

The multicomponent self-consistent Ornstein–Zernike application for CO₂, N₂, O₂ shock Hugoniot simulation

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Abstract. A multicomponent equation of state with wide range of applicability is required to simulate shock waves in C_xN_yO_z mixtures. This problem demands fine molecular interaction model due to competition between repulsion and attraction forces during shock compression process. A self-consistent Ornstein–Zernike application (SCOZA) based on distribution function integral equation theory can be used for it. The hypernetted-chain/soft core mean spherical approximation (HMSA) for SCOZA has been successfully applied to dense fluid systems with ambidextrous interactions. However, it was not designed to simulate mixtures, such as shock products of C_xN_yO_z system. The convenient way to simulate multicomponent systems is the van der Waals one-fluid model (vdW1f). It has been shown, that vdW1f is not good enough for CO₂ shock products at pressures higher, than 50 GPa. The multicomponent HMSA closure application based on partial version of the virial theorem has been offered in this paper. It is verified by molecular Monte-Carlo simulation at pressures up to 160 GPa with accuracy about 1–2%.

1. Introduction

Distribution function integral equation theory (DFIET) is one of the classical and well-known approaches in study of a dense fluid behavior. Amount of studies, based on multicomponent version of DFIET increases drastically during last decade. This growing of interest resides that, on the one hand, dense fluid mixtures is under the focus of different branches of science. On the other, DFIET provides fine simulation results with good computation efficiency, especially when compared with the Monte-Carlo (MC) methods.

A condition of self-consistency is required to simulate processes with wide range of thermodynamic parameters. In this way, hypernetted-chain/soft core mean spherical approximation (HMSA) closure [1] with EXP-6 pair potentials was successfully applied for dense and overcritical fluids with ambidextrous molecular interactions. Unfortunately, this closure was designed for a single component. The van der Waals one-fluid model (vdW1f) model was proposed by Ree [2] to overcome this drawback.

It has been shown [3], that vdW1f model is not fine enough for mixtures of components, which pair potential parameters differ drastically, such as CO₂ shock products. This discrepancy becomes unacceptable at pressures higher, than 50 GPa [4]. The main aim of this paper is to



present the application of HMSA closure for multicomponent systems, based on partial version of virial theorem for mixtures of shock products.

2. Theory

The full multicomponent equation of state (EOS), offered in this paper, is based on the Ornstein–Zernike (OZ) integral equation:

$$g_{ij}(r) = h_{ij}(r) + 1, \quad (1)$$

$$h_{ij}(r) = c_{ij}(r) + \sum_{k=1}^m \rho_k \int c_{ik}(\vec{s}) h_{kj}(|\vec{r} - \vec{s}|) d\vec{s}, \quad (2)$$

where g_{ij} represents radial distribution function of component i relatively to component j , h_{ij} —total correlation function, c_{ij} —pair correlation function, m —amount of components, ρ_k —numerical density of component k . An additional closure relation for pair and total correlation functions is needed [1] to compute radial distribution functions of system.

An ordinary form of EOS as a relation of three thermodynamic parameters can be obtained via virial equation for previously received distribution function:

$$P = \frac{\rho}{\beta} - \frac{2}{3}\pi \sum_{i=1}^m \sum_{j=1}^m \rho_i \rho_j \int_0^{+\infty} g_{ij}(r) \frac{d\phi_{ij}(r)}{dr} r^3 dr. \quad (3)$$

where ρ —numerical density, $\beta = \frac{1}{k_B T}$ —inverse temperature, k_B —Boltzmann constant, T —temperature, P —pressure, ϕ_{ij} —pair potential of molecular interaction.

