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Developing the evaluation method of heat capacity and speed of sound of real gases using fourth virial coefficient over Lennard-Jones (12-6) potential

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Abstract In this study, we suggest an effective method of the evaluation of HC and SS of real gases by using the FVC over Lennard-Jones (12-6) potential. As known, the determination of the FVC is a key step to correct evaluation of the thermal properties. As an example of application, the suggested method has been performed for gases of Ar, SF_6 and SiH_4. The obtained results of HC at constant pressure and SS of gases Ar, SF_6 and SiH_4 are in good agreement with the corresponding theory and experimental data in the range of temperature from 90 to 800 K and range of pressure from 0.09 to 100.7 atm. The precision and accuracy of obtained results from the suggested method have been validated by the literature observations.

List of symbols

VDW	Van der Waals
FVC	Fourth virial coefficient (cm^9 mol^{-3})
HC	Heat capacity (kJ/kg K)
SS	Speed of sound (m s^{-1})
$D(T)$	Fourth virial coefficient (cm^9 mol^{-3})
$f(r_{ij})$	Mayer function
$u(r_{ij})$	Intermolecular interaction
C_P	Heat capacities (kJ/kg K)
C_P^0	Heat capacities of ideal gases (kJ/kg K)
u	Speed of sound (m s^{-1})
T	Temperature (K)
k_B	Boltzmann constant (J K^{-1})
N_A	Avogadro number (mol^{-1})
ε	Depth of potential energy minimum (kcal/mol)
σ	Value of r at $u(r) = 0$ (Å)
P	Pressure (atm)
R	Universal gas constant (J/mol K)

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M Molecular weight (g/mol)
γ Heat ratio

1 Introduction

A research of the thermodynamic properties is significant in the understanding of the specific behavior of real gases for various pressure and temperature ranges [1, 2]. The leading work of VDW in 1873 caused the generation of new equations of state to investigate the thermal properties of gases [3]. Therefore, researchers have suggested many of equations of state for the determination of the thermal properties of fluids [4, 5]. The equations of state such as Soave–Redlich–Kwong [6], Redlich–Kwong [7], Beattie–Bridgeman [8] and the Peng–Robinson [9] have been used commonly for the study of fluid systems. The virial equation of state that defines thermal properties such as speed of sound, entropy, enthalpy and heat capacity at constant pressure for gases is one of these equations. The virial equation of state consists of the second, third, fourth virial coefficients, etc. The virial coefficients are important because there are strong relations between the interactions of the molecules in pairs, triplets, and so on [10]. The virial coefficients ensure a precious way to knowledge of the intermolecular forces since they depend on intermolecular interaction energy and temperature [10, 11]. Therefore, we preferred the virial coefficients which are suitable for calculating the HP and SS of used gases accurately for the industrial field in this work. The sufficient methods are presented for the second and third virial coefficients; however, precise determination of the fourth virial coefficient for different intermolecular potentials has not been completed yet [12]. Therefore, many researchers have proposed a lot of methods for the evaluation of fourth virial coefficient accurately. Katsura has tried to calculate the FVC over square well potential by utilization of Fourier transforms [13]. Also, Boys and Shavitt have calculated the FVC for Lennard-Jones (12-6) potential approximately by using the method based on Gaussian functions [14]. Barker and Monaghan have calculated the FVC over Lennard-Jones (12-6) and square well potentials by using Legendre polynomial expansion procedure [15]. But the FVC of different intermolecular potentials has not been calculated precisely and accurately so far. Nowadays, it is still quite difficult to determine the FVC and thermodynamic properties analytically according to the FVC [15–19].

We have suggested a new approach in this study for the computation of the HC and SS of real gases using the approach for the FVC over Lennard-Jones (12-6) potential. To our knowledge, this work is the initial approximation to the computation of HC at constant pressure and SS for real gases by FVC over Lennard-Jones (12-6) potential. This theoretical study strongly benefits the evaluation of HC at constant pressure and SS of real gases. Note that the obtained results are in a satisfactory agreement with the existing numerically evaluated data.

