Simple Volume-Explicit Equation of State for Mixtures of Non-additive Hard-Spheres

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ABSTRACT

A simple volume-explicit equation of state (EOS) for hard sphere mixtures has been developed on the basis of the pressure form of the virial expansion. The resulting equation yields the dependence of the compressibility factor on the packing fraction and mole fraction for different size ratios within the error estimates of simulation data in most cases. The new equation also gives the exact second and third pressure virial coefficients. An advantage of such equations of state is the fact that they yield easily the Gibbs energies and consequently hard-sphere diagrams. The equations also predict with good accuracy the compressibility factor of non-additive hard sphere mixture with a small negative or positive value of non-additivity parameter (Δ).

1. INTRODUCTION

Equations of state (EOS) are valuable tools in the calculations of thermodynamic properties and phase behavior. EOS that are based on sound statistical thermodynamics have more predictive capabilities compared to empirical equations. An important result of the theoretical study of fluids is that repulsive molecular forces are dominant at high densities. This result motivated researchers to build EOS around accurate repulsive equations. Examples of such EOS are the works of Chien et al. [1], Dohrn and Prausnitz [2] and Tao and Mason [3].

The most commonly used repulsive equation is that of hard spheres due to Carnahan and Starling [4]. This equation is explicit in pressure as most EOS are. In chemical engineering calculations, the pressure and temperature are the usually specified variables. This makes pressure-explicit equations inconvenient to use due to the added numerical procedure to find the correct volume root. It is therefore desirable to have a volume-explicit EOS that expresses the compressibility factor in terms of the independent variables pressure, *P* and temperature *T*.

It is the objective of this work to develop simple volume-explicit equations for mixtures of hard spheres that overcome these limitations. An advantage of such equations of state is the fact they yield easily Gibbs energies of the hard sphere mixtures and consequently the hard sphere phase diagram. The study of the phase behavior of the hard sphere systems is of both theoretical and practical interest and several papers have made clear this fact [5,6].

The developed equations of state will be tested against molecular dynamics simulation data of both additive [7] non-additive [8] mixtures of hard spheres over a wide range of size ratios, packing fractions and compositions.

2.   THEORY

2.1   Equations of state

In an earlier work [9], two forms of volume explicit equations of state for hard spheres were proposed. They are reproduced below:

$$Z = 1 + 4\wp + \frac{3}{4}\wp \ln\left(\frac{3+\wp}{3+25\wp}\right)$$ (1)

$$Z = 1 + 4\wp + a_1\wp\ln\left(\frac{(1+a_2\wp)(1+a_3\wp)}{(1+a_4\wp)(1+a_5\wp)}\right)$$ (2)

The constants in eq. 2 have been obtained by equating the first seven virial coefficients from the equation to the exact numerical values as reported by Janse van Rensburg [10]. The resulting values are:

$$a_1 = 0.403104, \quad a_2 = 0.067745, \quad a_3 = 1.28605,$$
$$a_4 = 7.55902, \quad a_5 = 8.67926$$ (3)

The reduced pressure, $\wp$ is defined as:

$$\wp = \frac{P\upsilon}{RT} = \frac{P}{RT}\frac{\pi\sigma^3}{6}N_A$$ (4)

where υ is the molar volume of spherical molecule with diameter σ and N_A is the Avogadro's number.

Both equations 1 and 2 give the exact second and third virial coefficients. Higher coefficients up to the eighth are represented with a maximum error of 1.4% by eq. 1. While eq. 2 predicts the eighth virial coefficient with only 0.07% error, compared to 15% for the common Carnahan-Starling equation [4].

2.2   Mixtures of Hard Spheres

It is our aim to generalize equations 1 and 2 to be used for mixtures of hard spheres. We will again make use of the virial coefficients; however the mixture pressure coefficients will be required. The mixture virial coefficients for hard molecules depend on both the composition and the size of the components. To start with, we generalize the equations to the form:

$$Z = 1 + b'_{m,2}\wp_m + \frac{3}{4}f\wp_m \ln\left(\frac{3+h\wp_m}{3+25h\wp_m}\right)$$ (5)

$$Z = 1 + b_{m,2}^{'} \wp_m + a_1 f \wp_m \ln\left(\frac{(1 + a_2 h \wp_m)(1 + a_3 h \wp_m)}{(1 + a_4 h \wp_m)(1 + a_5 h \wp_m)}\right) \quad (6)$$