An information about temperature dependence of distribution functions of the system is not represented in (1)–(2), so, it should be involved in a closure relation. Unfortunately, there are no theoretically proved closure relations for a general case of ambidextrous interactions. It can be constructed by interpolation between particular solutions in accordance with self-consistency conditions, given by theory. The HMSA [1] closure relation (4) is based on two asymptotic solutions analytically obtained for exponential repulsion at low radii and polynomial attraction at high radii:

$$g_{ij}(r) = e^{-\beta\phi_{ij}^R(r)} \left(\frac{e^{-f_{ij}(r)[h_{ij}(r)-c_{ij}(r)-\beta\phi_{ij}^A(r)]} - 1}{f_{ij}(r)} \right), \quad (4)$$

where ϕ_{ij}^R —repulsive potential, ϕ_{ij}^A —attractive potential, f_{ij} —switching function. The switching functions interpolates solutions with unknown parameters α_{ij} :

$$f_{ij}(r) = 1 - e^{-\alpha_{ij}^{sw} r} \quad (5)$$

to be determined from self-consistency conditions for each $m^2 - m$ pair interactions of components.

The first m conditions of self-consistency can be obtained from the virial theorem. There are two ways to compute an isothermal compressibility: through the definition relation [5] and through density derivatives of the virial equation (3):

$$\left(\frac{\partial(\beta P)}{\partial \rho_i} \right)_T^{vir} = \left(\frac{\partial(\beta P)}{\partial \rho_i} \right)_T \equiv 1 - 2\pi \sum_{j=1}^m \rho_j \int_0^{+\infty} c_{ij}(r) r^2 dr. \quad (6)$$

Another one is a Maxwell equation:

$$\left(\frac{\partial E}{\partial V} \right)_T = T^2 \frac{\partial}{\partial T} \left(\frac{P}{T} \right)_V, \quad (7)$$

where E —internal energy, P —volume.

Due to lack of self-consistency conditions, parameters were determined in this paper by numerical minimization of discrepancy between the definition and the finite difference virial derivative relations for isothermal compressibility:

$$\min_{\alpha_{ii}^{sw}} \left[\left(\frac{\partial(\beta P)}{\partial \rho_i} \right)_T - \left(\frac{\partial(\beta P)}{\partial \rho_i} \right)_T^{vir} \right] \quad (8)$$

provided linear interpolation for unknown cross component parameters

$$\alpha_{ij}^{sw} = \frac{\alpha_{ii}^{sw} + \alpha_{jj}^{sw}}{2}. \quad (9)$$

3. Algorithm

To solve the equation system (1)–(4), a change of variables should be done:

$$t_{ij} = h_{ij}(r) - c_{ij}(r), \quad (10)$$

$$C_{ij} = r c_{ij}(r), \quad (11)$$

$$T_{ij} = r t_{ij}(r). \quad (12)$$

The HMSA (4) equation in this term takes a form:

$$C_{ij} = -r - T_{ij}(r) + r e^{-\beta \phi_{ij}^R(r)} \left(\frac{e^{-f_{ij}(r) \left[\frac{T_{ij}(r)}{r} - \beta \phi_{ij}^A(r) \right]} - 1}{f_{ij}(r)} + 1 \right). \quad (13)$$

It should be noted, that HMSA produce a system of m algebraic equations in a multicomponent case. OZ equation, however, takes a form of matrix equation:

$$T_{ij}(r)r = \sum_{k=1}^m \rho_k (T_{ik}(r) + C_{ik}(r)) * C_{kj}(r). \quad (14)$$

A calculation of the convolution integral in (14) can be avoided by Fourier transform:

$$\widehat{T}_{ij}(\omega)\omega = \sum_{k=1}^m \rho_k \widehat{T}_{ik}(\omega) \widehat{C}_{kj}(\omega) + \sum_{k=1}^m \rho_k \widehat{C}_{ik}(\omega) \widehat{C}_{kj}(\omega). \quad (15)$$

Functions \widehat{T}_{ij} could be retrieved from (15) as:

$$\forall(i, j < m) : \sum_{k=1}^m \widehat{T}_{ik}(\omega) (\delta_{jk}\omega - \rho_k \widehat{C}_{kj}(\omega)) = \sum_{k=1}^m \rho_k \widehat{C}_{ik}(\omega) \widehat{C}_{kj}(\omega). \quad (16)$$

A solution of algebraic equation system (13) and matrix equation (16) could be found by performing direct iterations in the case of dense fluids, far enough from a critical point:

$$HMSA : C_{ij}^{l-1} = \mathbf{f}(\widehat{T}_{ij}^{l-1}), \quad (17)$$

$$OZ : \widehat{T}_{ij}^l = \mathbf{f}(\widehat{C}_{kl}^{l-1}), \quad (18)$$

where upper index l denotes number of iteration.