2 Definition and expressions of FVC and HC at constant pressure and SS

The FVC is given by

$$D(T) = D_1(T) + D_2(T) + D_3(T), \tag{1}$$

where the quantities $D_1(T)$, $D_2(T)$ and $D_3(T)$ can be written in the following forms [12, 15]:

$$D_1(T) = -\frac{3N_A^3}{8}\iiint f(r_{12})\ f(r_{14}) f(r_{23}) f(r_{34}) \mathrm{d}r_2 \mathrm{d}r_3 \mathrm{d}r_4, \tag{2}$$

$$D_2(T) = -\frac{3N_A^3}{4}\iiint f(r_{12})\ f(r_{13}) f(r_{14}) f(r_{23}) f(r_{34}) \mathrm{d}r_2 \mathrm{d}r_3 \mathrm{d}r_4, \tag{3}$$

$$D_3(T) = -\frac{N_A^3}{8}\iiint f(r_{12})\ f(r_{13}) f(r_{14}) f(r_{23}) f(r_{24}) f(r_{34}) \mathrm{d}r_2 \mathrm{d}r_3 \mathrm{d}r_4. \tag{4}$$

Here, $f(r_{ij}) = \left(e^{u(r_{ij})/k_B T} - 1\right)$ is Mayer function [12]. In Eqs. (2)–(4), angular coordinates are expressed as follows:

$$\eta_{ij} = \cos\theta_{ij}, \tag{5}$$

$$r_{ij}^2 = r_{li}^2 + r_{lj}^2 - 2r_{li}r_{lj}\cos\theta_{ij}, \tag{6}$$

$$\cos(\theta_{ij}) = \cos(\theta_{ik})\cos(\theta_{lj}) + \sin(\theta_{ik})\sin(\theta_{lj})\cos\vartheta. \tag{7}$$

By substituting Eqs. (5)–(7) into Eqs. (2)–(4) and considering Lennard-Jones (12-6) potential, we obtain the following formulae:

$$D_1(T) = -6\pi^2 b_0^3 \int_0^\infty\int_0^\infty\int_0^\infty\int_{-1}^1\int_{-1}^1 r_{12}^2\left(e^{-\frac{4\varepsilon}{T\,k_B}\left(\left(\frac{\sigma}{r_{12}}\right)^{12}-\left(\frac{\sigma}{r_{12}}\right)^{6}\right)}-1\right)$$
$$r_{13}^2\, r_{14}^2\left(e^{-\frac{4\varepsilon}{T\,k_B}\left(\left(\frac{\sigma}{r_{14}}\right)^{12}-\left(\frac{\sigma}{r_{14}}\right)^{6}\right)}-1\right)$$
$$\left(e^{-\frac{4\varepsilon}{T\,k_B}\left(\left(\frac{\sigma}{\sqrt{r_{12}^2+r_{13}^2-2r_{12}r_{13}\eta_{23}}}\right)^{12}-\left(\frac{\sigma}{\sqrt{r_{12}^2+r_{13}^2-2r_{12}r_{13}\eta_{23}}}\right)^{6}\right)}-1\right)$$
$$\left(e^{-\frac{4\varepsilon}{T\,k_B}\left(\left(\frac{\sigma}{\sqrt{r_{14}^2+r_{13}^2-2r_{14}r_{13}\eta_{34}}}\right)^{12}-\left(\frac{\sigma}{\sqrt{r_{14}^2+r_{13}^2-2r_{14}r_{13}\eta_{34}}}\right)^{6}\right)}-1\right)$$
$$\mathrm{d}r_{12}\mathrm{d}r_{13}\mathrm{d}r_{14}\mathrm{d}\eta_{23}\mathrm{d}\eta_{34} \tag{8}$$

$$D_2(T) = -12\pi^2 b_0^3 \int_0^\infty\int_0^\infty\int_0^\infty\int_{-1}^1\int_{-1}^1 r_{12}^2\left(e^{-\frac{4\varepsilon}{T\,k_\mathrm{B}}\left(\left(\frac{\sigma}{r_{12}}\right)^{12}-\left(\frac{\sigma}{r_{12}}\right)^{6}\right)}-1\right)$$
$$r_{13}^2\left(e^{-\frac{4\varepsilon}{T\,k_\mathrm{B}}\left(\left(\frac{\sigma}{r_{13}}\right)^{12}-\left(\frac{\sigma}{r_{13}}\right)^{6}\right)}-1\right) r_{14}^2\left(e^{-\frac{4\varepsilon}{T\,k_\mathrm{B}}\left(\left(\frac{\sigma}{r_{14}}\right)^{12}-\left(\frac{\sigma}{r_{14}}\right)^{6}\right)}-1\right)$$
$$\left(e^{-\frac{4\varepsilon}{T\,k_\mathrm{B}}\left(\left(\frac{\sigma}{\sqrt{r_{13}^2+r_{12}^2-2r_{13}r_{12}\eta_{23}}}\right)^{12}-\left(\frac{\sigma}{\sqrt{r_{13}^2+r_{12}^2-2r_{13}r_{12}\eta_{23}}}\right)^{6}\right)}-1\right)$$