where the mixture reduced pressure, $\wp_m$ is defined as:

$$\wp_m = \frac{P}{RT}\frac{\pi}{6}N_A \quad (7)$$

For hard spheres, the second and third density coefficients are known exactly [11]. For additive hard spheres, they are written as,

$$b_{m,2} = b_{m,2}^{'} = 3S_1 S_2 + S_3 \quad (8)$$

and

$$b_{m,3} = 3S_2^3 + 6S_1 S_2 S_3 + S_3^2 \quad (9)$$

where

$$S_j = \sum_k x_k \sigma_{kk}^j \quad (10)$$

where $b_{m,i}$ and $b_{m,i}^{'}$ are the mixture density and pressure virial coefficients respectively. The pressure mixture coefficients are related to the density coefficients. However, it should be noted that the second mixture density virial coefficient and that of the second pressure virial coefficient are identical { eq. 8 } for additive hard spheres.

The second pressure virial coefficient is also expressed as,

$$b_{m,2}^{'} = 4\sum_j \sum_k x_j x_k \sigma_{jk}^3 \quad (11)$$

Note that eq. 11 and eq. 8 are identical. The third pressure virial coefficient can be obtained from the density counterpart eq. 9 using the appropriate relationship as,

$$b_{m,3}^{'} = 3S_2^2 (S_2 - 3S_1^2) \quad (12)$$

f and *h* in eq.'s 5 and 6 are composition and size dependent quantities. They are to be obtained by expanding the respective equation and comparing the results with the pressure virial expansion. The third virial coefficient for eq.'s 5 and 6 leads to eq.'s 13 and 14 respectively.

$$f = \frac{-b_{m,3}^{'}}{6h} \quad (13)$$

$$f = \frac{-b_{m,3}^{'}}{a_1(-a_2 - a_3 + a_4 + a_5)h} \quad (14)$$

The next task is to evaluate h. We note that when equations 5 and 6 are expanded in powers of pressure, the quantity h appears in the same increasing powers as P. As noted in an earlier publication [9], the pressure virial coefficient are polynomials of degree $2(i-1)$ in mole fractions. To satisfy this requirement, the quantity h has to be a second order polynomial in composition. Thus, this leads to

$$h = \sum_i \sum_j x_i x_j h_{ij} \qquad (15)$$

where

$$h_{ii} = \sigma_{ii}^3 \qquad (16)$$

and

$$h_{ij} = h_0 \sigma_{ii}^3 + h_1 \sigma_{ij}^3 + h_0 \sigma_{jj}^3 \qquad (17)$$

For a binary mixture, eq.'s 15, 16 and 17 become

$$h = x_1^2 \, \sigma_{11}^3 + 2 x_1 x_2 h_{12} + x_2^2 \, \sigma_{22}^3 \qquad (18)$$

and

$$h_{12} = h_0 \sigma_{11}^3 + h_1 \sigma_{12}^3 + h_0 \sigma_{22}^3 \qquad (19)$$

and when

$$\sigma_{ii} = \sigma_{ij} = \sigma_{jj} \qquad (20)$$

then

$$h_1 = 1 - 2 h_0 \qquad (21)$$

The value of h_0 is selected such that it gives a good representation of the compressibility factor at high pressure. It was found that a value of **$h_0 = 0.327$** reproduces the high-pressure compressibility data accurately for eq. 5. While, a value of **$h_0 = 0.351$** gives the best representation of the compressibility data for eq. 6.

The quantity $\wp_m$ is evaluated from the packing fraction of the mixture, y given as

$$y = \frac{\pi}{6} N_A \sum_i x_i \sigma_{ii}^3 \rho \qquad (22)$$

and

$$Z = \frac{P}{\rho RT} \qquad (23)$$

Thus,

$$\wp_m = \frac{\pi P}{6RT} N_A = \frac{Zy}{\sum_i x_i \sigma_{ii}^3} \qquad (24)$$

Hence, from eq. 5

$$Z = \wp_m \frac{\sum_i x_i \sigma_{ii}^3}{y} = 1 + b'_{m,2}\, \wp_m + \frac{3}{4} f\, \wp_m\, \ln\!\left(\frac{3 + h\wp_m}{3 + 25\,h\wp_m}\right) \tag{25}$$

Similarly, for eq.6

$$Z = \wp_m \frac{\sum_i x_i \sigma_{ii}^3}{y} = 1 + b'_{m,2}\, \wp_m + a_1 f\, \wp_m\, \ln\!\left(\frac{(1 + a_2 h\wp_m)(1 + a_3 h\wp_m)}{(1 + a_4 h\wp_m)(1 + a_5 h\wp_m)}\right) \tag{26}$$

$\wp_m$ can be found by finding the root ($\wp_m$) of the eq.'s 25 and/or 26.

