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Equations of state for hard hypersphere fluids in high dimensional spaces

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Abstract
Plots for the comparison against the molecular dynamics (MD) computer simulations data of Luban and Michel and plots for the relative percent deviations from the molecular dynamics data of Luban Michel show that the empirical forms of the equations of state have a good agreement over full range of densities both for 4-D and 5-D. The equations of state for 4-D and 5-D hard hypersphere fluids with added additional parameters agree more closely with the available simulation data. It may also be reported here that the difference in compressibility factors below $\rho < 0.6$ is imperceptible for both 4-D and 5-D hard hyperspheres.

Keywords: Equations, state, hard hypersphere, dimensional

Introduction
The study of HS system with more than three dimensions (hard hypersphere) has the interest of being a general test for theoretical and computational technique. The addition of extra spatial dimensions to hard-sphere system is a relatively simple extension in the study of hard sphere fluid. One aspect of its study makes one to know the hard-hypersphere fluid properties such as virial coefficient [1, 7], equation of state [8, 13], fluid structure [14, 16] and the fluid-solid phase transition [14, 19]. These fluid properties may throw light into the study of higher dimensions. The other aspect of its study is that they provide a well-defined and very demanding approximations used in the construction of higher dimension theories.
In order to construct a new equation of state one should have an accurate knowledge of virial coefficients. Many different approaches have been employed for knowing virial coefficients and constructing equations of state. Out of these methods some has a large number of virial co-efficients to achieve high accuracy [9, 20] while other methods attain accuracy by using fewer virial co-efficients with a deepest physical understanding. The virial expansion can be written as the sum of first three known virial co-efficient plus a single unknown function. This unknown function must have all the information of the remaining virial coefficients of the expansion. A linear form representation for the unknown function is usually taken as a good approximation. The coefficients of the unknown function are determined by performing a least-square fit to available simulation data. If this is done for both 4-D and 5-D, the result obtained is an excellent agreement with the available simulation data over the full range of fluid densities. In 4-D and 5-D the first four virial coefficients have been used to construct both rational approximates and Padé approximates [3, 10]. The rational approximates have a simple denominator inspired by scaled particle theory [19, 21] and the numerator is a polynomial that is fixed by using the virial coefficients. Padé approximates have a polynomial structure for both the numerator and denominator that is fixed by using the virial co-efficients. The equations studied includes the virial equation [1, 3, 5, 9], Padé approximates, the rational approximates, the rational approximates of Baus and colot [2, 15], the Song, Mason and Stratt equation [19], Amros, Solana and Villar semi-empirical equations [17], regular close packed density approximant [7] and the Luban and Michels approximates [16]. In 5-D, both the Percus-Yevick [16, 18] virial and compressibility route were also examined. All of these equations were compared to the simulation data of Luban and Michel. It has been found that the Luban–Michel equation of state is still one of the most accurate over all density range. Our focus in this paper will be the study of hard sphere packing in 4-D and 5-D.

Equations of state

The infinite virial series expansion of the compressibility factor in powers of the density is:

$$Z = 1 + \sum_{n=2}^{\infty} B_n \rho^{n-1} \tag{1}$$

where B_n is the virial coefficients of the series expansion. An accurate equation of state for any fluid can be exactly determined if we have exactly known values of all the virial coefficients. Unfortunately, the expansion has only the few best known virial coefficients. In order to make virial expansion to converge rapidly, some approximants are proposed. These approximants are based on the fact that the series expansion of the proposed approximants must reproduce a given number of the known virial coefficients. The most widely used approximants is the Padé approximants. Padé approximants are quotients of polynomials in the density or in the so called packing fraction *y*. The packing fraction is the fraction of space $\left(\frac{\sigma}{2}\right)^d$ covered by the hard-spheres i.e., $y = \rho v_1\left(\frac{\sigma}{2}\right)$, σ is its diameter and v_1 is the volume of a *d*- dimensional sphere of radius $\frac{\sigma}{2}$, we have, $v_1\left(\frac{\sigma}{2}\right) = \frac{\pi^{d/2}}{\Gamma(1+d/2)}\left(\frac{\sigma}{2}\right)^d$ and, therefore, *y* may be expressed as: $y = \rho\frac{\pi^{d/2}}{\Gamma(1+d/2)}\left(\frac{\sigma}{2}\right)^d = \frac{\pi^{d/2}}{\Gamma(1+d/2)}\left(\frac{1}{2}\right)^d \rho^*$, $\Gamma(x)$ is the gamma function and $\rho^* = \rho\sigma^d$ is the reduced density. For solving the equations of state for *Z* we have limited ourselves to four virial coefficients for 4-D and five virial coefficients for 5-D hard-hypersphere respectively. We have plotted the values of *Z* obtained either from 4-D EOS or from 5-D EOS for all range of densities.

