Thermophysical Properties of Tetramethylmethane and Tetramethylsilane Gas Calculated by Means of an Isotropic Temperature-Dependent Potential

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An isotropic temperature-dependent potential (ITDP) is calculated for the description of binary interactions in gaseous tetramethylmethane, $C(CH_3)_4$, and tetramethylsilane, $Si(CH_3)_4$. The potential parameters of $C(CH_3)_4$ and $Si(CH_3)_4$ are determined by solving an inverse problem of minimization of the sum of weighted squared relative deviations between experimental and calculated pure gas viscosity (η), second (pVT)-virial coefficient (B), and second acoustic virial coefficient (β) data. At $T = 0$ K they are obtained for $C(CH_3)_4$ and $Si(CH_3)_4$, respectively, as repulsive parameter $n = 28.02(12)$ and $20.79(11)$, equilibrium distance $r_m = 5.7790(30) \times 10^{-10}$ and $5.9051(36) \times 10^{-10}$ m, potential well depth $\varepsilon/k_B = 586.32(42)$ and $674.75(91)$ K, and the first excited-level enlargement $\delta = 0.0141(3) \times 10^{-10}$ and $0.0188(3) \times 10^{-10}$ m. The influence of the temperature on the potential parameters $r_m(T)$ and $\varepsilon(T)$ is implied in the temperature dependence of the effective excited-state enlargement, calculated via the vibrational partition function. The calculated complete sets of normal vibrational frequencies for $C(CH_3)_4$ and $Si(CH_3)_4$ are consistent with the available experimental data. In addition, good agreement is observed between the calculations and new Raman spectroscopic measurements on $C(CH_3)_4$. Tables for recommended thermophysical properties (B, η, and self-diffusion ρD) and effective

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potential parameters (r_m and ε) of the two globular gases are given for the temperature range between 250 and 800 K.

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1. INTRODUCTION

The scientific interest in the thermophysical properties of polyatomic globular gases like tetramethylmethane (TMM; neopentane), $C(CH_3)_4$, and tetramethylsilane (TMS), $Si(CH_3)_4$, as well as their higher homologues $X(CH_3)_4$ ($X =$ Ge, Sn, Pb) has increased recently due to the growing number of their technical applications. These applications include plasma etching in the production of semiconductor devices, gas-phase epitaxy, and the like [1].

This series of gases is also interesting from an ecological point of view [2]. Volatile organic compounds are very important constituents of the troposphere. Depending on their concentration, they can have a strong direct adverse influence on the environment. Many of the hydrocarbon molecules in the atmosphere [including $C(CH_3)_4$] are initially present in fuels and are found in exhausts, as a consequence of incomplete fossil fuel combustion.

In this paper, we supply quantitative information on the transport (viscosity η, self-diffusion ρD) and equilibrium [second (pVT)-virial coefficient B, second acoustic virial coefficient β] properties of neopentane and tetramethylsilane in the temperature range between 250 and 800 K. It is obtained by means of an isotropic temperature-dependent potential (ITDP) [3]. This methodology has already been successfully applied to other heavy globular molecules (SF_6, WF_6, MoF_6, UF_6) [4] and their mixtures [5]. It requires knowledge of the complete set of normal vibrational frequencies, which, for the considered gases, is not available in the literature [6]. Therefore, in addition to the pure thermophysical investigations we have used Raman scattering experiments and density functional calculations to obtain the vibrational frequencies of TMM and TMS.

The ITDP is a semiempirical effective model which is based on the well-known enlargement of the molecule in higher vibrational levels. Despite the lack of a rigorous physical justification, it demonstrates a superior quality in describing thermophysical properties of globular or nearly globular molecules and their binary mixtures [4, 5]. However, it is worth mentioning that temperature-dependent intermolecular potential parameters have also been observed by other authors in their studies of collision-induced spectroscopic properties [7, 8] and in molecular dynamics (MD) calculations [9].

2. BINARY INTERACTIONS IN GASEOUS TMM AND TMS

Ordinarily, measured B or η data of TMM and TMS are approximated by means of an $(n-6)$ Lennard–Jones (L–J) potential [10, 11]. This approach has limited applicability. The intermolecular potentials derived from either B or η data cannot generally be used to produce an acceptable simultaneous fit of different properties (transport, equilibrium or spectroscopic).

The aim of this work is to explore the possibility of describing the binary interactions in TMM and TMS by means of an isotropic temperature-dependent potential ITDP [3]. This approach is a rationalized version of the model of the interactions between vibrationally excited states of molecules [12]. The ITDP was introduced to speed up the calculations for heavier globular molecules (UF_6, WF_6, MoF_6) and their mixtures [5].

Instead of a mixture of n_s different vibrational states [12], we consider the globular gas at given temperature T as one vibrationally excited state with an enlargement of the molecular radii $\delta^{(\mathrm{eff})}(T)$ averaged over all n_s states:

$$\delta^{(\mathrm{eff})}(T) = \sum_{k,\,m} \delta \times [\,C_k \times x_k(T) + C_m \times x_m(T)\,] \tag{1}$$

The harmonic oscillator force constants, C_k, are known and equal to the enlargement of the excited level k normalized to the enlargement of the first-level δ [12]. x_k is the relative population of the excited-state k.

