the first quantitatively successful one for the three-particle configurations we consider here.

One of the general problems one confronts in developing an adequate treatment of g_3 arises from the shear number of independent variables upon which g_3 depends. Even for a single-species homogeneous fluid for which the pair potential $\varphi_2(ij)$ is a function only of absolute distance $|\mathbf{r}_{ij}|$ between particles, g_3 is in general a function of three scalar coordinates (for example, of $r = |\mathbf{r}_{12}|$, $s = |\mathbf{r}_{23}|$ and θ, the angle defined by $\mathbf{r}_{12}$ and $\mathbf{r}_{32}$ at $\mathbf{r}_2$) and two independent thermodynamic variables (measuring, for example, number density ρ and temperature T). Thus we are dealing with a function of 5 scalar variables. [Notationally suppressing the thermodynamic dependence, we shall write $g_3(123) = g(r, s, cos\theta)$].

However, in an important subset of fluid-state applications [5-11,13], g_3 arises as a key function in theories using a hard-sphere reference system, in which the thermodynamic dependence of g_3 is reduced to that of a single variable, ρd^3, where d is the hard-sphere diameter (which we shall take to be unity in this note). Furthermore, in some of these applications [5,7,8,9,11] $g(r, s, cos\theta)$ is needed not over all configurations of three particles, but only over configurations of three spheres in rolling contact, so that $g(r, s, cos\theta) = g(1, 1, cos\theta)$, with θ the only free variable for given ρ. In other applications [9,13] a more general set of configurations is needed involving a pair of spheres in contact, with a third sphere in arbitrary position with respect to that pair. Here $g(r,s,cos\theta) = g(1,s,cos\theta)$. We give results for both types of configuration, compared with available computer-simulation data.

Our results can most easily be derived, discussed, and understood in the context of the function

$$g_2(13/2) = g_3(123)/g_2(12)g_2(23) \tag{1.1}$$

where $g_2(ij)$ is the pair distribution function of the fluid. The $g_2(12/3)$ was discussed in detail by one of us some time ago [2]. As we showed in that treatment, $g_2(12/3)$ is exactly the pair distribution function of the system of particles under consideration into which a particle is inserted at $\mathbf{r}_3$ and taken to be the source of the external field $\varphi(i,3)$ acting on the rest of the particles. It is $g_2(12/3)$, rather than $g_3(123)$ itself, that is the central function of interest of the theory developed in [1]. In fact, that theory is based upon use of Percus-Yevick (PY) approximation applied to $g_2(12/3)$. Moreover, it is $g_2(12/3)$, rather than $g_3(123)$, that most naturally appears in the treatments to which we have referred above as requiring knowledge of three-particle hard-sphere correlations.

As discussed in [2], several well-known and useful approximations for $g_3(123)$ can conveniently be characterized in terms of $g_2(12/3)$. For example, approximating $g_2(13/2)$ by $g_2(13)$ in Eq. (1.1) yield the Kirkwood superposition approximation (KSA)

$$g_3(123) = g_2(12)g_2(13)g_2(23) \tag{1.2}$$

For hard-spheres, this approximation appears to be at its worst for three particles in contact or nearly in contact in a linear or nearly linear array. For such configurations, on the other hand, an exact result in one dimension suggests a second approximation (also discussed in detail in [2]) which we shall call the "linear approximation". For any one-dimensional system of hard-core particles (of core length 1) in which the interparticle potentials $\varphi(ij)$ is felt only by neighboring particles, one has

$$g_3(123) = g_2(12)g_2(23)$$

when particle 2 is between particle 1 and 3. In other words

$$
\begin{aligned}
&g_3(13/2) = 1 \;\text{ for }\; |\mathbf{r}_{13}| > 2 \\
&\text{when }\; |\mathbf{r}_{13}| > |\mathbf{r}_{12}| \;;\; |\mathbf{r}_{13}| > |\mathbf{r}_{23}|
\end{aligned}
\tag{1.3}
$$

For three-dimensional hard spheres in rolling contact, (1.3) proves to be reasonably accurate as long as $\theta > 3\pi/4$, but it becomes highly inaccurate as θ approaches $2\pi/3$, for which all three spheres are in mutual contact. (See Fig. 1). Until our work reported here, no theoretical treatment of $g_3(123)$ has been demonstrated to give satisfactory results at liquid-state densities for rolling sphere configurations over all realizable θ, or for the more general set of configurations involving a pair of spheres in contact plus a third sphere at an arbitrary position.