We have considered 21 different equations of state for hard hyperspheres to compare with the simulation data of Michel and Luben. These equations of state were reported over a period of 25 years and they are found to produce a good agreement with simulation data. The table 1 shows the compressibility factors against the reduced density as reported by Michel and Luben.

Table1.Equation of state for hard sphere fluid

Table 1

ρ^*	Z **for4-D**	ρ^*	Z **for 5-D**
0.20	1.637	0.20	1.653
0.40	2.670	0.40	2.624
0.60	4.335	0.60	4.008
0.80	7.038	0.80	5.997
0.90	8.955	1.00	8.748
0.95	10.147	1.10	10.523
1.00	11.458	1.15	11.589
		1.18	12.217

Equations of state for 4-D Hard Hypersphere used in our work

1. We can write an equation of state from virial expansion as[17]:

$$Z = \frac{1+5y+11y^2+4y^3}{(1-y)^3} \tag{2}$$

2. Adding higher order term to the numerator of eqn.(2) and obtaining the coefficient of this term by fitting the simulation data[17]

$$Z = \frac{1+5y+11y^2+4y^3+9.8361y^4}{(1-y)^3} \tag{3}$$

3. One can write the following equation of state (a case of Padé approximants) form the knowledge of Percus-Yevick equation and Scaled particle theory as[17]:

$$Z = \frac{1+4y+6.4032y^2-8.1049y^3}{(1-y)^4} \tag{4}$$

4. Again adding higher order term to the numerator of eqn.(4) and obtaining the coefficient of this term by fitting the simulation data [17]:

$$Z = \frac{1+4y+6.4032y^2-8.1049y^3+1.9739y^4}{(1-y)^4} \qquad (5)$$

5. The asymptotic behavior of the virial expansion for the hard sphere fluid has a regular close packing density. This is because the matter in its crystalline state is perfectly ordered than in the liquid state which is the disordered fluid state called random close packing density. If there is a pole at regular close packing density then the equation of state for 4-D hard hypersphere is given by[17]

$$Z = 1+4\frac{y/y_0}{(1-y/y_0)}+36.300\frac{y^3}{(1-y)^3}+1.5154y+21.891y^2+24.121y^3 \qquad (6)$$

6. Equation of state when only second virial coefficient is exact and taking account of the density functional theory[7]:

$$Z = \frac{3+33y+58y^2+23y^3+8y^4}{3(1-y)^5} \qquad (7)$$

7. An extended rational approximate (RA) of Baus and Colot with a new value of virial coefficientint in 4-D is given by[4]

$$Z = \frac{1+4y+6.4058y^2-7.8779y^3-1.6057y^4+13.1048y^5-36.1409y^6+374.8526y^7}{(1-y)^4} \qquad (8)$$

Equations of state for 5-D Hard Hypersphere used in our work

8. Similar to section I(1), we have[17]

$$Z = \frac{1+12y+49y^2-26y^3+319y^4}{(1-y)^4} \qquad (9)$$

9. Using lest square fit, we have[17]

$$Z = \frac{1+12y+48y^2-26y^3+319y^4-923.10y^5}{(1-y)^4} \qquad (10)$$

10. Similar to section I(3), we have[17]

$$Z = \frac{1+11y+36y^2-74.44y^3+347.13y^4}{(1-y)^5} \qquad (11)$$

11. Using least square fit, we have [17]

$$Z = \frac{1+11y+36y^2-74.44y^3+347.13y^4-1068.56y^5}{(1-y)^5} \qquad (12)$$

12. Similar to section I (5), we have [17]

$$Z = 1+5\frac{y/y_0}{(1-y/y_0)}+200\frac{y^4}{(1-y)^4}+5.2532y+82.886y^2+255.915y^3+663.225y^4 \qquad (13)$$