Table 1 Parameters of Lennard-Jones (12-6) potential

Gases	ε/k_B (K)	σ (Å)
Ar	120	3.40
SF_6	206.85	5.783
SiH_4	193.65	4.539

$$\left(e^{-\frac{4\varepsilon}{T\,k_B}\left(\left(\frac{\sigma}{\sqrt{r_{12}^2+r_{14}^2-2r_{12}r_{14}\eta_{24}}}\right)^{12}-\left(\frac{\sigma}{\sqrt{r_{12}^2+r_{14}^2-2r_{12}r_{14}\eta_{24}}}\right)^{6}\right)}-1\right)$$
$$\mathrm{d}r_{12}\mathrm{d}r_{13}\mathrm{d}r_{14}\mathrm{d}\eta_{23}\mathrm{d}\eta_{24} \tag{9}$$

$$D_3(T)=-\pi^2 b_0^3\int_0^\infty\int_0^\infty\int_0^\infty\int_{-1}^1\int_{-1}^1\int_0^{2\pi} r_{12}^2\left(e^{-\frac{4\varepsilon}{T\,k_B}\left(\left(\frac{\sigma}{r_{12}}\right)^{12}-\left(\frac{\sigma}{r_{12}}\right)^{6}\right)}-1\right)$$
$$r_{13}^2\left(e^{-\frac{4\varepsilon}{T\,k_B}\left(\left(\frac{\sigma}{r_{13}}\right)^{12}-\left(\frac{\sigma}{r_{13}}\right)^{6}\right)}-1\right)r_{14}^2\left(e^{-\frac{4\varepsilon}{T\,k_B}\left(\left(\frac{\sigma}{r_{14}}\right)^{12}-\left(\frac{\sigma}{r_{14}}\right)^{6}\right)}-1\right)$$
$$\left(e^{-\frac{4\varepsilon}{T\,k_B}\left(\left(\frac{\sigma}{\sqrt{r_{12}^2+r_{14}^2-2r_{12}r_{14}\eta_{24}}}\right)^{12}-\left(\frac{\sigma}{\sqrt{r_{12}^2+r_{14}^2-2r_{12}r_{14}\eta_{24}}}\right)^{6}\right)}-1\right)$$
$$\left(e^{-\frac{4\varepsilon}{T\,k_B}\left(\left(\frac{\sigma}{\sqrt{r_{13}^2+r_{14}^2-2r_{13}r_{14}\eta_{34}}}\right)^{12}-\left(\frac{\sigma}{\sqrt{r_{13}^2+r_{14}^2-2r_{13}r_{14}\eta_{34}}}\right)^{6}\right)}-1\right)$$
$$\left(e^{-\frac{4\varepsilon}{T\,k_B}\left(\left(\frac{\sigma}{\sqrt{r_{12}^2+r_{13}^2-2r_{12}r_{13}\left(\eta_{24}\eta_{34}+\sqrt{1-\eta_{24}^2}\sqrt{1-\eta_{34}^2}\cos\vartheta\right)}}\right)^{12}-\left(\frac{\sigma}{\sqrt{r_{12}^2+r_{13}^2-2r_{12}r_{13}\left(\eta_{24}\eta_{34}+\sqrt{1-\eta_{24}^2}\sqrt{1-\eta_{34}^2}\cos\vartheta\right)}}\right)^{6}\right)}-1\right)$$
$$\mathrm{d}r_{12}\mathrm{d}r_{13}\mathrm{d}r_{14}\mathrm{d}\eta_{24}\mathrm{d}\eta_{34}\mathrm{d}\vartheta \tag{10}$$

where $b_0 = 2\pi N_A\sigma^3/3$. Note that the deviations from the ideal behavior are efficiently described by the second virial coefficient at low densities, but higher virial coefficients must be considered at higher densities [20]. Therefore, the HC and SS of gases may be expressed with the fourth virial coefficient approximately as follows [12, 21, 22], respectively:

$$C_P - C_P^0 = -\frac{1}{4R^4}\left(\frac{P}{T}\right)^3 D(T), \tag{11}$$

$$u^2 = \frac{\gamma RT}{M}\left(1+2\left(\frac{P}{RT}\right)^3\frac{(1+\gamma)}{\gamma}D(T)\right), \tag{12}$$

where $D(T)$ is the fourth virial coefficient and $\gamma = C_P/C_V$ is the heat capacity ratio. The symbol small zero $(^0)$ expresses the property of gas in its ideal state in Eqs. (11)–(12). We have suggested a new approach for calculating heat capacity at constant pressure and speed of sound according to the fourth virial coefficient by substituting Eq. (1) into Eqs. (11)–(12).