The interactions between excited molecules with an averaged effective size at given T can be described by means of a single isotropic $(n-m)$ or $(n-\exp)$ potential. If the $(n-6)$ model is chosen, then the effective potential $U(r, T)$ is

$$U(r, T) = \frac{\varepsilon^{(\mathrm{eff})}}{n-6} \left\{ 6\left[\frac{r_m^{(\mathrm{eff})}}{r}\right]^n - n\left[\frac{r_m^{(\mathrm{eff})}}{r}\right]^6 \right\} \tag{2}$$

where r is the distance between the centers of mass of the two molecules and n is the repulsive parameter.

In Eq. (2), the effective equilibrium distance is

$$r_m^{(\mathrm{eff})}(T) = r_m(T=0) + \delta^{(\mathrm{eff})}(T) \tag{3}$$

and the effective potential well depth is

$$\varepsilon^{(\mathrm{eff})}(T) = \varepsilon(T=0)\left[\frac{r_m(T=0)}{r_m^{(\mathrm{eff})}}\right]^6 \tag{4}$$

The relation of Eq. (4) follows from the assumption that the long-range forces are not influenced by vibrational excitation. This assumption is not valid at very high temperatures, which are not considered here.

In both Eq. (3) and Eq. (4), $r_m(T=0)$ and $\varepsilon(T=0)$ are parameters of the ground state–ground state interactions.

3. NORMAL VIBRATIONAL FREQUENCIES OF $C(CH_3)_4$ AND $Si(CH_3)_4$

It is obvious that the temperature dependence of $r_m^{(\text{eff})}$ is implied in the dependence $C_k x_k(T)$, which is specific for a particular globular gas. It can be calculated accurately by means of the vibrational partition function $z(T)$ and then approximated with a high precision. The relative populations x_k with $\sum_{k=0}^{n_s} x_k(T) \equiv 1$ of n_s vibrational states are calculated as functions of temperature through the vibrational partition function

$$z(T) = 1 + \sum_{n=1}^{\infty} \sum_{v_i=0}^{n} \cdots \sum_{v_N=0}^{n-v_1-\cdots-v_{N-1}} \prod_{i=1}^{N} g_{v_i} \exp(-v_i \theta_i/T) \qquad (5)$$

N is the total number of normal vibrations, v_i is the quantum number of the vibrationally excited level of the ith normal vibration, and g_{v_i} is the corresponding degeneracy; $\theta_i = h v_i/k_B$, where v_i is the ith normal vibrational frequency; and h and k_B are the Planck and Boltzmann constants, respectively. The relative population of the ground state is $x_0 = 1/z$. For temperatures $T > 300$ K practically all heavy globular molecules are already vibrationally excited, and the number of states n_s which ensures the convergence of the partition function is quite large (e.g., $n_s \approx 200,000$ for UF_6).

The calculation of the vibrational partition function of complex molecules consisting of many atoms like TMM and TMS is a problem because of the lack of a full set of accurate normal vibrational frequencies. Here their number is $N = 3l - 6 = 45$, l being the number of atoms in the molecule. The harmonic vibrations are of types

$$\tilde{A}_v = 3A_1 + A_2 + 4E + 4T_1 + 7T_2$$

which can be presented by means of their degeneracies g_{v_i} as $n_v(1, 1, 1, 1, 2, 2, 2, 2, 3, 3, 3, 3, 3, 3, 3, 3, 3, 3, 3)$.

We have calculated the harmonic vibrational frequencies for $C(CH_3)_4$ and $Si(CH_3)_4$ via gradient-corrected density functional theory using the Gaussian 94 [13] suite of programs. We used the hybrid B3LYP functional

[14, 15] with the double-zeta polarized 6–31G(d,p) basis set. This methodology is known to yield accurate structural, thermochemical, and spectroscopic data for a wide variety of systems [16–18].

The geometry was optimized to yield minimal energy with full tetrahedral symmetry. The experimental geometry of both tetramethyl compounds is reproduced with a deviation of less than 0.02 Å for the bond lengths and smaller than $2°$ for the bond angles [19]. Harmonic vibrational frequencies were subsequently computed at this fully optimized geometry.

To complete our study, Raman spectra of neopentane (supplied by Linde AG, Germany; purity, 99%) were recorded at a pressure of 1 atm

Table Ia. Comparison of Experimental, Theoretical, and Best-Estimated Vibrational Frequencies for $C(CH_3)_4$

		Frequency (cm^{-1})						
		Experimental						
				Gas				
				Raman				
No.	Mode	Liquid Raman [6]	IR [6]	[20]	[21]	This work[a]	Harmonic (theoretical)	Best estimate
1	A_2						239	239
2	T_1						308	308
3	E	335		334	331.4	334w	335	335
4	T_2	415	418		414.8	416vw	422	415
5	A_1	733		733	731.4	733vs	731	733
6	T_2	921	925	927		931m	935	921
7	T_1						969	953
8	E						1099	1075
9	T_2	1249	1256	1256	1257	1256m	1284	1249
10	T_2		1372				1413	1365
11	A_1						1451	1400
12	T_1						1500	1444
13	E	1451		1458		1467m	1508	1451
14	T_2		1475				1536	1477
15	T_2	2863	2876			2874m	3032	2863
16	A_1	2909		2922		2923s	3041	2909
17	T_1						3103	2954
18	E	2955		2962		2963w	3104	2955
19	T_2	2955	2959				3109	2959

