

Hard Sphere Compressibility Factors for Equation of State Development

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New molecular simulation data are reported for the compressibility factors of hard spheres covering the isotropic liquid, metastable fluid and solid ranges of density. These data provide a comprehensive set of values for the development of hard-sphere equations of state. In particular, they represent a substantial increase in the data available at high isotropic liquid densities. A comparison is reported with examples of accurate hard sphere equations. In contrast to literature comparisons, which are weighted towards existing lower density data, including these new higher density data indicates that the overall accuracy of current equations of state is considerably less than previously reported.

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Introduction

The concept of a hard body is useful in the development of theories of the liquid state. In particular, the properties of hard spheres provide the theoretical backbone of many equations of state for real fluids (Sadus, 1992; Wei and Sadus, 2000). The Carnahan-Starling (1969) equation provides an accurate representation of the compressibility factor (Z) as a function of reduced density ($\rho = N\sigma^3/V$, where N is the number of hard spheres of diameter σ and V is the volume) or packing fraction ($\eta = \pi N\sigma^3/6V$). Nonetheless, there is considerable interest in developing more accurate hard-sphere equations to improve predictions at high density, and for the higher virial coefficients. The rationale for such work is that a highly accurate representation of hard-sphere interactions might improve the prediction of real fluids.

The normal test used to determine the accuracy of a hard-sphere equation of state is to compare its Z - ρ behavior with exact hard sphere data obtained from molecular simulation (Sadus, 1999). There are eight main sources of simulation data in the literature for the compressibility factors of hard spheres (Alder and Wainwright, 1960; Alder et al., 1968; Hoover and

Ree, 1968; Barker and Henderson, 1971; Adams, 1974; Woodcock, 1976; Labik and Malijevsky, 1981; Erpenbeck and Wood, 1984). These data were reported over a period of 25 years, they were obtained by different simulation techniques, and they cover varying ranges of densities. Although, these different sources of data are in very good overall agreement with each other, for the purposes of evaluating different equations of state, it is desirable to have a common set of data, obtained by one simulation technique and covering the entire range of densities. In this work, we report comprehensive molecular simulation data for hard spheres, which can be used as reference data for the development of hard-sphere equations of state. The accuracy of several recently developed hard-sphere equations of state are evaluated with respect to these new data.

Theory

Molecular Simulation Details

Monte Carlo simulations were performed in the canonical ensemble. Hard spheres are athermal and as such, their properties are independent of temperature. This means the canonical ensemble becomes an NV -ensemble in which the number of particles (N) and volume (V) are the external control parameters. The system was typically composed of either 500 or 1372 identical hard spheres of dia. σ . In some cases up to 32,000

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hard spheres were used. The hard sphere intermolecular potential ($u(r)$) at different separations (r) has either a value of 0 ($r > \sigma$) or ∞ ($r \leq \sigma$) depending on whether or not the spheres overlap. At each density, the compressibility factor was obtained by using the formula for hard spheroids (Vieillard-Baron, 1972; Perram et al., 1984) that counts particle contacts. Conventional periodic boundary conditions were used, and the maximum displacement of translation was adjusted to have a 50% acceptance rate. The isotropic liquid and solid curves were both obtained by commencing the simulations from a face centered cubic lattice. The metastable extension of the isotropic fluid curve was obtained by using the final configuration of the previous density as the new initial starting point and re-equilibrating the system to eliminate any overlaps caused by the increase in density. By progressively adopting this procedure, we have been able to trace the metastable curve to $\eta = 0.6414$. This is consistent with literature estimates (Rintoul and Torquato, 1998) of the random close packing limit. The simulations were performed in cycles with each cycle representing 500 or 1372 attempted displacements. For the isotropic liquid range of densities, 4,800,000 cycles were used for equilibration followed by a further 4,800,000 cycles for post-equilibration. For the metastable and solid regions, typically, at least 200,000 cycles were used for equilibration and, at least, a further 200,000 cycles post-equilibration were performed to obtain ensemble averages of the compressibility factor. Therefore, the absolute statistical uncertainty of data reported here is very low, typically $\leq 0.1\%$.