Table 2 Comparative results of heat capacity at constant pressure of Ar

P (atm)	T (K)	Density (kg m^{-3}) [27]	Density (kg m^{-3}) [22]	C_P (kJ/kg K)	C_P (kJ/kg K) [23]	Standard deviation	C_P (kJ/kg K) [27]	Standard deviation	C_P (kJ/kg K) [22]	Standard deviation
0.789539	90	4.378	–	0.520286	0.5203	0.00000989949	0.55397	0.0238182	–	–
	150	2.577	–	0.520286	0.5203	0.00000989949	0.526184	0.00417052	–	–
	200	1.926	–	0.520286	0.5203	0.00000989949	0.52293	0.00186959	–	–
	250	1.539	–	0.520286	0.5203	0.00000989949	0.521929	0.00116178	–	–
	300	1.282	–	0.520286	0.5203	0.00000989949	0.521178	0.000630739	–	–
	360	1.068	–	0.520286	0.5203	0.00000989949	0.520927	0.000453255	–	–
	400	0.9610	–	0.520286	0.5203	0.00000989949	0.520927	0.000453255	–	–
3.94769	150	13.19	–	0.520286	0.5203	0.00000989949	0.550966	0.021694	–	–
	200	9.723	–	0.520286	0.5203	0.00000989949	0.533443	0.0093034	–	–
	250	7.729	–	0.520286	0.5203	0.00000989949	0.527686	0.00523259	–	–
	300	6.422	–	0.520286	0.5203	0.00000989949	0.525183	0.0034627	–	–
	360	5.342	–	0.520286	0.5203	0.00000989949	0.52343	0.00222314	–	–
	400	4.805	–	0.520286	0.5203	0.00000989949	0.52293	0.00186959	–	–
9.86923	120	47.18	47.202	0.520148	0.5203	0.00010748	0.75423	0.165521	0.75594	0.16673
	150	34.55	34.551	0.520285	0.5203	0.0000106066	0.60779	0.0618754	0.60857	0.0624269
	200	24.75	24.743	0.520285	0.5203	0.0000106066	0.529689	0.00664963	0.55560	0.0249715
	300	16.11	16.111	0.520286	0.5203	0.00000989949	0.532442	0.00859559	0.53235	0.00853054
	340	14.17	14.171	0.520145	0.5203	0.000109602	0.529438	0.00657114	0.52917	0.00638164
	400	12.01	12.014	0.520286	0.5203	0.00000989949	0.526685	0.00452478	0.52632	0.00426668
	500	–	9.5926	0.520145	0.5203	0.000109602	–	–	0.52388	0.00264104
	600	–	7.9885	0.520145	0.5203	0.000109602	–	–	0.52266	0.00177837
	700	–	6.8458	0.520145	0.5203	0.000109602	–	–	0.52197	0.00129047
14.8038	150	54.16	54.157	0.520142	0.5203	0.000111723	0.66937	0.10552	0.67030	0.106178