II. METHODS AND RESULTS

A general method for determining $g_3(12/3)$ for a simple atomic fluid has been given previously by one of us [1]. Briefly, that method requires that the spherically inhomogeneous Ornstein-Zernike equation, one of the exact equations for the density profile, and a closure approximation relating the inhomogeneous pair correlation functions, be solved simultaneously when the external potential is the pair potential of the simple fluid. Explicit data were obtained for the bulk thermodynamic properties and the triplet correlation function of a hard-sphere fluid using the Treizenberg-Zwanzwig density relation and the Percus-Yevick closure. This procedure was designated PY3 because the closure is applied at the triplet level; it is more accurate but more numerically demanding than the usual analytic solution obtained at the pair level.

The data presented here were obtained by the same procedure described in detail in the original paper [1]. However, they do represent a more accurate numerical solution to the PY3 approximation since the number of grid points, the bulk cutoff, and the fineness of the grid were all significantly increased. Specifically, the number of angular nodes were increased from 60 to 75, the number of layers in the radial direction was 250, compared to 120 originally, and the distance beyond which bulk properties were assumed grew from 9 to 11 diameters, giving a mesh of 25 compared to 15 layers per diameter originally. In addition, the convolution integral which remains in the Legendre expanded Ornstein-Zernike equation was now evaluated using Simpson's rule rather than the trapezoidal rule used previously. These improvements have little effect for low and moderate densities, but have led to more reliable data for $\rho d^3 \approx 0.7$ and higher.

Table I represents an extensive tabulation of the PY3 inhomogeneous pair probability distribution of two hard-spheres in contact with a third, $g(1,1,cos\theta)/g(1)^2$. (The angle is that subtended by the two hard-spheres at the center of the third with which they are in contact; the hard-sphere diameter is taken as the unit of length). Perhaps the most convenient accurate way to obtain the full three-particle probability distribution for this particular geometry is to utilize the contact value of the radial distribution function given by the Carnahan-Starling equation of state. The number of significant figures retained in the table reflects the accuracy of the solution to the PY3 equations rather than the accuracy of that approximation itself; we discuss the latter shortly.

The inhomogeneous pair function near contact ($cos\theta = 0.5$) is only close to the homogenenous pair correlation function at very low density whereas the Kirkwood superposition approximation identifies these two functions at all densities. In fact a reasonable approximation is $g(1,1,1/2) \approx g(1)^2[1+g(1)]/2$. Also the two particles become uncorrelated for nearly linear configuration [$g(1,1,cos\theta) \rightarrow\sim g(1)^2$, $cos\theta \rightarrow -1$], which again contradicts the KSA, but indicates that the linear approximation $g(r,s,cos\theta) = g(r)g(s)$ is quite successful for nearly linear configurations [12].

The accuracy of the PY3 approximation itself can best be gauged from the comparison with the simulation data given in Figure 1. In general the agreement with the simulation is highly satisfactory, especially considering the rather high density, $\rho^3 = 0.83685$. The data attributed to Bellemans and Orban [3] was derived by dividing their simulated $g(1,1,cos\theta)$ by the square of the contact value obtained by extrapolating their MC data to contact, $g(1) = 4.330$. This value appears to underestimate the true value somewhat. The PY 3 contact value is $g(1) = 4.511$, and hence a comparison of the full PY3 three particle probability distribution would systematically overestimate the simulated quantity. Use of the Carnahan-Starling equation of state, $g(1) = 4.403$, would give better agreement with the simulation of the full quantity. The bulk radial distribution function $g(t)$ is included in the figure for comparison (where $t = (2 - 2cos\theta)^{1/2}$); for this purpose the PY3 approximation to this quantity can be taken as exact. It is clear that $g(t)$ does not have as much structure as the inhomogeneous quantity, $g(1,1,cos\theta)/g(1)^2$, and that at this density $g(1)$ greatly overestimates the contact value $g(1,1,1/2)/g(1)^2$. The disparity between the two pair functions graphically illustrates the error in the Kirkwood superposition approximation. Finally, Bellemans and Orban [1968] have utilized a quantity A_3 in their theory for the entropy of mixing of nearly identical hard-spheres. A_3 is essentially the angular integral of the three particle distribution function (rolling contact), and they found it to be equal to 231 ± 2 at $\rho d^3 = 0.77254$ and 343 ± 2 at $\rho d^3 = 0.83685$. The PY3 values are 232.4 and 355.2; most of the error for the higher density is attributable to the overestimation of the contact value discussed above.