Up to 10 000 iterations for (17)–(18) and 30 iterations for (8) were performed in this work to obtain accuracy about 0.1% for isothermal compressibility. Unfortunately, the convergence of this method is not satisfactory for near- and supercritical fluids with compressibility factor $\frac{\beta P}{\rho} > 16$. More sophisticated methods are required [6] for this case.

4. Simulation and results

All simulations in this paper were performed using EXP-6 pair potentials:

$$\phi_{ij}(r) = \begin{cases} +\infty & : r < r_{ij}^{max} \\ \frac{\epsilon_{ij}}{\alpha_{ij}-6} \left(6 \exp \left[\alpha_{ij} \left(1 - \frac{r}{r_{ij}^{min}} \right) \right] - \alpha_{ij} \left(\frac{r_{ij}^{min}}{r} \right)^6 \right) & : r \geq r_{ij}^{max} \end{cases} \quad (19)$$

$$\phi(r_{ij}^{max}) = \max_r \phi(r), \quad (20)$$

$$\phi_{ij}^R(r) = \begin{cases} \phi_{ij}(r) - \phi_{ij}(r_{ij}^{max}) & : r < r_{ij}^{min} \\ 0 & : r \geq r_{ij}^{min} \end{cases}, \quad (21)$$

$$\phi_{ij}^R(r) = \begin{cases} \phi_{ij}(r_{ij}^{min}) & : r < r_{ij}^{min} \\ \phi_{ij}(r) & : r \geq r_{ij}^{min} \end{cases}, \quad (22)$$

$$\phi(r_{ij}^{min}) = \min_r \phi(r), \quad (23)$$

where ϵ_{ij} —potential well depth, α_{ij} —stiffness of exponential repulsion, r_{ij}^{max} —radius of potential maximum, r_{ij}^{min} —radius of potential minimum (figure 1). Internal cutoff radius r_{ij}^{max} is not a free parameter. It should be determined from ϵ_{ij} , α_{ij} and r_{ij}^{min} . External cutoff radius was 20.48 times higher than r_{ij}^{min} in this paper.

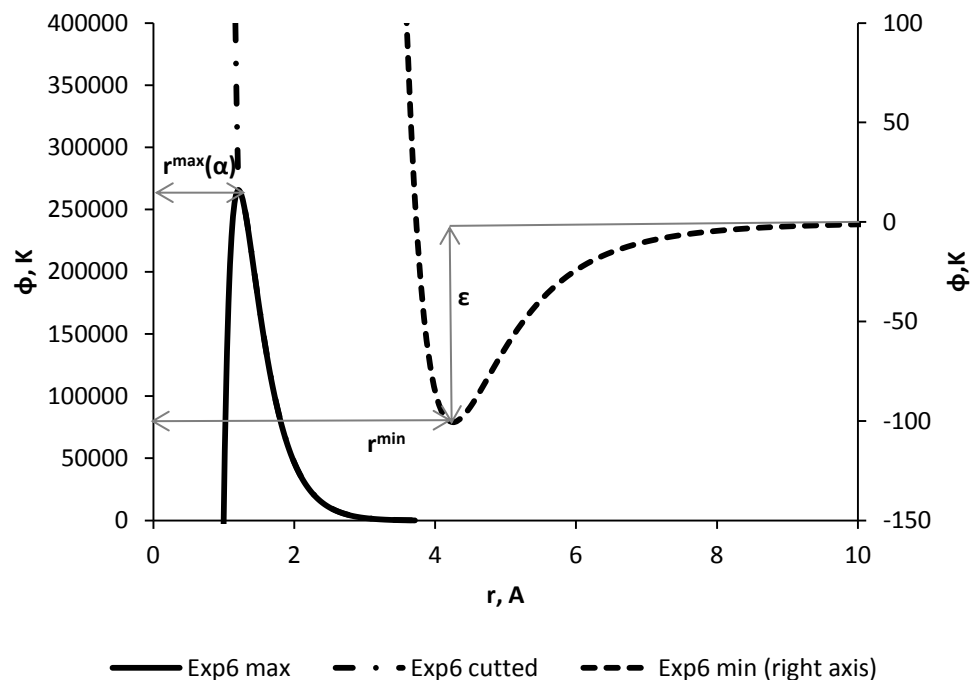


Figure 1. EXP-6 pair potential for N₂–N₂.