Table 2 continued

P (atm)	T (K)	Density (kg m^{-3}) [27]	Density (kg m^{-3}) [22]	C_P (kJ/kg K)	C_P (kJ/kg K) [23]	Standard deviation	C_P (kJ/kg K) [27]	Standard deviation	C_P (kJ/kg K) [22]	Standard deviation
	200	37.70	37.686	0.520144	0.5203	0.000110309	0.573996	0.0380791	0.57523	0.0389517
	300	24.24	24.237	0.520145	0.5203	0.000109602	0.5387	0.0131204	0.53847	0.0129577
	340	21.28	21.285	0.520145	0.5203	0.000109602	0.533944	0.00975737	0.53362	0.00952826
	400	18.02	18.021	0.520145	0.5203	0.000109602	0.529689	0.00674863	0.52930	0.00647356
	500	–	14.376	0.520145	0.5203	0.000109602	–	–	0.52564	0.00388555
	600	–	11.968	0.520145	0.5203	0.000109602	–	–	0.52381	0.00259155
	700	–	10.255	0.520145	0.5203	0.000109602	–	–	0.52277	0.00185616
29.6077	150	129.0	128.93	0.520139	0.5203	0.000113844	1.02934	0.360059	1.0311	0.361304
	200	79.11	79.075	0.520143	0.5203	0.000111016	0.641334	0.085695	0.64370	0.087368
	300	48.87	48.876	0.520145	0.5203	0.000109602	0.557725	0.0265731	0.55719	0.0261948
	340	42.71	42.723	0.520145	0.5203	0.000109602	0.547962	0.0196696	0.54705	0.0190247
	400	36.02	36.036	0.520145	0.5203	0.000109602	0.539201	0.0134746	0.53826	0.0128092
	500	–	28.671	0.520145	0.5203	0.000109602	–	–	0.53086	0.00757665
	600	–	23.847	0.520145	0.5203	0.000109602	–	–	0.52723	0.00500985
	700	–	20.429	0.520145	0.5203	0.000109602	–	–	0.52517	0.00355321
49.3462	200	141.2	141.19	0.520136	0.5203	0.000115966	0.759487	0.169247	0.76303	0.171752
	300	82.27	82.275	0.520144	0.5203	0.000110309	0.583509	0.0448115	0.58287	0.0443596
	340	71.47	71.487	0.520144	0.5203	0.000110309	0.566236	0.0325976	0.56508	0.0317802
	400	59.99	60.011	0.520145	0.5203	0.000109602	0.551467	0.0221544	0.55001	0.0211241
	500	–	47.592	0.520145	0.5203	0.000109602	–	–	0.53769	0.0124126
	600	–	39.543	0.520145	0.5203	0.000109602	–	–	0.53168	0.00816284
	700	–	33.866	0.520145	0.5203	0.000109602	–	–	0.52828	0.00575868

Table 3 Comparative results of speed of sound of Ar

P (atm)	T (K)	Density (kg m^{-3}) [27]	Density (kg m^{-3}) [22]	u (m s^{-1})	u (m s^{-1}) [23]	Standard deviation	u (m s^{-1}) [27]	Standard deviation	u (m s^{-1}) [22]	Standard deviation
0.789539	90	4.378	–	176.742	176.7	0.0296985	174.3	1.72675	–	–
	150	2.577	–	228.174	228.1	0.0523259	227.6	0.405879	–	–
	200	1.926	–	263.473	263.4	0.0516188	263.3	0.122329	–	–
	250	1.539	–	294.572	294.5	0.0509117	294.5	0.0509117	–	–
	300	1.282	–	322.687	322.6	0.0615183	322.7	0.00919239	–	–
	360	1.068	–	353.486	353.4	0.0608112	353.5	0.00989949	–	–
	400	0.9610	–	372.607	372.5	0.0756604	372.6	0.00494975	–	–
3.94769	150	13.19	–	228.175	228.1	0.053033	225.6	1.8208	–	–
	200	9.723	–	263.473	263.4	0.0516188	262.7	0.546594	–	–
	250	7.729	–	294.572	294.5	0.0509117	294.5	0.0509117	–	–
	300	6.422	–	322.687	322.6	0.0615183	322.9	0.150614	–	–
	360	5.342	–	353.486	353.4	0.0608112	353.9	0.292742	–	–
	400	4.805	–	372.607	372.5	0.0756604	373.1	0.348604	–	–
9.86923	120	47.18	47.202	204.084	–	–	189.1	10.5953	189.35	10.4185
	150	34.55	34.551	228.181	228.1	0.0572756	221.6	4.65347	221.67	4.60397
	200	24.75	24.743	263.475	263.4	0.053033	261.7	1.25511	261.59	1.3329
	300	16.11	16.111	322.688	322.6	0.0622254	323.5	0.574171	323.44	0.531744
	340	14.17	14.171	343.558	343.4	0.111723	344.7	0.807516	344.66	0.779232
	400	12.01	12.014	372.607	372.5	0.0756604	374.1	1.05571	374.06	1.02743
	500	–	9.5926	416.625	416.5	0.0883883	–	–	418.25	1.14905
	600	–	7.9885	456.39	456.2	0.13435	–	–	458.06	1.18087
	700	–	6.8458	492.957	492.8	0.111016	–	–	494.61	1.16885
14.8038	150	54.16	54.157	228.217	228.1	0.0827315	218.1	0.0827315	218.16	0.0403051