[a] Spectral conditions: laser line, 514.5 nm; laser power, 1500 mW; resolution, 2.5 cm^{-1}. vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

and a temperature of 296 K. To this end, a Spectra Physics 2017-06S Ar$^+$ laser was used as the excitation source, a Coderg T800 triple monochromator was used for the analysis, and an RCA C31034A photomultiplier was used for the detection of the 90° scattered radiation. No polarization analyzer was used.

Our calculated and experimental vibrational frequencies, as well as those available in the literature [6, 20, 21], for the liquid and the gas phase are presented in the corresponding columns in Tables Ia and Ib. The lowest seven modes involve C–C torsions, C–C–C deformations, and C–C stretches. For all these modes, the theoretical harmonic frequencies are quite accurate. The rest of the frequencies involve significant anharmonic hydrogen motions and, therefore, deviate systematically from the experiment. Due to the high

Table Ib. Comparison of Experimental, Theoretical, and Best-Estimated Vibrational Frequencies for $Si(CH_3)_4$

		Frequency (cm^{-1})					
			Experimental				
				Gas			
				Raman			
No.	Mode	Liquid Raman [6]	IR [6]	[21]	[20]	Harmonic (theoretical)	Best estimate
1	A_2	145				153	153
2	T_1	145				157	157
3	E	199		190.7	190.5	180	180
4	T_2	245		239.0	239	223	223
5	A_1	593		592.2	593	573	573
6	T_2	694	696	694.5	698	692	683
7	T_1	829	829			700	690
8	E	859	871		870	845	827
9	T_2					900	879
10	T_2	1250	1253		1257	1309	1264
11	A_1	1263			1271	1316	1270
12	T_1	1416	1416			1472	1417
13	T_2	1418	1430			1474	1419
14	E	1418			1421	1489	1433
15	A_1	2900			2913	3034	2888
16	T_2	2900	2900			3037	2891
17	E	2957			2964	3111	2960
18	T_2	2957	2957			3112	2961
19	T_1	2966	2966			3115	2964

frequencies of these vibrations, this slight mismatch does not introduce any significant error in the vibrational partition function at temperatures below 800 K.

4. COMPUTATIONAL PROCEDURE

The procedure for determining the ITDP parameters n, $\varepsilon^{(\text{eff})}(T)$, and $r_m^{(\text{eff})}(T)$ is based on solving an ill-posed problem of minimization of the sum F of squared deviations between calculated and measured B, η, and β normalized to their relative experimental error a_{exp} [22]. In all cases we have used classical formulas for the calculation of the thermophysical properties. In the case of TMM and TMS, quantum corrections are found to be completely negligible at temperatures $T > 250$ K [23].

The processing of the data requires several rather elaborate and time-consuming computational procedures, such as calculation of the normal vibrational frequencies and the vibrational partition function. The next equally complicated step is the scanning of the multidimensional function in wide limits of the potential parameters. This procedure permits the localization of several minima of $F(M, n, \varepsilon, r_m, \delta)$, M being the number of experimental input data. After scanning, the Newton method for detection of minima is applied. More details can be found in Ref. 4.

5. EXPERIMENTAL INPUT DATA

In Table IIa, we present a short review of all published thermophysical and spectroscopic measurements of gaseous $C(CH_3)_4$ which report on properties which can be used in this work. The thermophysical data used for $Si(CH_3)_4$ are given in Table IIb.

5.1. Tetramethylmethane

The second (pVT)-virial coefficients B have been reported in 13 works for pure $C(CH_3)_4$ [24–36] and in one for mixtures with CH_4 (B_{mix}) [25]. Strictly speaking, the results in Refs. 26 and 32 should be considered as spectroscopic data since they have been derived from measured refractivities. However, these published data depend on some models with unknown input parameters. Therefore, they are not considered in what follows. The data of Schramm's group [33, 34] have also been given only for the sake of completeness. These data, as already mentioned by Ewing et al. [37, 38], are systematically in error [39] and are not taken into account.