Figure 2 compares the PY3 approximation to the inhomogeneous pair probability distribution function with the simulations of Uehara et al. [12], for the case when two spheres are in contact at a moderate density of $\rho d^3 = 0.5261$. We have plotted $g(1,s,cos\theta)/[g(1)g(s)]$ for $s = 1, 1.2$, and 1.6. Note that the respective MC values are $g(s) = 2.262$, 1.470 and 0.908, and those given by PY3 are $g(s) = 2.2876$, 1.4701, and 0.9039. The simulation data are derived from Table II of Uehara et al, by multiplying their simulated quantity $\delta(r,s,1)$ by their BGY2 values for $g(r)$, rather than by the more coarsely tabulated simulation data of Ree et al. [11]; the small errors in the BGY2 results are not relevant for the comparison presented here. Again the PY3 approximation is seen to perform very satisfactorily, indicating that it is probably a good approximation for the full three-particle probability distribution function for all configurations of the hard-spheres, and not only the rolling contact most explicitly addressed in this paper. We are currently actively pursuing extensions of our approach to potentials lacking a hard core (e.g., the Lennard-Jones potential).

Tables of the PY3 $g(1,s,cos\theta)/g(1)g(s)$ for representative s,θ, and ρ are available from either author upon request.

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REFERENCES

[1] P. Attard, J. Chem. Phys. **91**, (1989) 3072.

[2] G. Stell in **The Equilibrium Theory of Classical Fluids**, ed. by H. Frisch and J.L. Lebowitz (Benjamin, New York, 1964).

[3] A. Bellemans and J. Orban, Chem. Phys. Lett. **2**, (1968) 253 and unpublished results.

[4] D.G. Chae, F.H. Ree, and T. Ree, J. Chem. Phys. **50**, (1969) 1581.

[5] A. Bellemans, Phys. Rev. Lett. **21**, (1968) 527.

[6] I. de Schepper, A.F.E.M. Haffmans, H. van Beijeren, Phys. Rev. Lett. **57**, (1986) 1715.

[7] I. de Schepper and E.D.G. Cohen, Phys. Lett. **55A**, (1976) 385.

[8] W.G. Gibson, Mol. Phys. **30**, (1975) 13.

[9] A.F.E.M. Haffmans, et al, Phys. Rev. A **37**, (1988) 2698.

[10] J.A. Leegwater and H. van Beijeren, J. Stat. Phys. **57**, (1989) 585.