13. An extended rational approximate (RA) of Baus and Colot with a new value of virial coefficient in 5-D is given by [4]

$$Z = \frac{1+11y+36y^2-68.8166y^3+192.5313y^4-1098.6489y^5+8279.8312y^6}{(1-y)^5} \qquad (14)$$

14. A slightly more sophisticated equation of state is the rescaled Padé approximant proposed by Maeso *et al.* [23], which reads

$$Z = \frac{1+12.912y+57.027y^2}{(1-y)^5(1+1.912y)} \qquad (15)$$

15. A general equation of state for 5-D is given by Baus-Colot [15] proposal as:

$$Z = \frac{1+11y+36y^2}{(1-y)^5} \quad (16)$$

16. An equation of state for 5-D given by Song, Mason-Stratt [19] as:

$$Z = 1+\frac{16y(1+1.625y)}{(1-y)^5} \quad (17)$$

17. Another semiempirical equation of state is that of Maseo *et al.* [23]

$$Z = -4+5.253y+82.902y^2+261.537y^3+\frac{1.861}{(0.465-y)}+276.88y^4\left(\frac{1}{(1-y)^4}-1\right) \quad (18)$$

18. Equation of state when only third virial coefficient is exact and taking account of the density functional theory [7]:

$$Z = \frac{2+22y+72y^2+32y^3-3y^4}{2(1-y)^5} \quad (19)$$

19. One of the most accurate proposals given by Luban and Michels[16], which is presented as:

$$Z = 1+\frac{16y\left\{1+\left[6.625-(1.07416+0.35096y)2.936\right]y\right\}}{1-\left[2.936(1.07416+0.35096y)y\right]+19.449\left[(1.07416+0.35096y)-1\right]y^2} \quad (20)$$

20. A new equation of state proposed by Santos is the linear combination of the PY compressibility (Z_{PY-c}) and PY virial (Z_{PY-v}) equations[21]:

$$Z_{CS} = Z_{PY-c}+Z_{PY-v} \quad (21)$$

We have plotted the figures (1-16) representing the compressibility factors *Z* in *y* –direction and the reduced density ρ^* in *x*-direction. From figures (1, 2 and 4), we observe that at high densities $(\rho > 0.6)$ the difference between the compressibility factors are perceptible. Therefore, the equations of state are less accurate at high densities than at low densities. The dashed line in figure.3 has an exact coincidence with the simulation data because of the additional added terms in the numerator by using least square fit. A single line figure.3 illustrates the results for the eqn.(4) and eqn.(5) and shows differences in the compressibility factors predicted by the two equations are imperceptible for the above range of reduced densities.

Comparison of simulation data with the data of equations of state

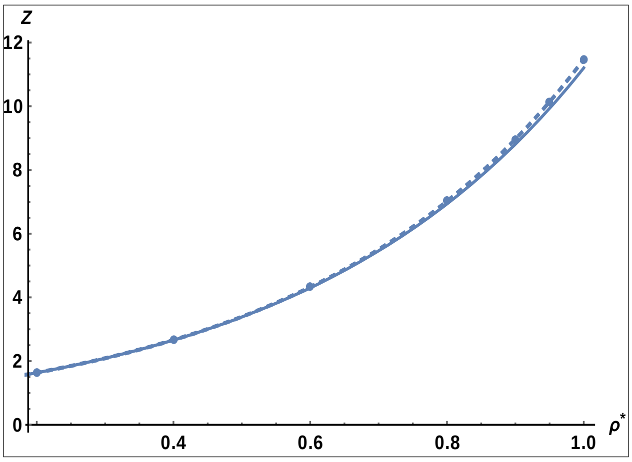

Fig 1: [Eqn (2) -,Eqn. (3) - -and simulation data.]

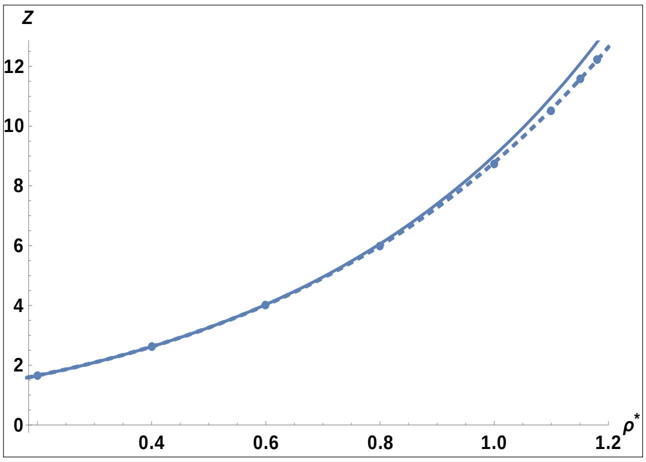

Fig 2: [Eqn (9) -, Eqn. (10) - - and simulation data.]