3.   RESULTS AND DISCUSSION

In Figures 1-3, comparisons were made between the mixture compressibility factors for additive hard sphere mixtures. Simulation data of Barosova et al. [7] were compared with predictions from our proposed equations 25 and 26. The figures indicate fair agreement between the predicted and the simulation results. The accuracy generally declines as the packing fraction increases, most especially for the size ratio (σ_{22}/σ_{11}) of 0.3. Furthermore, eq. 26 appears to predict the simulation better than eq. 25.

Figure 1 shows the variation of the compressibility factor, Z, with composition for a size ratio, $\sigma_{22}/\sigma_{11} = 0.9$ at different packing fractions, y. A good agreement is achieved generally between the predicted values and simulation data most especially the predictions of eq. 26. The situation is also similar for $\sigma_{22}/\sigma_{11} = 0.6$ depicted in figure 2 where a good agreement is achieved between the predicted values and simulation data at low packing fractions, but the predictions begin to worsen at high packing fractions most especially the predictions of eq. 25. In figure 3, where comparison for the size ratio of $\sigma_{22}/\sigma_{11} = 0.3$ is plotted, deviation begins to appear similar to figure 2 at the highest packing fraction. From the comparison made in the figures, the good predictive ability of the proposed equations is obvious, most especially eq. 26 for additive hard sphere mixtures.
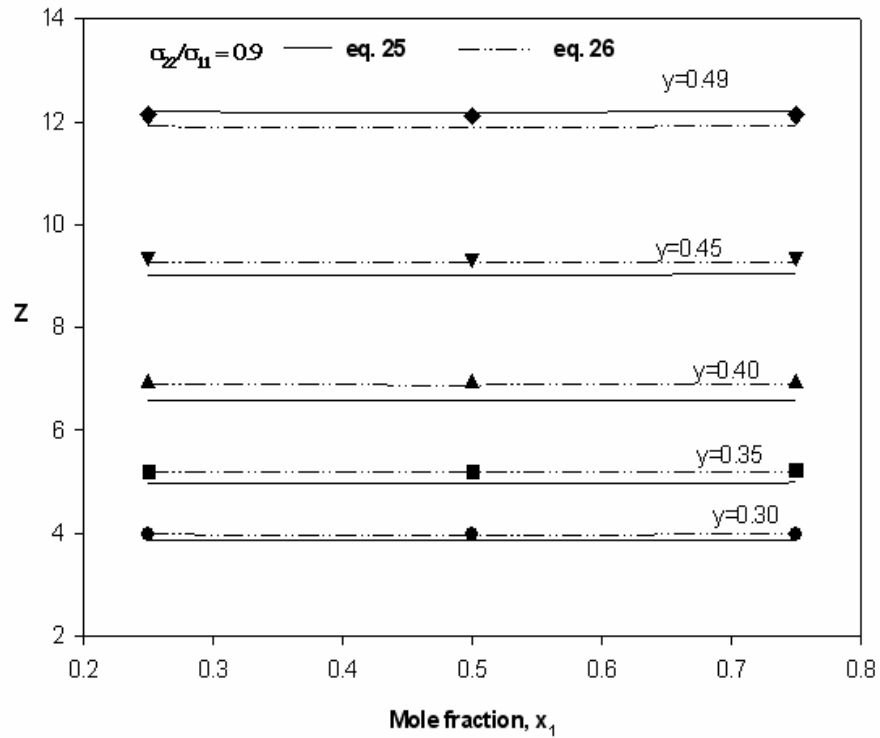
Figure 1: Comparison of mixture models (lines) with molecular dynamics simulations (points for hard sphere mixtures with ($\sigma_{22}/\sigma_{11} = 0.9$).
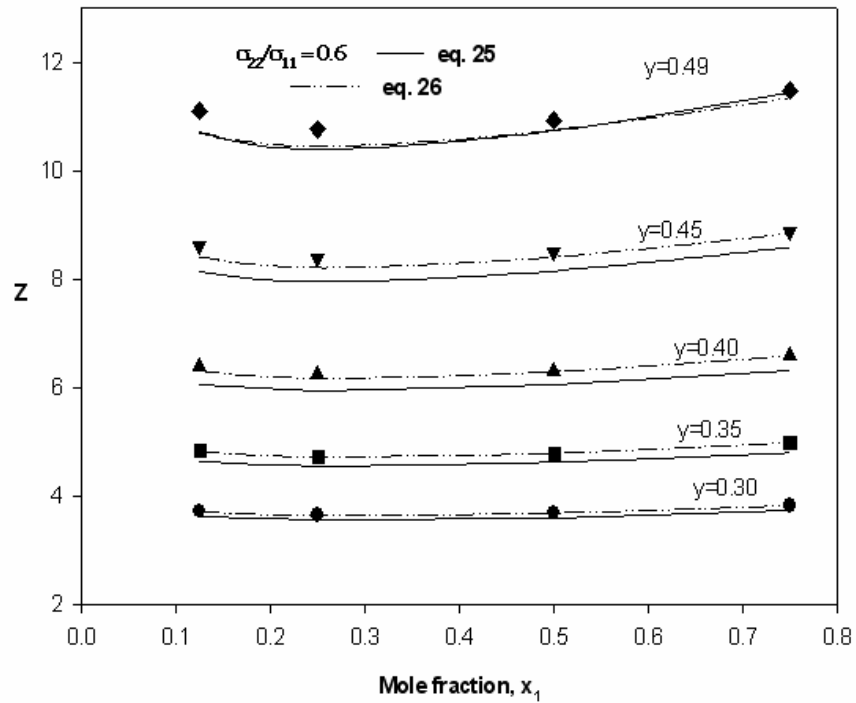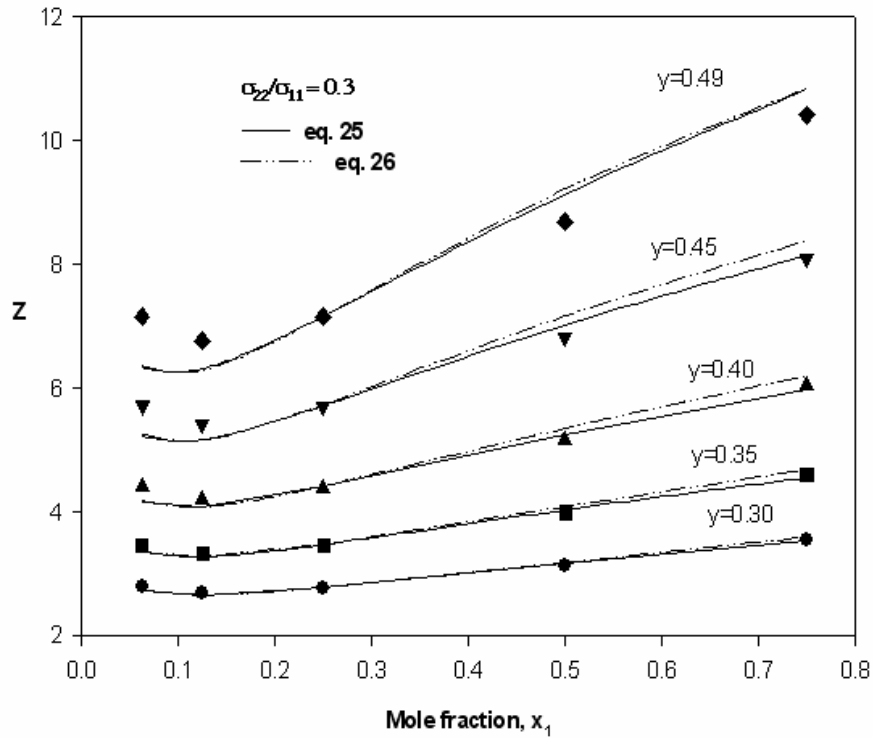

Figure 2: Comparison of mixture models (lines) with molecular dynamics simulations (points) for hard sphere mixtures with ($\sigma_{22}/\sigma_{11} = 0.6$).