Table IIa. Experimental Data of TMM

Property	Reference	Substance[a]	M^b	ΔT (K)	$a_{exp}^{\ c}$ (%)
Second (pVT)-virial coefficient					
Pure gas					
1	Beatie et al., 1952 [24]		6 (*B*)	433.75–548.15	10
2	Hamann et al., 1955 [25]		11 (*B*)	303.15–403.15	10
3	Ashton and Halberstadt, 1958 [26]		4 (*B*)	300.35–342.30	10
4	Heichelheim and McKetta, 1963 [27]		9 (*B*)	303.15–473.15	1.2–3
5	Perez Masia et al., 1963 [28]		5 (*B*)	303.22–397.70	1.6–3
6	Silberberg et al., 1967 [29]		9 (*B*)	303.15–473.15	2
7	Dawson et al., 1973 [30]		9 (*B*)	348.15–498.15	0.8–1.5
8	Das et al., 1977 [31]		14 (*B*)	303.15–548.15	5
9	Kerl and Häusler, 1984 [32]		9 (*B*)	260.74–365.70	1–4
10	Strein et al., 1971 [33]		11 (*B*)	296.15–492.6	1
11	Bellm et al., 1974 [34]		10 (*B*)	300.0–550.0	1–3
12	Ewing and Marsh, 1979 [35]		3 (*B*)	303.15–346.15	0.5–0.8
13	Hossenlopp and Scott, 1981 [36]		8 (*B*)	264.81–303.50	1–2.6
	All *B* data		108		

Mixtures

14	Hamann et al., 1955 [25]	$C(CH_3)_4 + CH_4$	40 (B_{mix})	303.15–403.15	10
			8 (B_{12})		
15	Dantzler Siebert and Knobler, 1971 [40]	$C(CH_3)_4 + CF_4$	1 (B_{12})	323.15	10
16	Boughan et al., 1975 [41]	$C(CH_3)_4 + CH_4$	7 (B_{12})	199.9–258.9	10
17	Strein et al., 1971 [33]	$C(CH_3)_4 + CH_4$	11 (B_{12})	296.15–492.6	1–3
18	Bellm et al., 1974 [34]	$C(CH_3)_4 + SF_6$	10 (B_{12})	300.0–550.0	>10
	All B_{mix} data		40		
	All B_{12} data		37		

Second acoustic virial coefficient

19	Ewing et al., 1987 [37]		8 (β)	250.00–323.15	1

Viscosity

20	McCubrey, 1957 [42]		6 (η)	305.2–457.5	1
21	Gonzales et al., 1968 [43]		5 (η)	310.2–444.2	1
22	Diaz Pena and Esteban, 1966 [44]		16 (η)	263.35–393.15	1
23	Lambert et al., 1955 [45]		4 (η)	323.15–351.15	1
	All η data		31		

[a] Unless otherwise noted, the substance is neat $C(CH_3)_4$.
[b] Number of experimental data.
[c] Accepted relative experimental error.

Table IIb. Experimental Data of TMS

Property	Reference	M^a	ΔT (K)	$a_{exp}{}^b$ (%)
Second (pVT)-virial coefficient (pure gas)				
1	Hamann et al., 1955 [25]	6	323.0–403.0	10
2	Bellm et al., 1974 [34]	10	300.0–550.0	?
3	Bottomley and Nairn, 1977 [46]	32	333.0–539.0	0.5–2.2
4	Marcos et al., 1983 [47]	7	423.0–572.0	10
	All B	55	300.0–572.0	
Viscosity				
5	Diaz Pena and Esteban, 1966 [44]	17	263.0–413.0	1

[a] Number of experimental data.
[b] Accepted relative experimental error.

Measured second acoustic virial coefficients β of neopentane are reported by Ewing et al. [37, 38]. The second mixture, B_{mix} (TMM–CH_4 [25]), and interaction second virial coefficients B_{12} (TMM–CF_4 [40], TMM–CH_4 [25, 33, 41], and TMM–SF_6 [34]) in Table IIa have been used only for comparison with our calculations.

Experimental data on pure gas viscosities have been published in four works [42–45]. The set of normal frequencies for TMM (Table Ia) was used to calculate the vibrational partition function $z(T)$ [Eq. (5)] and to define $C_k x_k$ in the temperature range $T = 200$ to 900 K. To scan the potential surface, we put into the minimization procedure 74 experimental values of B [24, 25, 27–31, 35, 36], all 31 pure-gas viscosities η [42–45], and 8 experimental data for the second acoustic virial coefficient β [37]. The experimental viscosity values in Refs. 42 and 43 are measured with an accuracy of 1% and are in good agreement in the complete temperature range $T = 300$ to 460 K. In the case of the other η values, we also assume a 1% accuracy, although no error bars are given in the literature [44, 45]. The accuracy of the second acoustic virial coefficients is also set to 1%.

5.2. Tetramethylsilane

The thermophysical properties of TMS are much less investigated than those of TMM. Altogether 55 values of B measured in the temperature range between 323 and 572 K have been reported in four papers [25, 34, 46, 47]. The results in Ref. 47 resolved the existing discrepancy between already published data and finally confirmed those in Refs. 25 and 46 against those in Ref. 34. The viscosity was measured only by Diaz Pena and Esteban [44], who determined 17 values of η in the range between 263 and 413 K. As in the case of TMM, the accuracy has not been discussed by the authors, and we assumed 1% as a reliable estimate. Unfortunately, in the case of TMS no second acoustic virial coefficients β are available in the literature. Recently it has been shown by different authors that precisely determined β values are an important experimental source for the determination of intermolecular interaction potentials [48, 49]. Therefore, the minimization was carried out only with the B data reported in Refs. 25, 46, and 47 and the viscosities given in Ref. 44.