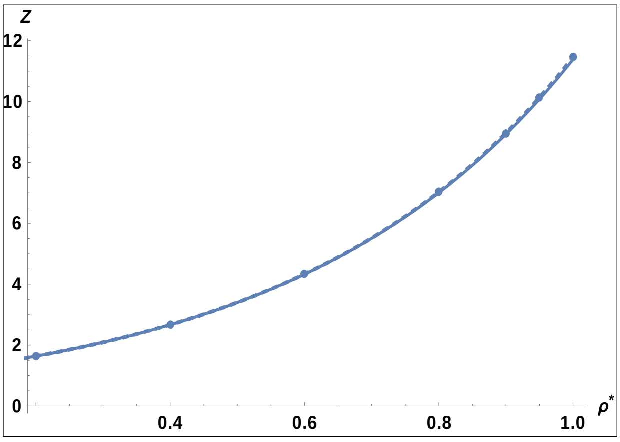

Fig 3: [Eqn (4) -, Eqn. (5) - -and simulation data.]

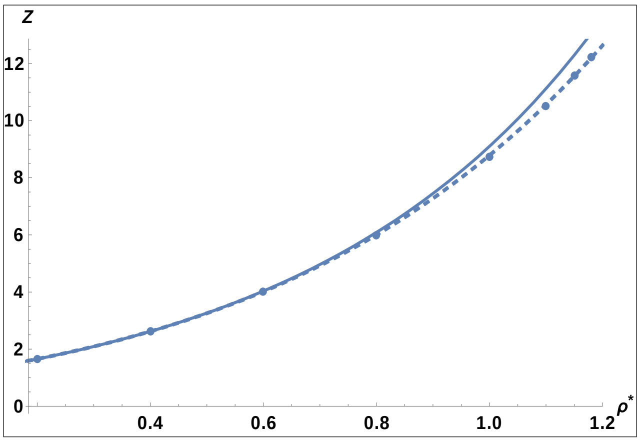

Fig 4: [Eqn (11) -, Eqn. (12) - - and simulation data.]

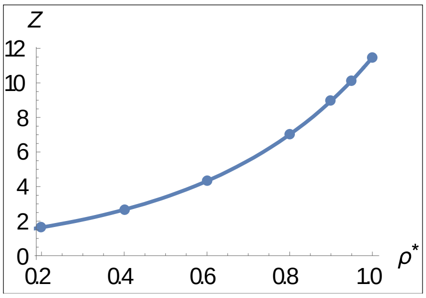

Fig 5: [Eqn (6) - and simulation data.]

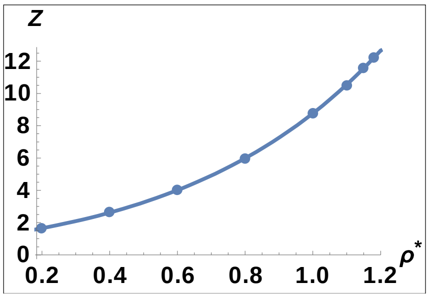

Fig 5: [Eqn (13) - and simulation data.]

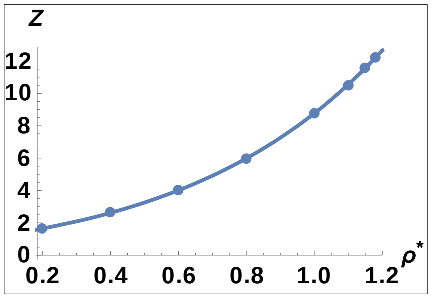

Fig 6: [Eqn (15) - and simulation data.]