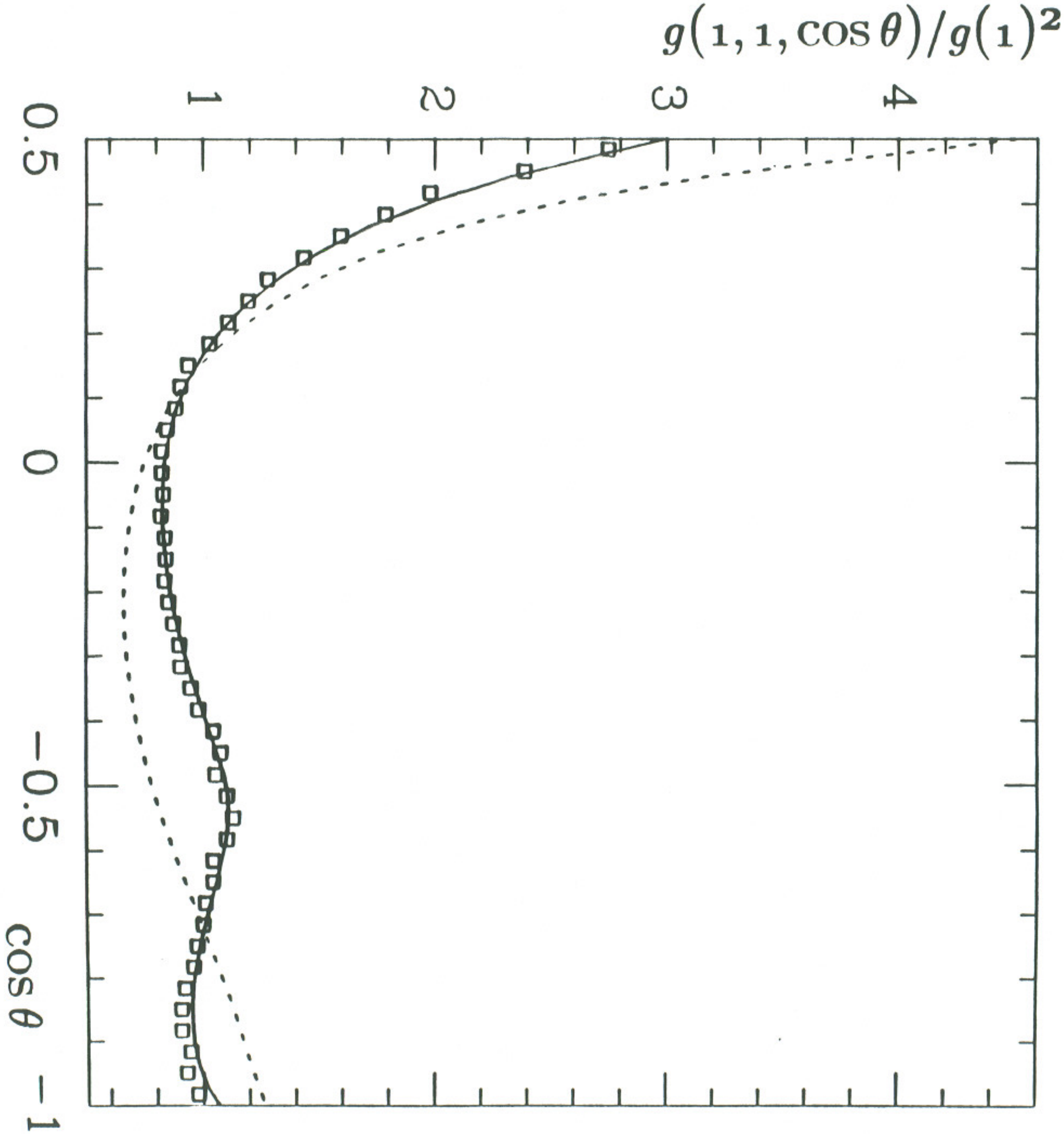
[11] F.H. Ree. Y.-T. Lee, and T. Ree, J. Chem. Phys. **55**, (1971) 234.

[12] Y. Uehara, Y.-T. Lee, T. Ree, F.H. Ree, J. Chem. Phys. **70**, (1979) 1884.