Hard-sphere equations of state for fluids

The most widely used hard-sphere equation of state is that of Carnahan and Starling (1969) (CS)

$$Z = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \quad (1)$$

Several improved hard-sphere equations have been proposed. The equation of Kolafa (K) (Boublik, 1986) introduces an additional term to the denominator of the CS equation

$$Z = \frac{1 + \eta + \eta^2 - \frac{2}{3}(\eta^3 + \eta^4)}{(1 - \eta)^3} \quad (2)$$

The equation of Malijevsky and Veverka (1999) (MV) is

$$Z = \frac{1 + 1.056\eta + 1.6539\eta^2 + 0.3262\eta^3}{(1 - \eta)^3(1 + 0.056\eta + 0.5979\eta^2 + 0.3076\eta^3)} \quad (3)$$

In contrast to the above equations, Yelash and Kraska (2001) (YK) reported an equation of state without a pole at $\eta=1$

$$Z = \frac{3 + 8\eta + 14\eta^2 + 14\eta^3 + \frac{40}{3}\eta^4}{3 - 4\eta} \quad (4)$$

Table 1. Molecular Simulation Compressibility Factor Data for Hard Spheres*

Isotropic Liquid		Metastable Fluid		Solid	
ρ	Z	ρ	Z	ρ	Z
0.04	1.0894(1)	0.98	14.26(1)	0.96	9.6146(5)
0.07	1.1630(1)	0.99	14.79(1)	0.965	9.6727(3)
0.1	1.2413(1)	1.01	15.96(1)	0.97	9.7540(8)
0.13	1.3289(1)	1.02	16.56(2)	0.98	9.9099(3)
0.16	1.4223(1)	1.03	17.19(1)	0.99	10.099(5)
0.19	1.5232(2)	1.04	17.76(2)	1.0	10.304(5)
0.22	1.6332(2)	1.11	23.70(3)	1.05	11.609(3)
0.25	1.7526(2)	1.13	29.22(2)	1.1	13.457(5)
0.28	1.8817(2)	1.14	32.59(1)	1.12	14.390(2)
0.31	2.0231(3)	1.15	34.82(3)	1.14	15.470(2)
0.34	2.1762(3)	1.16	41.06(3)	1.16	16.741(4)
0.37	2.3433(3)	1.17	50.11(1)	1.18	18.238(4)
0.4	2.5255(3)	1.18	59.89(1)	1.2	20.025(5)
0.43	2.7254(4)	1.19	75.22(3)	1.22	22.190(5)
0.46	2.9403(4)	1.195	87.39(4)	1.24	24.893(4)
0.49	3.1806(5)	1.2	95.65(2)	1.26	28.334(5)
0.52	3.4418(4)	1.203	114.03(4)	1.28	32.841(3)
0.54	3.6298(5)	1.205	114.63(5)	1.3	39.006(5)
0.56	3.8305(7)	1.207	138.59(4)	1.32	47.884(5)
0.58	4.0427(7)	1.209	155.84(7)	1.34	61.728(8)
0.6	4.2952(4)	1.21	181.65(6)	1.36	85.675(6)
0.65	4.9494(3)			1.38	133.06(1)
0.7	5.7286(4)			1.4	200.36(1)
0.75	6.6566(5)				
0.8	7.7662(4)				
0.85	9.1168(5)				
0.9	10.762(3)				
0.91	11.131(5)				
0.92	11.519(3)				
0.93	11.925(2)				
0.94	12.348(2)				
0.95	12.786(3)				

*The values in brackets represent the standard error in the last digit.