6. RESULTS AND DISCUSSION

The parameters ε/k_B, r_m, n, and δ of the isotropic temperature-dependent potentials at $T = 0$ K of TMM and TMS are given in Table III.

Table III. Parameters of the Isotropic Temperature-Dependent Potentials at $T = 0$ K
Determined in this Work

Substance	r_m (10^{-10} m)	ε/k_B (K)	N	δ (10^{-12} m)
$C(CH_3)_4$	5.7790(30)	586.32(42)	28.02(12)	1.41(3)
$Si(CH_3)_4$	5.9051(36)	674.75(91)	20.79(11)	1.88(3)

To visualize the temperature dependence of these potentials, we have plotted them for three temperatures in Fig. 1.

The corresponding B, η, and β deviation plots for TMM and TMS (Figs. 2a and 2b, respectively) show how the experimental values of the different authors differ from our calculations (zero line). The so-called "jack-knife" [50] procedure proved the self-consistency of all data.

In the case of TMM, we observe a rms deviation of all input data of $1.20a_{exp}$. For about 85% of all 113 points, the deviation is within the frame of $\pm 1.5a_{exp}$, and for approximately 67% it does not exceed $\pm 1a_{exp}$. The deviations are symmetrically situated with respect to the zero line. The largest deviations are found at temperatures of 300 and 370 K.
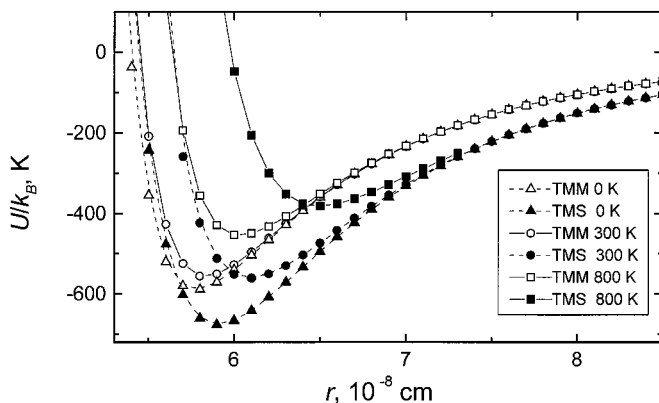

Fig. 1. Isotropic temperature-dependent potentials of TMM and TMS
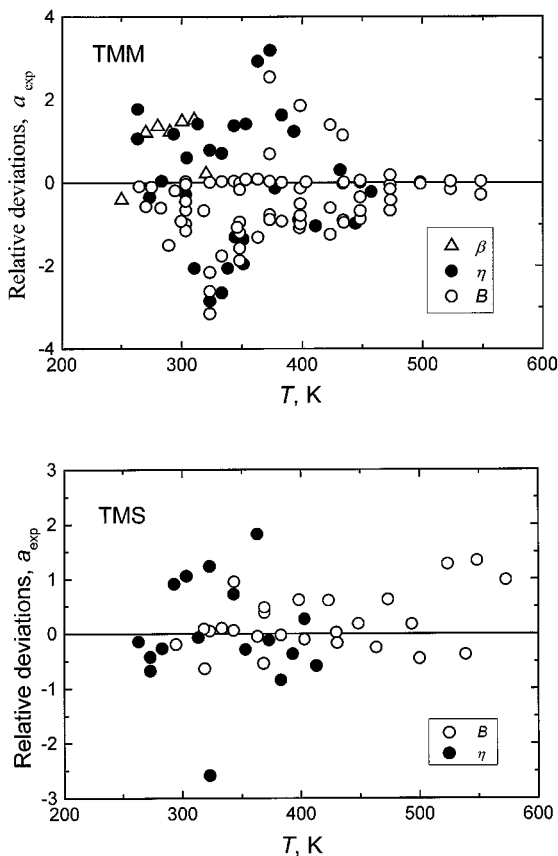obtained in this work.

Fig. 2. Relative deviation between experimental and calculated values normalized to their experimental uncertainty a_{exp}. (a) TMM. (b) TMS.

For TMS, the deviation plot in Fig. 2b illustrates an acceptably good fit in the whole temperature range between the experimental values of B and η, respectively, and our calculations. The two of the three viscosity deviations exceeding $1a_{exp}$ are obviously a random effect because, measured at almost-equal temperatures, they have also different signs (1.24 % at 322.9 K and -2.56 % at 323.12 K). The majority of B and η deviations are in the frame of one experimental error a_{exp}. No systematic deviations are observed, and the rms deviation is $0.68a_{exp}$.