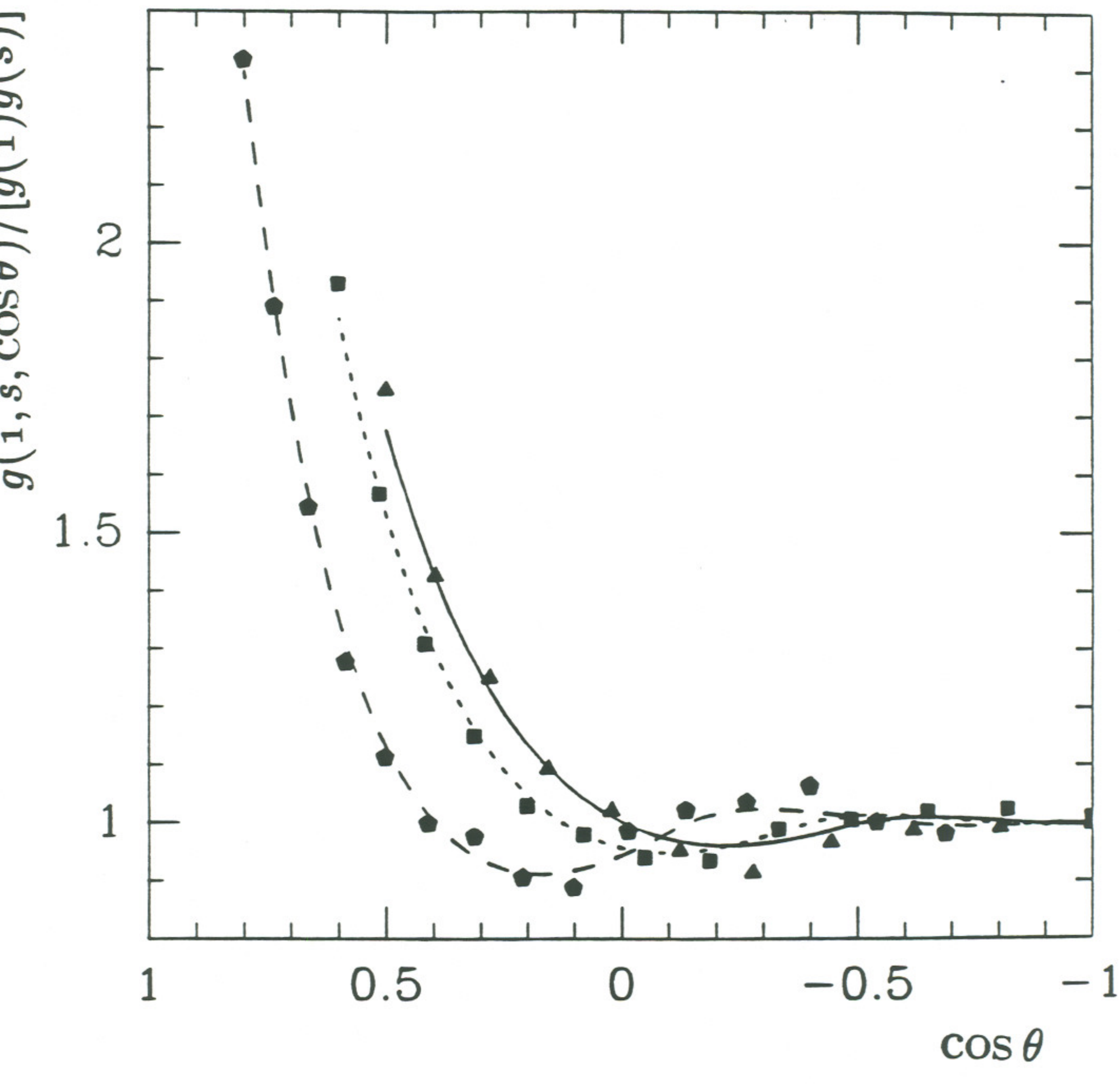
[13] H. van Beijeren, Phys. Lett. **105A**, (1984) 191.

Table I. PY3 values for the inhomogeneous pair probability distribution for two hard-spheres rolling around a third, $g(1,1,\cos\theta)/g(1)^2$, for various densities, ρd^3.