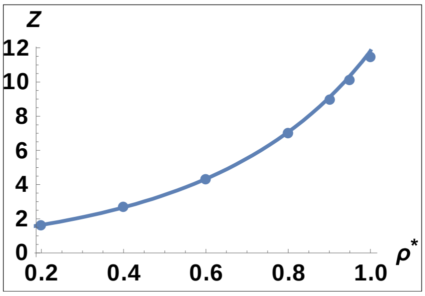

Fig 8: [Eqn (8) - and simulation data.]

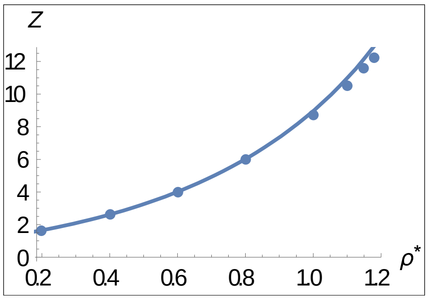

Fig 9: [Eqn (16) - and simulation data.]

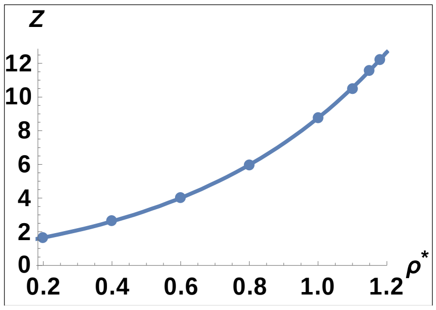

Fig 10: [Eqn (18) - and simulation data.]

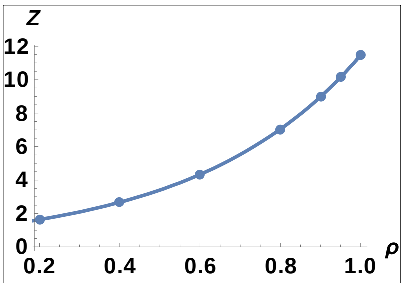

Fig 11: [Eqn (14) - and simulation data.]

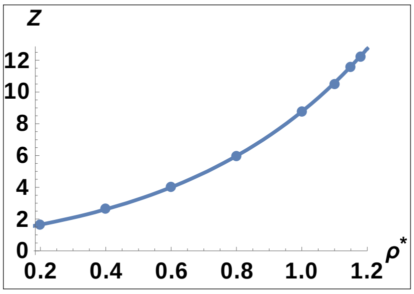

Fig 12: [Eqn (20) - and simulation data.]

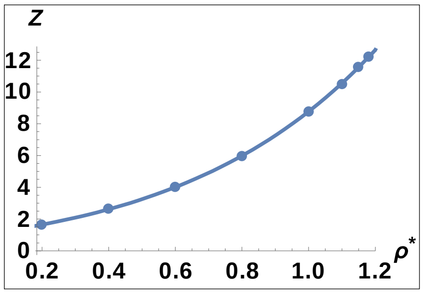

Fig 13: [Eqn (21) - and simulation data.]

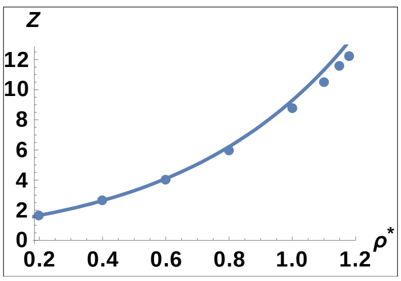

Fig 14: [Eqn (17) - and simulation data.]

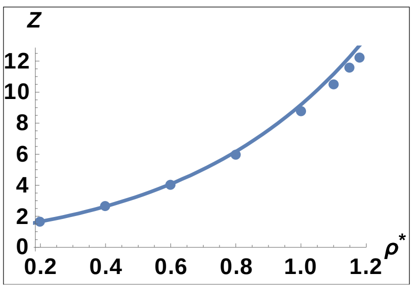

Fig 15: [Eqn (7) - and simulation data.]

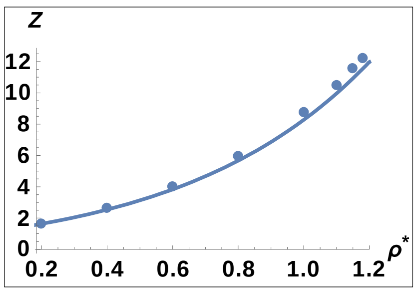

Fig 16: [Eqn (19) - and simulation data.]