Table 3 continued

P (atm)	T (K)	Density (kg m^{-3}) [27]	Density (kg m^{-3}) [22]	u (m s^{-1})	u (m s^{-1}) [23]	Standard deviation	u (m s^{-1}) [27]	Standard deviation	u (m s^{-1}) [22]	Standard deviation
	200	37.70	37.686	263.505	263.4	0.0742462	260.9	1.84201	260.76	1.94101
	300	24.24	24.237	322.718	322.6	0.0834386	324.0	0.906511	323.91	0.842871
	340	21.28	21.285	343.559	343.4	0.11243	345.4	1.30178	345.32	1.24522
	400	18.02	18.021	372.642	372.5	0.100409	374.9	1.59665	374.87	1.57543
	500	–	14.376	416.626	416.5	0.0890955	–	–	419.16	1.79181
	600	–	11.968	456.39	456.2	0.13435	–	–	458.99	1.83848
	700	–	10.255	492.958	492.8	0.111723	–	–	495.53	1.81868
29.6077	150	129.0	128.93	228.369	228.1	0.190212	205.8	15.9587	205.67	16.0506
	200	79.11	79.075	263.561	263.4	0.113844	259.0	3.22511	258.67	3.45846
	300	48.87	48.876	322.728	322.6	0.0905097	325.8	2.17223	325.58	2.01667
	340	42.71	42.723	343.567	343.4	0.118087	347.6	2.85176	347.46	2.75277
	400	36.02	36.036	372.647	372.5	0.103945	377.4	3.36088	377.41	3.36795
	500	–	28.671	416.629	416.5	0.0912168	–	–	421.95	3.76252
	600	–	23.847	456.392	456.2	0.135765	–	–	461.82	3.83818
	700	–	20.429	492.959	492.8	0.11243	–	–	498.32	3.7908
49.3462	200	141.2	141.19	263.792	263.4	0.277186	257.7	4.30769	257.20	4.66125
	300	82.27	82.275	322.772	322.6	0.121622	328.7	4.19173	328.37	3.95838
	340	71.47	71.487	343.601	343.4	0.142128	350.9	5.16117	350.74	5.04804
	400	59.99	60.011	372.671	372.5	0.120915	381.0	5.88949	381.06	5.93192
	500	–	47.592	416.644	416.5	0.101823	–	–	425.81	6.48134
	600	–	39.543	456.402	456.2	0.142836	–	–	465.68	6.56054
	700	–	33.866	492.965	492.8		–		502.09	6.45235

Table 4 Comparative results of heat capacity at constant pressure of SF_6

P (atm)	T (K)	Density (kg m^{-3}) [28]	C_P (kJ/kg K)	C_P (kJ/kg K) [23]	Standard deviation	C_P (kJ/kg K) [28]	Standard deviation
0.986923	210	8.6767	0.494126	0.4940	0.0000890955	0.51414	0.014152
	300	5.9203	0.667694	0.6676	0.000066468	0.67184	0.00293166
	400	4.4095	0.797155	0.7972	0.0000318198	0.79899	0.00129754
	500	3.5190	0.879521	0.8792	0.000226981	0.88004	0.000366988
	600	2.9295	0.931329	0.9320	0.000474469	0.93244	0.000785596
4.93462	250	39.44	0.577726	0.5778	0.0000523259	0.63846	0.0429454
	300	31.041	0.667694	0.6676	0.000066468	0.69206	0.0172294
	400	22.416	0.797155	0.7972	0.0000318198	0.80617	0.00637457
	500	17.710	0.879521	0.8792	0.000226981	0.88375	0.00299035
	600	14.681	0.931329	0.9320	0.000474469	0.93467	0.00236244
9.86923	300	66.523	0.667693	0.6676	0.0000657609	0.72807	0.042693
	400	45.799	0.797154	0.7972	0.0000325269	0.81598	0.013312
	500	35.707	0.879521	0.8792	0.000226981	0.88854	0.0063774
	600	29.441	0.931329	0.9320	0.000474469	0.94703	0.0111023
14.8038	300	108.68	0.66769	0.6676	0.0000636396	0.78676	0.0841952
	400	70.230	0.797154	0.7972	0.0000325269	0.82686	0.0210053
	500	53.986	0.879521	0.8792	0.000226981	0.89350	0.00988465
	600	44.273	0.931329	0.9320	0.000474469	0.94036	0.00638588