Recently, Eu and Ohr (2003) (EO) proposed the following equation of state

$$Z = \frac{\eta(1 + \eta + \eta^2)}{(1 - \eta)^3} - 54\lambda \ln(1 - \eta) - \frac{54\lambda\eta}{(1 - \eta)^5} \left(1 - \frac{9}{2}\eta + \frac{47}{6}\eta^2 - \frac{77}{12}\eta^3 + \frac{157}{60}\eta^4 - \frac{1}{3}\eta^5 \right) \quad (5)$$

where $\lambda = 0.05$ is an adjustable parameter. Speedy (1994) (S) reported a purely empirical relationship that is only valid for packing fractions at which the fluid is metastable

$$Z = \frac{2.67}{(1 - 1.543\eta)} \quad (6)$$

Results and Discussion

The compressibility factors obtained from molecular simulation are summarized in Table 1. The uncertainties in the ensemble averages are given as standard errors (Bevington and Robinson, 2003). The standard errors were calculated by dividing the post-equilibrium data into 10 equal size blocks, and comparing the block averages with the ensemble average. Data are included for both the isotropic fluid and the metastable

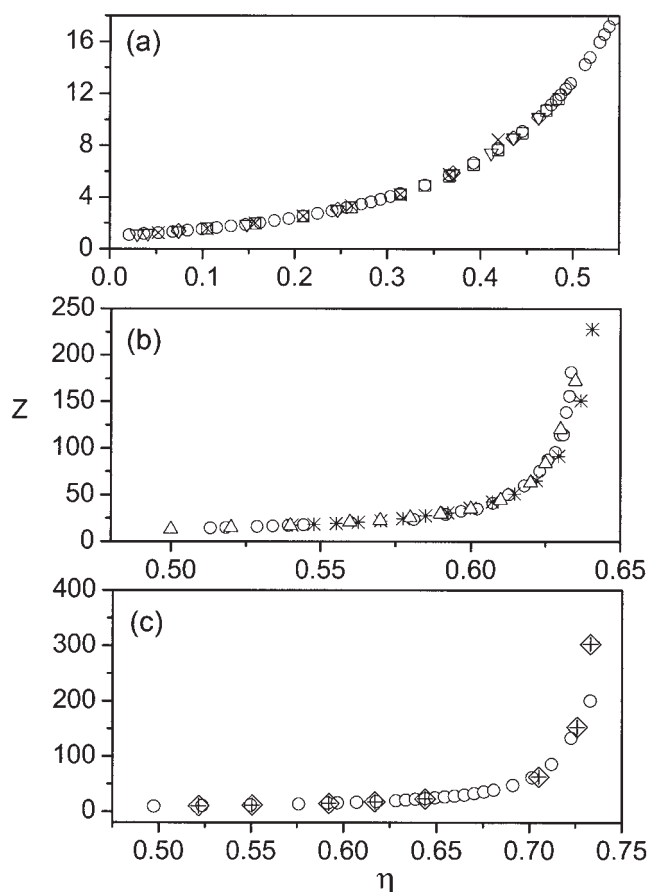


Figure 1. Compressibility factors of hard spheres, as a function of packing fraction, obtained in this work (O) with literature data from Alder and Wainwright, 1960 (diamonds); Alder et al., 1968 (+); Barker and Henderson, 1971 (squares); Adams, 1974 (X); Erpenbeck and Wood, 1984 (▽); Speedy, 1994 (*); and Rintoul and Torquato, 1988 (Δ).

Results are given separately for the (a) isotropic liquid, (b) metastable fluid, and (c) solid phases.

extension of the isotropic curve, which occurs after the freezing transition. Data for the solid phase are also included for the benefit of completeness. We will not consider the solid data further because the focus of this work is on equations of state for fluids. An example of an equation of state for solids is available elsewhere (Hall, 1970).

Figure 1 shows that there is generally very agreement between our simulation data and literature data for the isotropic liquid (Figure 1a) and solid phases (Figure 1c) over most of the η range. The new data reported here and illustrated in Figure 1a considerably increases the data available for the isotropic fluid at $\eta > 0.45$. The different sets of data for the metastable fluid (Figure 1b) do not agree for $\eta > 0.62$. This reflects the increased uncertainties involved in determining metastable equilibria compared with thermodynamically stable properties. The results are likely to be sensitive to factors, such as the number of particles, the criterion of overlap, and the length of

the simulation. Erpenbeck and Wood (1984) have discussed estimating values at the thermodynamic limit. We repeated our simulations for up to 32,000 spheres. We did not observe any significant size dependency in the compressibility factors for systems containing 1372 or more spheres. That is, the results for the larger systems were generally within the combined standard errors. Our simulations have the benefit of much larger pre and post-equilibrium periods than reported previously in the literature.