The potential parameters (table 1) was found in [7, 8] by solving the inverse problem of shock waves and isothermal compression simulations through method of characteristic function extremum (MCFE) with Kang-Lee-Ree-Ree thermodynamic perturbation theory (KLRR-T) and vdW1f model. Chemical composition in view of dissociation and recombination was found by the same way via IVTANTHERMO [9] thermodynamic potentials available at <http://www.chem.msu.su/rus/handbook/ivtan/>.

Table 1. Pair potential parameters.

	ϵ/k , K	r_{ij}^{min} , Å	α		ϵ/k , K	r_{ij}^{min} , Å	α
N ₂ – N ₂	100.6	4.25	12.3	CO ₂ – O ^{LB}	252.5	3.39	12.6
N ₂ – N	109.9	3.45	11.3	CO – CO	103.5	4.12	14.0
N – N	120.0	2.65	10.4	CO – O ₂	99.8	3.96	14.3
CO ₂ – CO ₂	230.2	4.22	13.8	CO – O	169.3	3.35	12.7
CO ₂ – CO	154.4	4.17	13.9	O ₂ – O ₂	96.2	3.79	14.7
CO ₂ – O ₂	148.8	4.00	14.2	O ₂ – O	163.2	3.18	13.0
CO ₂ – O ^{non-LB}	252.5	3.09	12.6	O – O	277.0	2.57	11.5

An independent realization of MCFE is required to validate the multicomponent HMSA closure application (MHMSA) for shock products simulation; so, it is not a goal of this paper. But perspectives of it can be assessed by joint verification of MHMSA, HMSA+vdW1f and KLRR-T+vdW1f via molecular Monte-Carlo (MC) simulation with the same composition. The MC simulation was performed by MCCC'S Towhee software [10–12] available at <http://towhee.sourceforge.net/>. Each run for system of 1000 molecules included 500 000 configurations.

The simulation of shock wave experiments [13–15]. was performed at first. During it, N₂ at $T = 77$ K, $\rho = 0.808$ g/cm³, $E = -2.842$ kcal/mole was shocked up to 90 GPa. No significant discrepancy was found for any theory (table 2) due to close values of pair interaction potential parameters for the dissociation products N₂ and N. Maximal deviation of pressure was about 1% for MHMSA and 4% for KLRR-T+vdW1f relatively to MC results. MCFE with KLRR-T+vdW1f provides accuracy about 7% relatively to experimental data.

Table 2. N₂ shock simulation.

T , K	V , cm ³ /mol	N ₂ , mol fr	N, mol fr	P_{MC} , GPa	P_{MHMSA} , GPa	P_{KLRR-T} , GPa
6250.62	13.9775	0.99	0.01	27.8175	28.0658	27.9144
7762.14	12.8458	0.95	0.05	35.3262	35.6305	35.2586
8691.28	11.9067	0.90	0.10	41.2595	41.6046	40.915
9372.67	11.1152	0.85	0.15	46.4226	46.7977	45.7627
9951.11	10.4045	0.80	0.20	51.3316	51.7311	50.3328
10477	9.74999	0.75	0.25	56.1382	56.5819	54.8113
10974.9	9.1387	0.70	0.30	60.9504	61.4330	59.2931
11458.7	8.5627	0.65	0.35	65.7961	66.3336	63.8355
11936.2	8.01554	0.60	0.40	70.7165	71.3315	68.4757
12418.3	7.49594	0.55	0.45	75.7019	76.3980	73.2429
12896.7	6.99902	0.50	0.50	80.7324	81.5564	78.1373
13379.6	6.52214	0.45	0.55	85.7994	86.8342	83.1793
13884.7	6.06323	0.40	0.60	91.0303	92.2862	88.4176
14449.3	5.62074	0.35	0.65	96.3131	98.0327	93.9669

The same result (table 3) was obtained for O₂ experiment [13]. Initial state was at $T = 77$ K, $\rho = 1.202$ g/cm³, $E = -1.413$ kcal/mole. Maximal deviation of pressure was about 1% for MHMSA and 7% for KLRR-T+vdW1f relatively to MC results. MCFE with KLRR-T+vdW1f provides accuracy about 8% relatively to experimental data.