Figure 3: Comparison of mixture models (lines) with molecular dynamics simulations (points) for hard sphere mixtures with (σ_{22}/σ_{11} = 0.3).

Figures 4-7 show comparisons made between the mixture compressibility factors for non-additive hard sphere mixtures. These mixtures are characterized by non-additive cross collision diameters σ_{ij},

$$\sigma_{ij} = (1+\Delta_{ij})\frac{\sigma_{ii}+\sigma_{jj}}{2} \qquad \Delta \geq -1$$

An earlier reported simulation data [8] were compared with predictions from the proposed equations 25 and 26.

Figure 4 shows the compressibility factor versus the packing fraction(density) for an equimolar binary mixture with a size ratio of 3 and a small negative value of the non-additivity parameter Δ = -0.05. At low and moderate densities, the two proposed models perform extremely well. This is expected as both the two equations give the exact second and third virial coefficients. At high densities however, slight errors begin to appear with eq. 25 giving the highest deviations.

Figure 5 is similar to figure 4, except that the comparison here is for a small positive value of non-additivity Δ = 0.05. The two proposed equations also perform very well. Slight deviations begin to appear at the highest densities.

Figure 6 shows the variation of the compressibility factor with size ratio from 1 to 4 at moderate non-additivity of Δ = 0.2 where x_1 = 0.25. The two proposed models show higher deviations for small size ratio than for large size ratios. Furthermore, this suggests that the two equations are not very good with high non-additivity parameter.
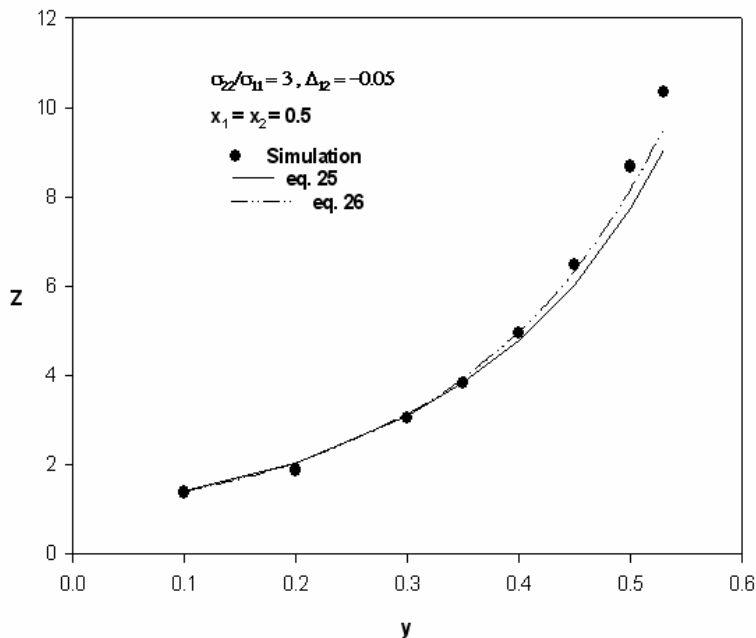

Figure 4: Comparison of mixture models (lines) with molecular dynamics simulations (points) for equimolar mixtures of hard spheres (σ_{22}/σ_{11} = 3 and Δ_{12} = -0.05).
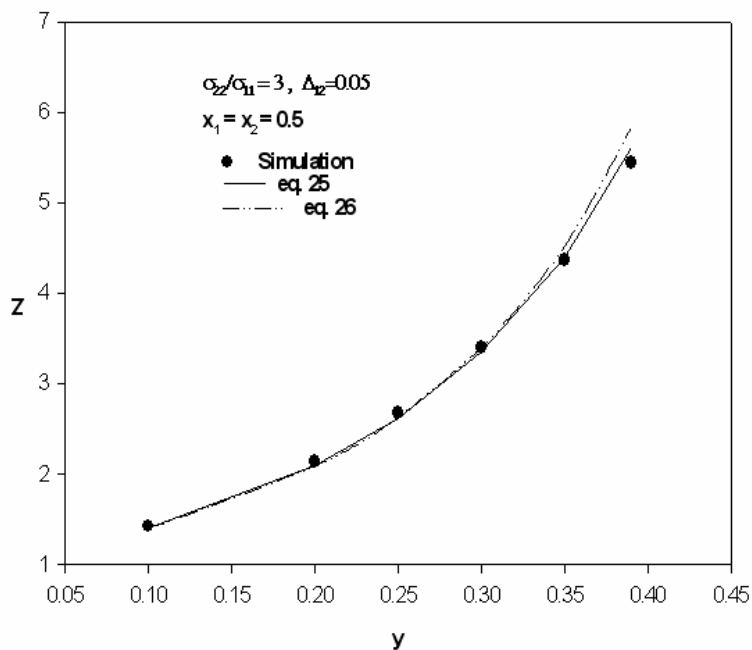