The difference in the compressibility factors predicted from various simulation studies and the predictions obtained from the Carnahan-Starling equation of state are compared in Figure 2 for the isotropic liquid. For values of $\eta < 0.35$, the various simulation results agree with the predictions of the Carnahan-Starling equation to within 0.1% in the worse case. For values of $\eta > 0.35$, the results of Alder and Wainwright (1960) and Erpenbeck and Wood (1984) and our results remain in very good agreement with the predictions of the Carnahan-Starling equation of state. The compressibility factors reported by Baker and Henderson (1971) for values of η between 0.35 and 0.45 are systematically smaller. However, their two data points at high packing fractions deviate from the trend.

Figure 3 compares our data with the predictions of the CS, K, MV, YK, and EO hard-sphere equations of state. There are many other hard-sphere equations of state in the literature (Mulero et al., 2001), and these equations were chosen solely as recent examples of equations of state. In all cases, the agreement between theory and simulation for the isotropic liquid appears good. To provide an objective quantitative measure of the relative accuracy of the equations of state, we calculated the average absolute deviation (AAD) between theory and simulation defined by

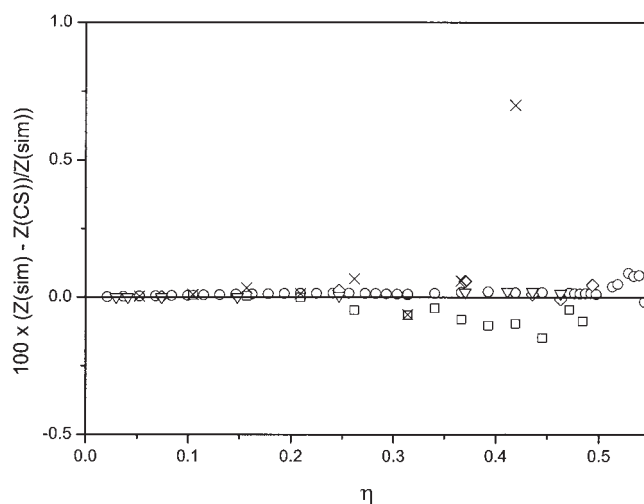


Figure 2. Relative percentage difference between compressibility factors from simulation and the predictions of the Carnahan-Starling equation of state.

Results are compared for the simulation data obtained by Alder and Wainwright, 1960 (diamonds); Barker and Henderson, 1971 (squares); Adams, 1974 (X); Erpenbeck and Wood, 1984 (▽), and this work (O).

$$AAD = \frac{1}{n} \sum_{i=1}^n \left| \frac{Z_{i, \text{sim}} - Z_{i, \text{eos}}}{Z_{i, \text{sim}}} \right| \quad (7)$$

Values of the AADs are summarized in Table 2. We separately analyzed the isotropic liquid and metastable fluid regions. Our data enables a comparison with equations of state predictions for the entire range of isotropic liquid densities. In contrast, different sources of data must be combined to make an equivalent comparison from the literature. For the isotropic fluid, our analysis indicates that the CS equation is accurate. The K and MV equations are more accurate than the CS equation but the improvement in accuracy is small. The comparisons with our data indicate that the YK and EO equations are less accurate than the CS, K and MV equations.

Our values of AADs are larger than reported elsewhere in the literature (Mulero et al. 2001), which are typically < 0.2%. We attribute this difference to both the larger density range and amount of data used in our comparison. In particular, we have used considerably more data at high densities ($\rho > 0.9$) than was previously available in the literature. It is well known that the equations of state are less accurate at high densities than low densities, which is consistent with the larger values of AADs that we obtained. Until now, hard-sphere equations of state have been developed and tested against simulation data that was mainly confined to the lower range of isotropic fluid densities. It is apparent that the very small AAD values obtained at lower densities are misleading indicators of the overall accuracy of the equations of state. The increases in AADs caused by including more high density data indicate that there is scope to further improve the accuracy of the equations of state. The high-density data reported here are likely to be useful in the future development of equations of state.