Table 3. O₂ shock simulation.

T , K	V , cm ³ /mol	O ₂ , mol fr	O, mol fr	P_{MC} , GPa	P_{MHMSA} , GPa	P_{KLRR-T} , GPa
3533.09	12.8809	0.99	0.01	23.2491	23.0117	23.2718
4505.07	11.916	0.95	0.05	30.8252	30.5381	30.5578
5186.43	11.1469	0.90	0.10	36.9711	36.6546	36.2525
5751.1	10.5094	0.85	0.15	42.4354	42.0936	41.1891
6295.9	9.97	0.80	0.20	47.3658	46.9971	45.5495
6826.28	9.44414	0.75	0.25	52.6903	52.3128	50.2653
7377.19	8.95463	0.70	0.30	58.1664	58.1651	55.087
7964.26	8.49512	0.65	0.35	63.8318	63.4103	60.0871
8602.66	8.06122	0.60	0.40	69.7347	69.2981	65.3319
9310.18	7.64964	0.55	0.45	75.9348	75.4866	70.8958
10108.3	7.25788	0.50	0.50	82.5106	82.0414	76.8657
11026.5	6.88387	0.45	0.55	89.5346	89.0577	83.3579
12106.8	6.52594	0.40	0.60	97.1429	96.6729	90.5357
13412.9	6.18262	0.35	0.65	105.5880	105.1029	98.6447

One may suggest more interesting results for liquid CO₂ because of rich set of pair potential parameters of products. The initial state was at $T = 218$ K, $\rho = 1.173$ g/cm³, $E = -98.486$ kcal/mole [16]. Two simulations were performed. The chemical composition of the first (table 4) one was represented as binary mixture of CO₂ and O.

Table 4. CO₂ two-component shock simulation.

T , K	V , cm ³ /mol	CO ₂ , mol fr	O, mol fr	P_{MC} , GPa	P_{MHMSA} , GPa	P_{KLRR-T} , GPa
5526.71	14.3819	0.90	0.10	45.773	45.3499	44.2675
5818.85	13.5348	0.85	0.15	49.407	48.9652	46.9546
6179.9	12.6746	0.80	0.20	54.038	53.5671	50.5793
6598.3	11.8423	0.75	0.25	59.254	58.7436	54.7552
7097.12	11.0381	0.70	0.30	65.182	64.6240	59.6382
7708.12	10.2619	0.65	0.35	71.995	71.3965	65.4399
8479.81	9.51365	0.60	0.40	80.003	79.3351	72.4686
9120.13	8.89867	0.55	0.45	85.142	84.4260	77.0644
10917.5	8.10127	0.50	0.50	101.67	100.8251	92.4499
11897.9	7.58011	0.45	0.55	107.23	106.3643	98.2409
14138.6	7.00222	0.40	0.60	121	120.0366	112.003

All theoretical and experimental data are in a good agreement up to 50 GPa (figure 2). The HMSA+vdW1f and KLRR-T+vdW1f schemes coincide with each other but underestimate the pressure relatively to MC at higher pressures. High accuracy was found for MHMSA model with the same closure relation as HMSA. Therefore, the reason of previous lack is in vdW1f model. The accuracy of MCFE with KLRR-T+vdW1f can be analyzed via comparison of density-temperature dependency (figure 3) with first-principle models [17–19].