Calculated $r_m^{(eff)}(T)$, $\varepsilon^{(eff)}(T)$, $B(T)$, $\eta(T)$, and $\rho D(T)$ for the temperature range 250 to 800 K are given in Table IVa for TMM and Table IVb

Table IVa. Recommended Thermophysical Properties of Gaseous TMM Calculated by Means of ITDP

T (K)	r_m (10^{-8} cm)	ε/k_B (K)	$-B(T)$ (cm$^3 \cdot$ mol^{-1})	η (μPa $\cdot$ s)	ρD (g $\cdot$ m$^{-1} \cdot$ s^{-1})	β (cm$^3 \cdot$ mol^{-1})
250.0	5.8201	561.87	1293.97	6.111	7.958	−2125.66
260.0	5.8235	559.92	1184.09	6.321	8.239	−1984.91
270.0	5.8269	557.96	1088.37	6.531	8.519	−1837.32
277.0						−1744.24
280.0	5.8304	555.98	1004.32	6.741	8.798	
287.0						−1622.89
290.0	5.8339	553.98	929.96	6.951	9.077	
300.0	5.8374	551.95	863.73	7.1612	9.356	−1482.32
310.0	5.8411	549.90	804.37	7.372	9.634	−1386.62
320.0	5.8448	547.82	750.90	7.583	9.911	
323.15						−1259.22
330.0	5.8485	545.71	702.49	7.794	10.187	
340.0	5.8523	543.59	658.46	8.006	10.462	
350.0	5.8562	541.45	618.26	8.217	10.737	
360.0	5.8601	539.30	581.41	8.428	11.010	
370.0	5.8640	537.13	547.52	8.638	11.282	
390.0	5.8719	532.78	487.29	9.060	11.824	
400.0	5.8760	530.59	460.42	9.271	12.094	
420.0	5.8841	526.22	412.10	9.692	12.631	
440.0	5.8923	521.84	369.85	10.112	13.165	
460.0	5.9005	517.47	332.60	10.529	13.693	
480.0	5.9089	513.09	299.49	10.942	14.210	
500.0	5.9173	508.72	269.87	11.351	14.718	
520.0	5.9258	504.36	243.20	11.757	15.222	
540.0	5.9344	500.01	219.07	12.161	15.723	
560.0	5.9430	495.68	197.11	12.562	16.220	
580.0	5.9517	491.37	177.05	12.958	16.710	
600.0	5.9604	487.09	158.64	13.346	17.192	
620.0	5.9691	482.83	141.69	13.728	17.663	
640.0	5.9778	478.62	126.02	14.104	18.125	
660.0	5.9865	474.44	111.50	14.475	18.580	
680.0	5.9953	470.29	97.99	14.843	19.029	
700.0	6.0041	466.19	85.39	15.207	19.472	
720.0	6.0128	462.13	73.62	15.566	19.909	
740.0	6.0216	458.11	62.58	15.918	20.339	
760.0	6.0303	454.14	52.22	16.263	20.761	
780.0	6.0391	450.21	42.47	16.600	21.176	
800.0	6.0478	446.34	33.27	16.931	21.584	

Table IVb. Recommended Thermophysical Properties of Gaseous TMS Calculated by Means of ITDP

T (K)	r_m $(10^{-8}$ cm$)$	ε/k_B (K)	$-B(T)$ $(\text{cm}^3 \cdot \text{mol}^{-1})$	η $(\mu\text{Pa} \cdot \text{s})$	ρD $(\text{g} \cdot \text{m}^{-1} \cdot \text{s}^{-1})$
250.00	6.0539	581.10	1769.41	6.017	7.871
260.00	6.0623	576.27	1605.90	6.230	8.162
270.00	6.0708	571.49	1465.17	6.444	8.455
280.00	6.0792	566.75	1342.93	6.661	8.748
290.00	6.0876	562.05	1235.86	6.879	9.042
300.00	6.0961	557.39	1141.39	7.098	9.337
310.00	6.1045	552.78	1057.46	7.319	9.632
320.00	6.1130	548.20	982.44	7.541	9.927
330.00	6.1214	543.67	915.01	7.764	10.221
340.00	6.1299	539.18	854.09	7.987	10.514
350.00	6.1384	534.74	798.81	8.211	10.807
360.00	6.1468	530.33	748.41	8.435	11.100
370.00	6.1553	525.97	702.30	8.660	11.392
380.00	6.1638	521.65	659.94	8.886	11.685
390.00	6.1722	517.38	620.91	9.112	11.979
400.00	6.1807	513.15	584.82	9.339	12.272
420.00	6.1976	504.81	520.26	9.788	12.856
440.00	6.2144	496.65	464.17	10.235	13.432
460.00	6.2313	488.66	414.99	10.687	13.995
480.00	6.2480	480.84	371.51	11.140	14.549
500.00	6.2648	473.19	332.78	11.584	15.103
520.00	6.2814	465.71	298.07	12.017	15.656
540.00	6.2980	458.40	266.76	12.444	16.202
560.00	6.3145	451.25	238.38	12.866	16.734
580.00	6.3310	444.26	212.53	13.286	17.251
600.00	6.3474	437.43	188.87	13.700	17.755
620.00	6.3636	430.75	167.14	14.107	18.250
640.00	6.3798	424.23	147.10	14.504	18.739
660.00	6.3960	417.86	128.55	14.892	19.220
680.00	6.4120	411.63	111.34	15.270	19.695
700.00	6.4279	405.54	95.30	15.639	20.162
720.00	6.4438	399.60	80.34	16.001	20.619
740.00	6.4595	393.78	66.33	16.355	21.064
760.00	6.4752	388.11	53.19	16.703	21.497
780.00	6.4907	382.57	40.83	17.043	21.918
800.00	6.5061	377.16	29.20	17.376	22.329