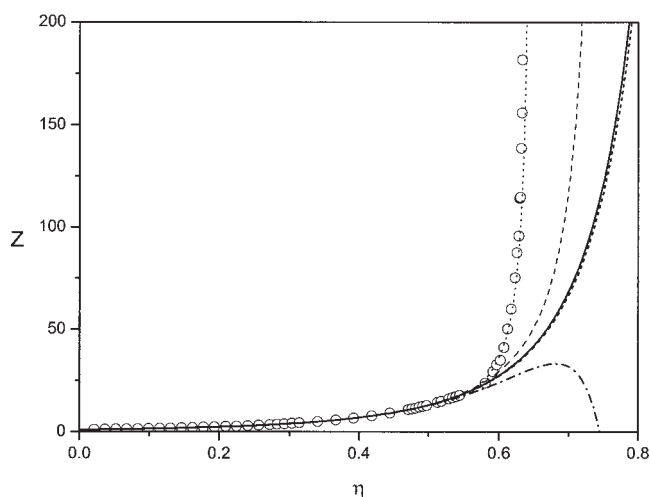


Figure 3. Compressibility factors of hard spheres, as a function of packing fraction, obtained in this work (O) with calculations using the CS/MV (—), YK (---), K (- · -), EO (- · ·), and S (···) equations of state.

A single line illustrates the results for the CS and MV because differences in the compressibility factor predicted by the two equations are imperceptible for the above range packing fractions.

Table 2. Average Absolute Deviations in the Compressibility Factor Obtained by Comparing Equation of State Predictions with Simulation Data

Equation	Isotropic Liquid (% AAD)	Metastable Fluid (% AAD)
	$0.04 \leq \rho \leq 0.95$	$0.98 \leq \rho \leq 1.21$
CS	0.333	34.4
K	0.247	34.8
MV	0.228	34.2
YK	0.530	31.5
EO	0.918	40.5
S		10.8

It is unrealistic to expect conventional equations of state for fluids to give good agreement for the metastable region because it has a considerable degree of structure that is absent in the isotropic fluid. Nonetheless, for the benefit of completeness, we also examined the predictions of the equations of state in the metastable region. It is clear from Figure 3 and Table 2 that all the equations of state are inaccurate for the isotropic metastable fluid. For the metastable region, the YK equation is the most accurate alternative whereas the EO equation totally breaks down at high density. The failure of conventional equations of state in the metastable region of densities is not an important problem for the development of equations of state for fluids because most real fluid properties occur at lower densities. The accurate prediction of the properties of the metastable region requires specially formulated equations of state (Speedy, 1994). This is demonstrated in Figure 3 and Table 2 by the reasonable results obtained using the purely empirical S equation.

Although the K and MV equations are slightly more accurate, the CS equation remains a very good choice for the accurate prediction of the Z - ρ behavior of hard spheres in the isotropic liquid phase. It is also mathematically the simplest choice without any significant compromise in accuracy. Of course, it should be noted that there are other valid reasons for using the alternative equations of state, such as their improved ability to predict higher virial coefficients and the absence of a pole in the numerator.

Conclusions

Molecular simulation results for the compressibility factor of hard spheres are reported which can be used as reference data for the development of equation of state for hard spheres. The amount of data at high densities has been increased considerably. Comparison of these data with some recently proposed hard-sphere equations of state confirms the usefulness of the CS equation of state for the isotropic liquid. The higher liquid density data reported here may have a useful role in future improvements to equations of state.

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Note Added in Proof: Recently, some hard sphere compressibility factors were reported elsewhere (J. Kolafa, S. Labik and A. Malijevsky, *Phys. Chem. Chem. Phys.*, 6, 2335 (2004) for reduced densities between 0.2, and 1.03. Our compressibility factors are in good agreement with these data.

Notation

AAD = average absolute deviation
 n = number of data points
 N = number of hard spheres
 u = intermolecular potential
 V = volume
 Z = compressibility factor

Greek Letters

η = packing fraction
 ρ = reduced density
 σ = hard sphere diameter

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