Table 5 Comparative results of speed of sound of SF_6

P (atm)	T (K)	Density ($kg\ m^{-3}$) [28]	u ($m\ s^{-1}$)	u ($m\ s^{-1}$) [23]	Standard deviation	u ($m\ s^{-1}$) [28]	Standard deviation	T (K)	P (atm)	u ($m\ s^{-1}$)	Experimental data u ($m\ s^{-1}$) [2]	Standard deviation
0.986923	210	8.6767	116.27	116.2	0.0494975	113.01	2.3057	298.15	15.3773	136.576	112.52	17.0102
	300	5.9203	136.676	136.6	0.0537401	135.41	0.89597		14.6232	136.482	113.97	15.9184
	400	4.4095	156.639	156.6	0.0275772	156.08	0.395273		13.507	136.482	116.06	14.4405
	500	3.5190	174.5	174.5	0.00000	174.23	0.190919		12.3168	136.435	118.20	12.8941
	600	2.9295	190.789	190.7	0.0629325	190.66	0.0912168		11.1591	136.396	120.20	11.4523
4.93462	250	39.44	125.7	125.6	0.0707107	114.40	7.99031		9.05798	136.345	123.62	8.99793
	300	31.041	136.686	136.6	0.0608112	130.24	4.55801		8.13225	136.328	125.06	7.96768
	400	22.416	156.642	156.6	0.0296985	154.00	1.86818		7.28942	136.316	126.33	7.06117
	500	17.710	174.501	174.5	0.00070717	173.38	0.792667		6.52258	136.307	127.46	6.25577
	600	14.681	190.789	190.7	0.0629325	190.40	0.275065		5.83074	136.301	128.47	5.53735
9.86923	300	66.523	136.753	136.6	0.108187	123.00	9.72484		3.68715	136.289	131.46	3.41462
	400	45.799	156.66	156.6	0.0424264	151.39	3.72645		2.92031	136.287	132.50	2.67781
	500	35.707	174.508	174.5	0.00565685	172.36	1.51887					
	600	29.441	190.794	190.7	0.066468	190.13	0.469519					
14.8038	300	108.68	136.935	136.6	0.236881	114.53	15.8427					
	400	70.230	156.711	156.6	0.0784889	148.79	5.60099					
	500	53.986	174.526	174.5	0.0183848	171.40	2.21042					
	600	44.273	190.806	190.7	0.0749533	189.91	0.633568					

Table 6 Comparative results of heat capacity at constant pressure and of SiH_4

P (atm)	T (K)	C_P (kJ/kg K)	C_P (kJ/kg K) [17]	Standard deviation	P (atm)	T (K)	C_P (kJ/kg K)	C_P (kJ/kg K) [17]	Standard deviation
0.29608	200	2.19643	2.1965	0.0000494975	29.6077	200	2.19646	2.1965	0.0000282843
	400	2.512	2.5120	0.00000000		400	2.51199	2.5120	0.00000707107
	500	2.55677	2.5568	0.0000212132		500	2.55677	2.5568	0.0000212132
	600	2.58775	2.5877	0.0000353553		600	2.58775	2.5877	0.0000353553
	800	2.64386	2.6441	0.000169706		800	2.64386	2.6441	0.000169706
0.986923	200	2.19643	2.1965	0.0000494975	49.3462	200	2.19656	2.1965	0.0000424264
	400	2.512	2.5120	0.00000000		400	2.51198	2.5120	0.0000141421
	500	2.55677	2.5568	0.0000212132		500	2.55676	2.5568	0.0000282843
	600	2.58775	2.5877	0.0000353553		600	2.58774	2.5877	0.0000282843
	800	2.64386	2.6441	0.000169706		800	2.64386	2.6441	0.000169706
4.93462	200	2.19643	2.1965	0.0000494975	69.0846	200	2.19677	2.1965	0.000190919
	400	2.512	2.5120	0.00000000		400	2.51194	2.5120	0.0000424264
	500	2.55677	2.5568	0.0000212132		500	2.55674	2.5568	0.0000424264
	600	2.58775	2.5877	0.0000353553		600	2.58773	2.5877	0.0000212132
	800	2.64386	2.6441	0.000169706		800	2.64472	2.6442	0.000367696
14.8038	200	2.19643	2.1965	0.0000494975	100.666	200	2.19749	2.1965	0.000700036
	400	2.512	2.5120	0.00000000		400	2.51181	2.5120	0.00013435
	500	2.55677	2.5568	0.0000212132		500	2.55668	2.5568	0.0000848528
	600	2.58775	2.5877	0.0000353553		600	2.58769	2.5877	0.00000707107
	800	2.64386	2.6441	0.000169706		800	2.64471	2.6442	0.000360624