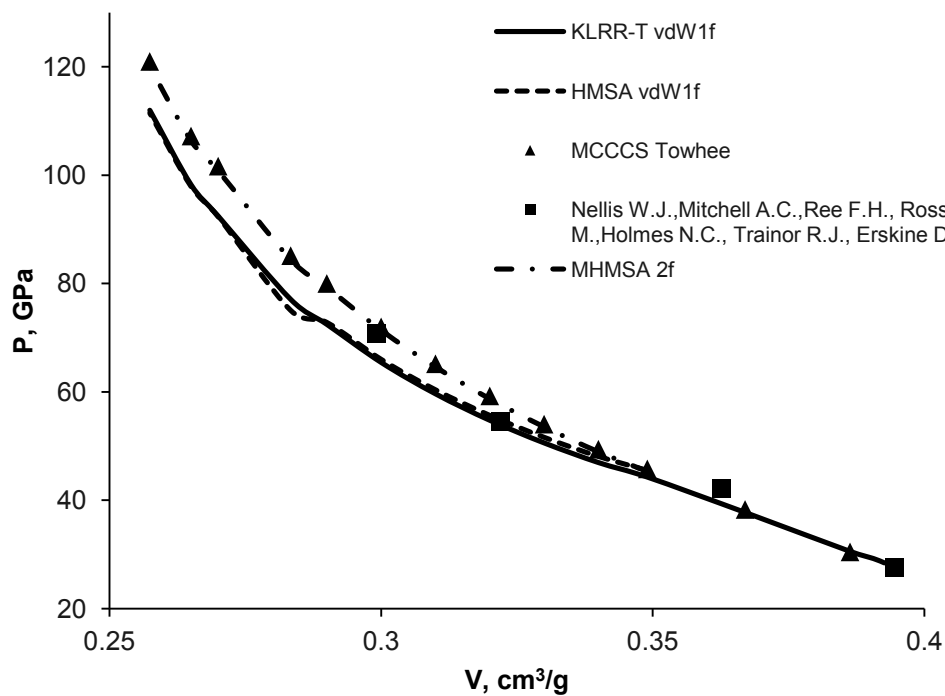


Figure 2. Shock Hugoniot for CO_2 in P - V .

The goal of another simulation (table 5) was to verify MHMSA scheme on rich $\text{CO}_2 - \text{CO} - \text{O}_2 - \text{O}$ composition by MC. The maximal deviation of pressure was about 1–2%.

Table 5. CO_2 four-component shock simulation.

T , K	V , cm^3/mol	CO_2 , mol fr	CO , mol fr	O_2 , mol fr	O , mol fr	P_{MC} , GPa	P_{MHMSA} , GPa
3272.45	17.6642	0.991	0.005	0.005	0.000	24.6922	24.5493
3959.25	16.7319	0.962	0.019	0.019	0.000	31.1241	30.9075
4657.8	15.6798	0.910	0.045	0.045	0.000	39.1896	39.1696
5419.44	14.5754	0.842	0.079	0.078	0.000	49.8404	49.7790
6076.94	13.6104	0.790	0.089	0.121	0.001	61.6153	62.1243
7362.91	12.4214	0.683	0.159	0.158	0.001	81.3286	81.9168
8649.5	11.4451	0.603	0.199	0.197	0.001	103.4664	104.4469
10184.9	10.5787	0.529	0.236	0.234	0.001	131.1494	132.1105
11989.9	9.82976	0.466	0.268	0.265	0.001	163.5806	165.0193