$\cos\theta$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0.5000	1.0713	1.1610	1.2753	1.4225	1.6164	1.878	2.238	2.751	3.52
0.4419	1.0603	1.1342	1.2252	1.3384	1.4806	1.662	1.895	2.198	2.60
0.4042	1.0539	1.1186	1.1966	1.2908	1.4051	1.544	1.713	1.916	2.16
0.3658	1.0479	1.1042	1.1704	1.2476	1.3376	1.442	1.558	1.682	1.80
0.3268	1.0422	1.0908	1.1463	1.2087	1.2778	1.352	1.427	1.491	1.53
0.2872	1.0370	1.0785	1.1244	1.1738	1.2252	1.275	1.317	1.337	1.31
0.2471	1.0321	1.0672	1.1044	1.1421	1.1781	1.208	1.222	1.209	1.14
0.2066	1.0277	1.0569	1.0865	1.1144	1.1376	1.151	1.146	1.110	1.02
0.1657	1.0237	1.0476	1.0704	1.0898	1.1024	1.103	1.083	1.031	0.93
0.1245	1.0199	1.0391	1.0561	1.0681	1.0719	1.062	1.032	0.970	0.86
0.0831	1.0166	1.0316	1.0434	1.0494	1.0462	1.029	0.991	0.924	0.82
0.0416	1.0135	1.0250	1.0324	1.0335	1.0250	1.003	0.961	0.893	0.79
0.0000	1.0108	1.0191	1.0229	1.0198	1.0069	0.981	0.936	0.869	0.77
-0.0416	1.0085	1.0140	1.0148	1.0087	0.9932	0.965	0.921	0.858	0.77
-0.0831	1.0064	1.0096	1.0081	0.9996	0.9822	0.953	0.911	0.853	0.78
-0.1245	1.0046	1.0060	1.0026	0.9926	0.9743	0.946	0.906	0.855	0.79
-0.1657	1.0032	1.0030	0.9983	0.9874	0.9692	0.943	0.907	0.864	0.82
-0.2066	1.0020	1.0007	0.9951	0.9839	0.9664	0.942	0.912	0.877	0.84
-0.2471	1.0010	0.9989	0.9928	0.9819	0.9658	0.945	0.920	0.896	0.88
-0.2872	1.0003	0.9977	0.9915	0.9814	0.9673	0.950	0.933	0.919	0.92
-0.3268	0.9998	0.9969	0.9910	0.9819	0.9702	0.957	0.947	0.944	0.96
-0.3658	0.9995	0.9966	0.9913	0.9838	0.9750	0.967	0.964	0.974	1.01
-0.4042	0.9993	0.9966	0.9921	0.9862	0.9803	0.977	0.982	1.002	1.06
-0.4419	0.9992	0.9970	0.9934	0.9894	0.9867	0.989	1.001	1.034	1.11
-0.4788	0.9993	0.9975	0.9950	0.9930	0.9934	1.000	1.019	1.062	1.15
-0.5149	0.9995	0.9981	0.9966	0.9963	0.9993	1.010	1.034	1.082	1.18
-0.5501	0.9995	0.9986	0.9979	0.9988	1.0034	1.016	1.040	1.087	1.17
-0.5844	0.9997	0.9990	0.9989	1.0006	1.0061	1.019	1.042	1.082	1.15
-0.6176	0.9998	0.9994	0.9997	1.0018	1.0075	1.019	1.039	1.069	1.11
-0.6498	0.9998	0.9997	1.0002	1.0026	1.0082	1.019	1.034	1.054	1.07
-0.6809	0.9998	0.9998	1.0005	1.0030	1.0080	1.017	1.028	1.037	1.03
-0.7108	0.9999	1.0000	1.0008	1.0032	1.0075	1.014	1.021	1.020	0.99
-0.7394	0.9999	1.0001	1.0009	1.0030	1.0065	1.011	1.013	1.005	0.96
-0.7668	0.9999	1.0002	1.0010	1.0028	1.0055	1.008	1.007	0.992	0.94
-0.7928	1.0000	1.0002	1.0009	1.0024	1.0043	1.005	1.001	0.981	0.92
-0.8175	1.0000	1.0002	1.0009	1.0021	1.0032	1.003	0.996	0.974	0.92
-0.8407	1.0000	1.0002	1.0007	1.0016	1.0020	1.000	0.992	0.969	0.91
-0.8625	1.0000	1.0002	1.0007	1.0012	1.0010	0.998	0.989	0.967	0.92
-0.8828	1.0000	1.0002	1.0005	1.0008	1.0001	0.997	0.988	0.967	0.92
-0.9016	1.0000	1.0002	1.0004	1.0004	0.9993	0.996	0.987	0.970	0.94
-0.9188	1.0000	1.0001	1.0003	1.0001	0.9987	0.995	0.987	0.974	0.95
-0.9344	1.0000	1.0001	1.0002	0.9998	0.9982	0.995	0.989	0.981	0.98
-0.9484	1.0000	1.0001	1.0001	0.9996	0.9978	0.995	0.990	0.988	1.00
-0.9608	1.0000	1.0001	1.0000	0.9994	0.9976	0.995	0.993	0.997	1.03
-0.9715	1.0000	1.0001	0.9999	0.9992	0.9975	0.995	0.995	1.006	1.05
-0.9805	1.0000	1.0000	0.9999	0.9991	0.9975	0.996	0.998	1.015	1.08
-0.9878	1.0000	1.0000	0.9998	0.9991	0.9975	0.996	1.000	1.024	1.10
-0.9934	1.0000	1.0000	0.9998	0.9990	0.9975	0.997	1.002	1.031	1.13
-0.9973	1.0000	1.0000	0.9997	0.9990	0.9975	0.997	1.004	1.036	1.14
-0.9995	1.0000	1.0000	0.9997	0.9990	0.9976	0.998	1.005	1.040	1.15



$g(1,1,\cos\theta)/g(1)^2$
1
2
3
4
0.5
0
−0.5
−1
$\cos\theta$



g(1, s, cos θ)/[g(1)g(s)]
2
1.5
1
1
0.5
0
−0.5
−1
cos θ