for TMS. In the case of $r_m^{(\mathrm{eff})}(T)$, $\varepsilon^{(\mathrm{eff})}(T)$, $\eta(T)$, and $\rho D(T)$, these data were fitted according to

$$P = \sum_{i=1}^{3} A_i (T/K)^{i-1} \tag{6}$$

where P is the property under consideration. In the case of $B(T)$, it is well known that an approximation of the following type is more suitable:

$$B(T) = \sum_{i=1}^{4} A_i (T/K)^{1-i} \tag{7}$$

The fitting constants A_i are given in Table V. They can be used for rapid and accurate estimations of the potential parameters and thermophysical properties in the range between 250 and 800 K. In the case of $\beta(T)$ reported for neopentane, we have made calculations only at the temperatures used by Ewing et al. [37]. To calculate this property, data on the heat capacities c_p must be known. However, to avoid further approximations, only the c_p data given in Ref. 37 are used.

Table V. Fit Parameters of Eqs. (6) and (7) Valid in the Temperature Range $T = 250$ to 800 K

	$C(CH_3)_4$				
Property	A_1	A_2	A_3	A_4	Δ (rms)[a]
r_m (10^{-8} cm)	5.72894(95)	$3.385(38) \times 10^{-4}$	$7.70(36) \times 10^{-8}$	—	0.00063
ε/k_B (K)	618.75(54)	$-0.2265(22)$	$1.27(21) \times 10^{-5}$	—	0.36
$B(T)$ (cm³·mol⁻¹)	316.7(1.7)	$-2.896(22) \times 10^5$	$2.451(93) \times 10^7$	$-1.317(12) \times 10^{10}$	0.36
η (μPa·s)	0.180(35)	0.02461(14)	$-4.52(14) \times 10^{-6}$	—	0.024
ρD (g·m⁻¹·s⁻¹)	0.138(23)	0.033050(94)	$-7.767(89) \times 10^{-6}$	—	0.016

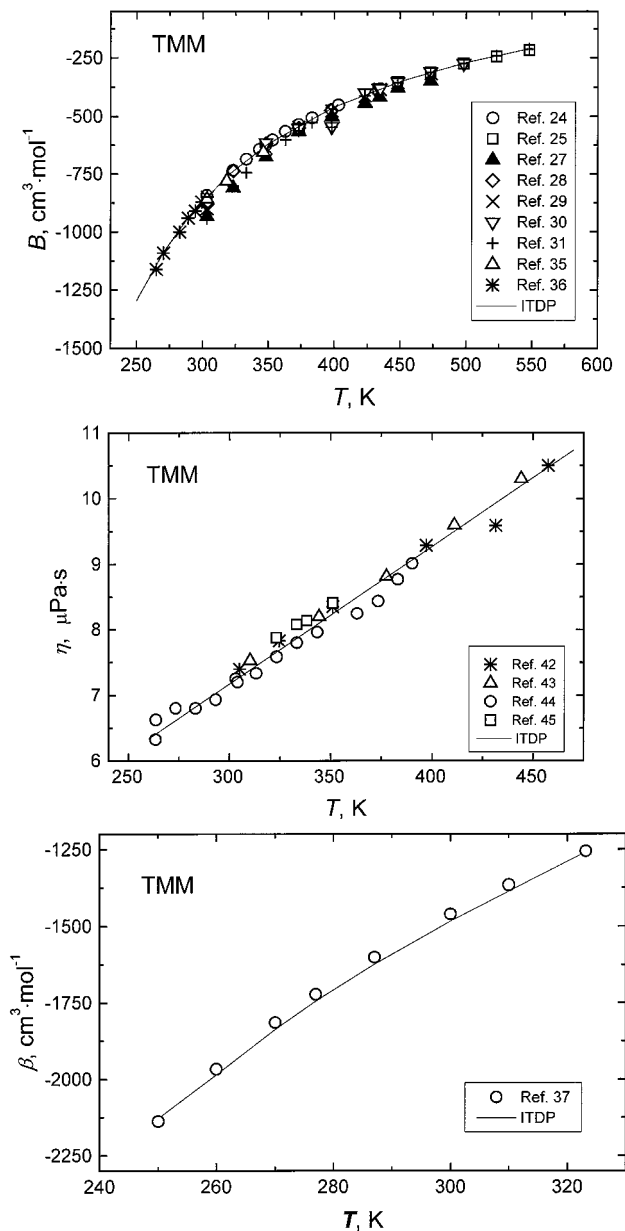|	$Si(CH_3)_4$				
Property	A_1	A_2	A_3	A_4	Δ (rms)[a]
r_m (10^{-8} cm)	5.83170(57)	$9.033(23) \times 10^{-4}$	$-7.42(22) \times 10^{-8}$		0.00038
ε/k_B (K)	713.77(20)	$-0.58211(83)$	$2.0226(78) \times 10^{-4}$		0.14
$B(T)$ (cm³·mol⁻¹)	444.0(4.3)	$-4.206(57) \times 10^5$	$6.52(24) \times 10^7$	$-2.454(31) \times 10^{10}$	0.93
η (μPa·s)	$-0.516(68)$	0.02709(28)	$-5.79(26) \times 10^{-6}$		0.046
ρD (g·m⁻¹·s⁻¹)	$-0.722(51)$	0.03630(20)	$-9.27(19) \times 10^{-6}$		0.034

[a] Standard deviation of fit.