From figures (5-13) there is an excellent agreement of the compressibility factors with the simulation data of Michel and Lubin over the entire density range. Figures (14-16) there is remarkable differences form the simulation data above $(\rho > 0.6)$.

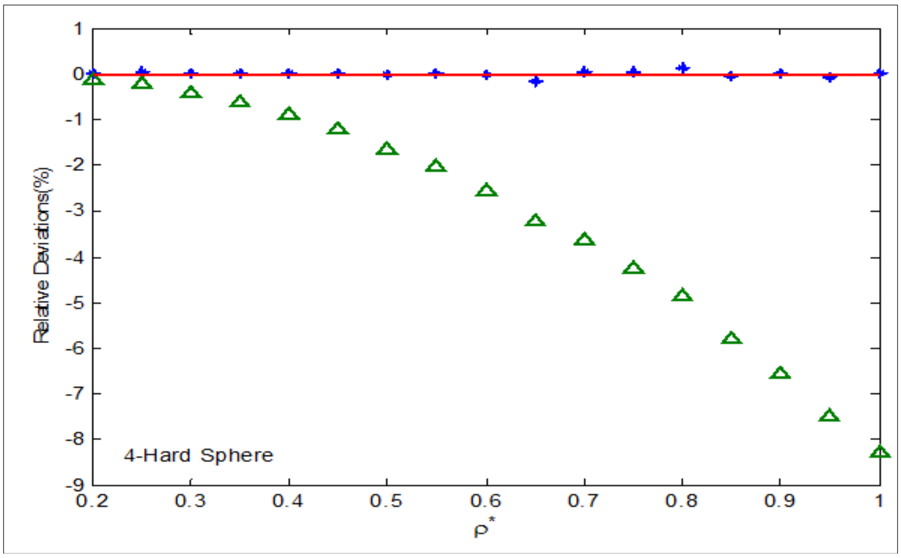

Fig 17: represents the relative percent deviations (%) of compressibility factors over the entire density range. The deviations are calculated from computed data of equations of state and the available simulation data of Michel and Luben. [eqn.(8) Δ, eqn.(20) *]

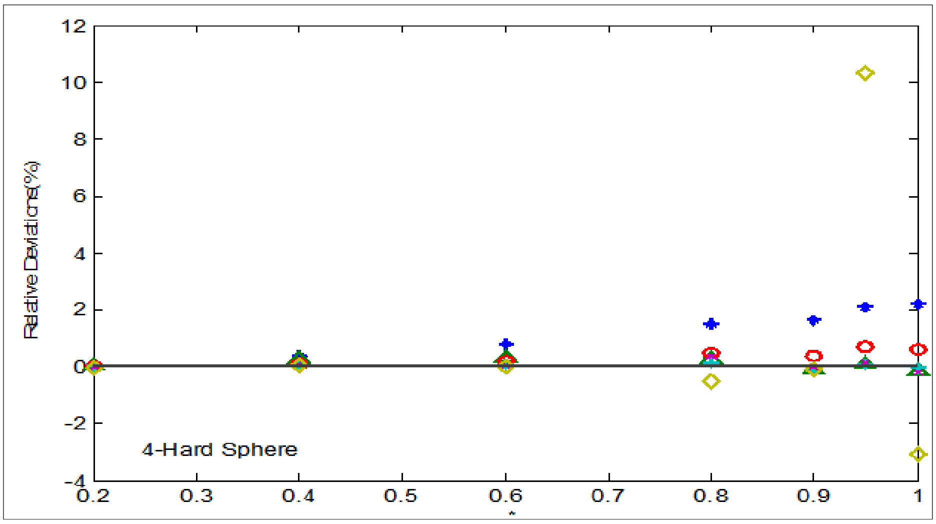

Fig 18: represents the relative percent deviations (%) of compressibility factors over the entire density range. The deviations are calculated from computed data of equations of state and the available simulation data of Michel and Luben. [eqn.(2) *, eqn.(3) Δ, eqn.(4) o,eqn.(5) +,eqn.(6) x]