Figure 5: Comparison of mixture models (lines) with molecular dynamics simulations (points) for equimolar mixtures of hard spheres (σ_{22}/σ_{11} = 3 and Δ_{12} = 0.05).
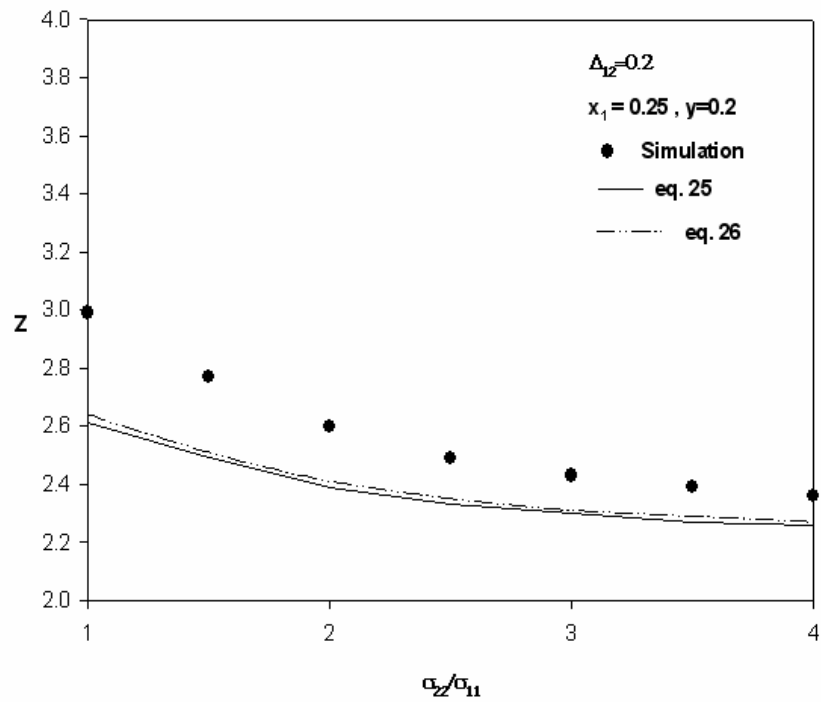
Figure 7: Comparison of mixture models (lines) with molecular dynamics simulations (points) for equimolar mixtures of hard spheres (y=0.2, x_1 = 0.25 and Δ_{12} = 0.2).

4. CONCLUSIONS

Volume-explicit equations of state for mixture of hard spheres have been developed based on a summation of the pressure virial expansion. The equation accurately predicts the dependence of compressibility factor on both composition and packing fraction over a broad range of size ratios for additive hard-spheres. Prediction accuracy however tends to worsen at high packing fractions. The two proposed models also performed very well in predicting the compressibility factor of binary hard sphere mixture with a small negative or positive value of non-additivity parameter Δ. However, the equations are not very satisfactory for mixtures with large non-additivity.

5. ACKNOWLEDGMENTS

6. List of symbols

$b'_{m,2}$	Second pressure mixture virial coefficient
$b_{m,2}$	Second density mixture virial coefficient
$b'_{m,3}$	Third pressure mixture virial coefficient
f	Composition-dependent quantity
h	Size-dependent quantity
N_A	Avogadro's number
P	Pressure
$\wp$	Dimensionless pressure
R	Idea gas constant
T	Absolute temperature
x_i	Mole fraction of component i
y	Packing fraction
Z	Compressibility factor
υ	Molar molecular volume
Δ	Non-additivity parameter
σ_{ij}	Collision diameter of molecular pair i,j

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