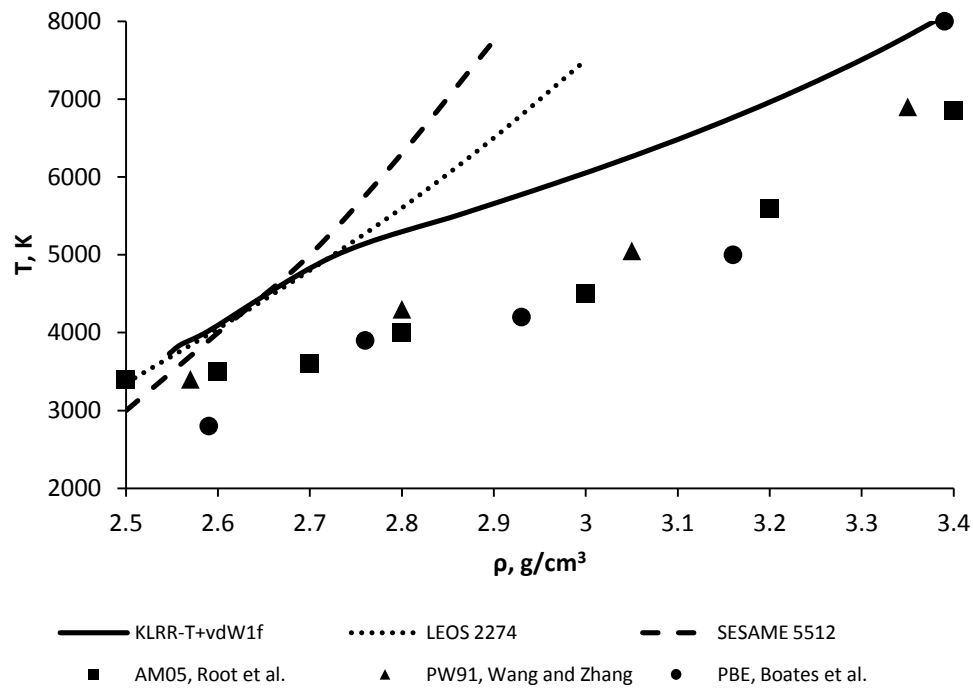


Figure 3. Shock Hugoniots for CO_2 in T - ρ .

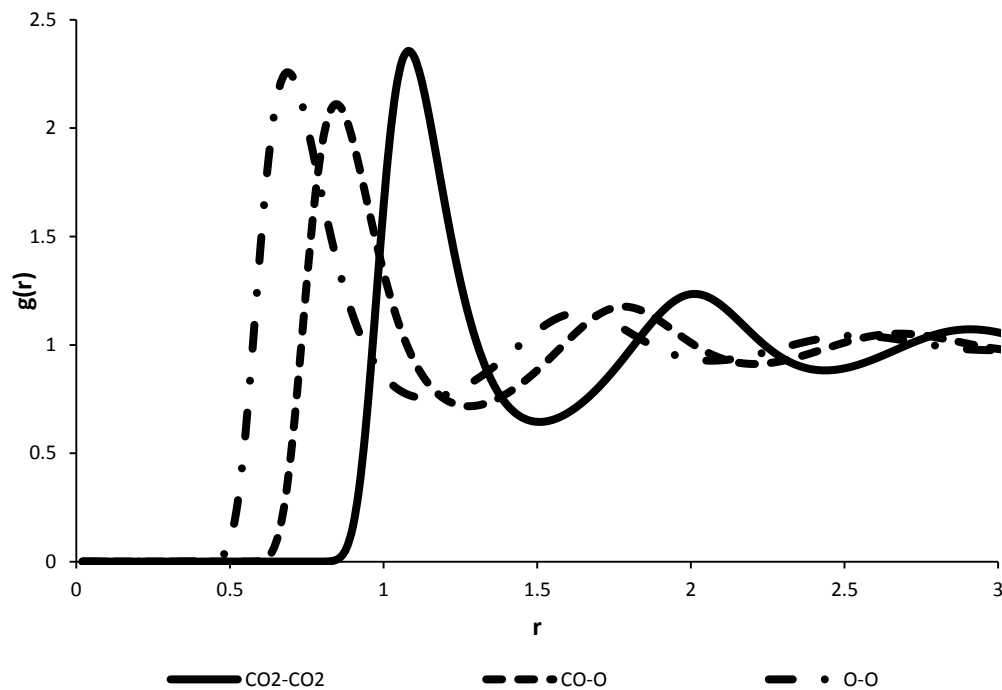


Figure 4. Four-component radial distribution functions for CO_2 at 164 GPa.

The structure of multicomponent fluid mixture can be analyzed by visualization of radial distribution functions (figure 4). One may see discrepancies between amplitudes as well as radii of maxima. Therefore, the disadvantage of vdW1f one fluid model is not surprising.

5. Conclusions

Multicomponent equations of state with wide range of applicability have been verified by MC for $C_xN_yO_z$ shock products mixture simulation. The drawback of vdW1f model has been confirmed at pressures, higher than 50 GPa. The new application of multicomponent HMSA closure for self-consistent OZ application has been offered. The multicomponent EOS for CO_2 with accuracy about 1–2% at pressures up to 160 GPa was developed.

Acknowledgments

We are deeply grateful to S B Victorov and P R Levashov for consulting and cooperation. Our work was performed using resources of NRNU MEPhI high-performance computing cluster.

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