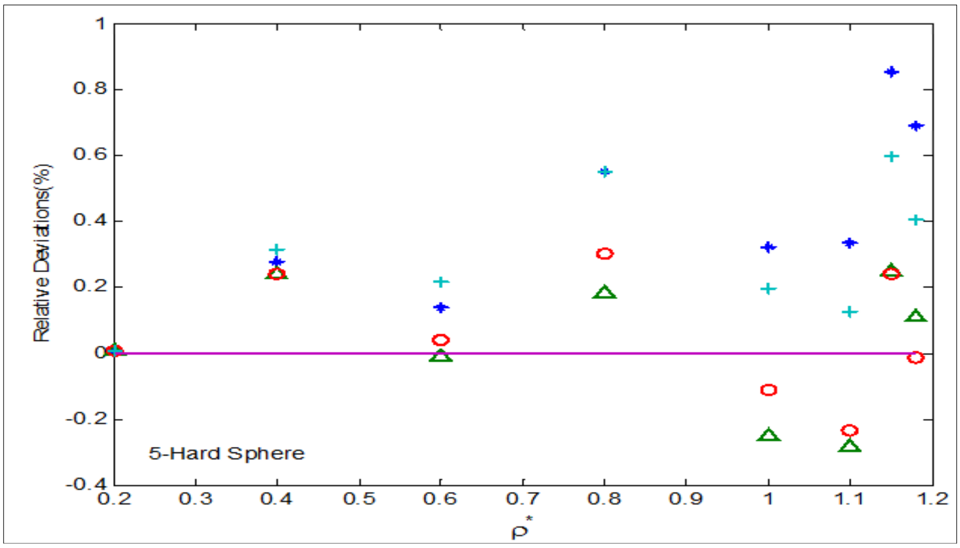

Fig 19: represents the relative percent deviations (%) of compressibility factors over the entire density range. The deviations are calculated from computed data of equations of state and the available simulation data of Michel and Luben. [eqn.(15) *, eqn.(20) Δ, eqn.(18) o, eqn.(8) +]

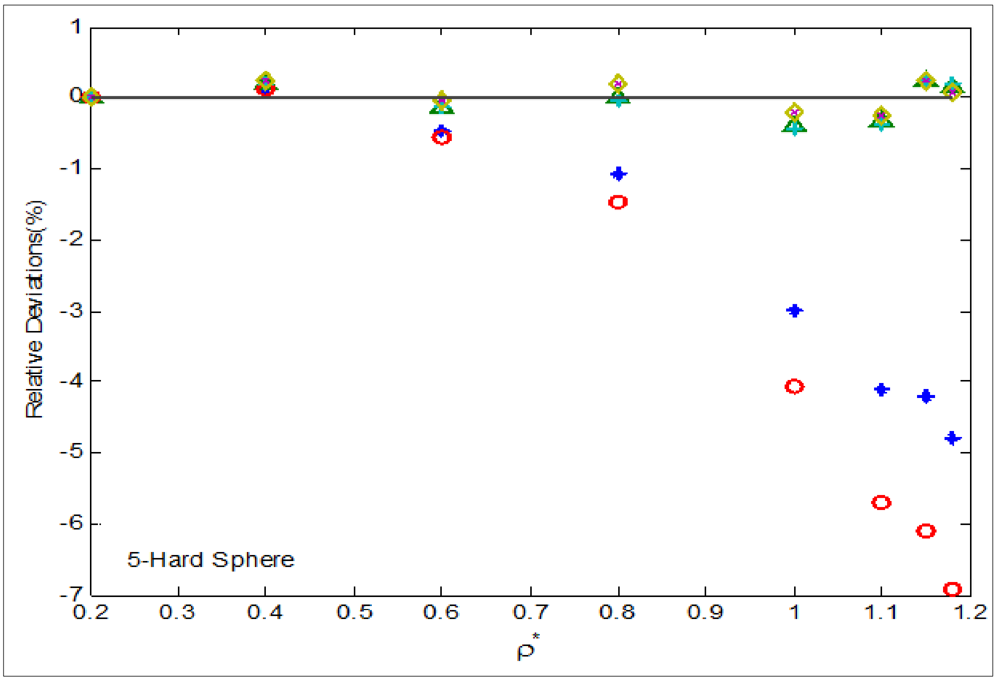

Fig 20: represents the relative percent deviations (%) of compressibility factors over the entire density range. The deviations are calculated from computed data of equations of state and the available simulation data of Michel and Luben. [eqn.(9) *, eqn.(10) Δ, eqn.(11) o, eqn,(12) + and eqn.(13) x]

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