Table 7 Comparative results of speed of sound of SiH_4

P (atm)	T (K)	u (m s^{-1})	u (m s^{-1}) [17]	Standard deviation	P (atm)	T (K)	u (m s^{-1})	u (m s^{-1}) [17]	Standard deviation
0.29608	200	368.185	368.1	0.0601041	29.6077	200	367.65	368.1	0.318198
	400	510.89	510.8	0.0636396		400	511.024	510.8	0.158392
	500	569.898	569.8	0.0692965		500	569.97	569.8	0.120208
	600	623.345	623.2	0.10253		600	623.395	623.2	0.137886
	800	717.875	717.7	0.123744		800	717.9	717.7	0.141421
0.986923	200	368.185	368.1	0.0601041	49.3462	200	365.7	368.1	1.69706
	400	510.89	510.8	0.0636396		400	511.512	510.8	0.50346
	500	569.898	569.8	0.0692965		500	570.232	569.8	0.30547
	600	623.345	623.2	0.10253		600	623.575	623.2	0.265165
	800	717.875	717.7	0.123744		800	717.992	717.7	0.206475
4.93462	200	368.182	368.1	0.0579828	69.0846	200	361.326	368.1	4.78994
	400	510.89	510.8	0.0636396		400	512.594	510.8	1.26855
	500	569.898	569.8	0.0692965		500	570.813	569.7	0.78701
	600	623.346	623.2	0.103238		600	623.975	623.2	0.548008
	800	717.875	717.7	0.123744		800	718.169	717.7	0.331633
14.8038	200	368.118	368.1	0.0127279	100.666	200	346.523	368.1	15.2572
	400	510.906	510.8	0.0749533		400	516.145	510.8	3.77949
	500	569.907	569.8	0.0756604		500	572.723	569.7	2.13758
	600	623.352	623.2	0.10748		600	625.29	623.2	1.47785
	800	717.878	717.7	0.125865		800	718.844	717.6	0.879641

3 Numerical results and discussion

A new approach to calculate the HC at constant pressure and SS for real gases using the FVC is presented. The utility approach for calculating HC and SS of gases is proposed, and it can be applied to any gases. We made some mathematical transformations on the fourth virial coefficient to make it numerically solvable. Equations (11)–(12) have been evaluated using the numerical method. This work is the first approach to the calculation of HC at constant pressure and SS for real gases by FVC over Lennard-Jones (12-6) potential, as far as we know. The Lennard-Jones (12-6) parameters for gases of Ar, SF_6 and SiH_4 are given in Table 1 [24–26]. The Mathematica 7.0 software system has been used to compute the HC at constant pressure and SS. The obtained results are given for HC at constant pressure and SS of gases of Ar, SF_6 and SiH_4 in Tables 2, 3 and 4. The calculation results of Eqs. (11)–(12) have been compared with those obtained by literature data [2, 22, 23, 27, 28]. The results are in well agreement with the existing literature at a varying temperature ranging from 90 to 800 K and at a varying pressure ranging between 0.09 and 100.7 atm [2, 23]. The standard deviation is given for the sound of speed and heat capacities of Ar, SF_6 and SiH_4 in Tables 2, 3, 4, 5, 6 and 7. The obtained results of the HC at constant pressure for gases of Ar, SF_6 and SiH_4 are compared with theoretical data [22, 23, 27, 28]. The calculated results of SS for gases Ar, SF_6 and SiH_4 are compared with theoretical and experimental data [2, 22, 23, 27]. It is well known that the real gases begin to switch into the liquid phase at low temperatures and high pressures. Therefore, as seen in Tables 2, 4 and 6, the computation results of the heat capacities by using the FVC deviate a little from literature data at high pressures and low temperatures [22, 27, 28]. Also, as the pressure increases at a constant temperature, the agreement between the obtained calculation results for SS and the experimental data is demonstrated in Table 5. As seen from Tables 2, 3, 4, 5, 6 and 7, note that the FVC is implemented at the private temperature and pressure ranges that molecule indicates the gas behavior. As known, the deviations from the ideal behavior at low densities are efficiently expressed by the second virial coefficient; however, higher virial coefficients are taken into regard at higher densities. One of the advantages of this work is the utilization of the FVC for the accepted formulae of HC and SS for gases at higher densities. Therefore, the established formulae for the FVC to calculate HC and SS are suitable in the arbitrary range of values of parameters. As seen from the calculation results, the suggested approach displays good results in various ranges of parameters. Therefore, the calculation results obtained from this work will be beneficial for a different perspective of industry and technology.

4 Conclusion

A new approach has been proposed in this study to calculate the HC at constant pressure and SS of real gases at different temperature and pressure ranges using the fourth virial coefficient. As seen from the results, the present theoretical approximation is general and provides a useful guidance for a correct assessment of the other thermal properties of gases.

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