Fig. 3. (a) Comparison of measured and calculated second (pVT)-virial coefficients $B(T)$ of TMM. (b) Comparison of measured and calculated viscosities $\eta(T)$ of TMM. (c) Comparison of measured and calculated second acoustic virial coefficients $\beta(T)$ of TMM.

In Figs. 3a–3c (TMM) and 4a and 4b (TMS), the experimental input data are compared to the results obtained using our ITDP. In all cases, an acceptable agreement can be seen. The viscosities in Fig. 3b show a considerable scatter, and only the data given by Lambert et al. [45] appear to be systematically too high. The second speed-of-sound virial coefficients β in Fig. 3c are slightly underestimated by our ITDP; however, the deviations are in the range of the accepted experimental uncertainties.
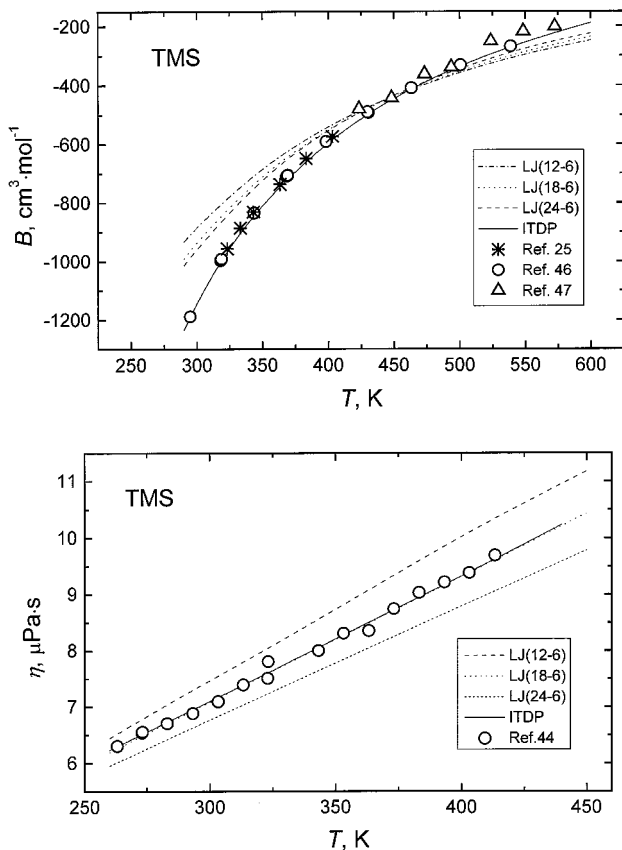
Fig. 4. (a) Comparison of measured and calculated second (pVT)-virial coefficients $B(T)$ of TMS. The solid line was obtained with our ITDP; the dashed lines, with other potentials (see text). (b) Comparison of measured and calculated viscosities $\eta(T)$ of TMS. The solid line was obtained with our ITDP; the dashed lines, with other potentials (see text).

6.1. TDP and Comparison with Other Available Potentials

In the case of TMM, we have also fitted the whole set of experimental input data to a Lennard–Jones (12–6) and a Lennard–Jones $(n-6)$ potential. In the first case, we obtain the parameters $\varepsilon/k_B = 368.0$ K and $r_m = 6.306 \times 10^{-10}$ m, whereas the latter gives $n = 34.906$, $\varepsilon/k_B = 573.8$ K, and $r_m = 5.806 \times 10^{-10}$ m. The rms deviation for all data points is $4.31 a_{\exp}$ in the case of the (12–6)-potential and $1.93 a_{\exp}$ for the $(n-6)$-potential. This demonstrates the superior quality of our ITDP. Collision-induced light scattering (CILS) is another valuable source for obtaining intermolecular interaction potentials. In some cases, CILS also gives a hint of a possible temperature dependence for these (effective) potentials [7, 8]. In the case of TMM, there is only one published work on the CILS spectra [10] in which the author has referred to the (12–6) Lennard–Jones potential with $\varepsilon/k_B = 417$ K and $\sigma_{(U(\sigma) = 0)} = 5.22 \times 10^{-10}$ m. This potential has not been published, and it is not clear why σ/r_m reported for a given value of $r_m = 6.09 \times 10^{-10}$ m is larger than $2^{1/6}$ as it should be for (12–6) L–J potentials.

In Fig. 5, different L–J $(n-6)$ potentials of TMS are compared with our ITDP, which is calculated for 400 K. An essential disagreement between the different potentials can be seen. This disagreement is also revealed in Figs. 4a and 4b, where the second (pVT)-virial coefficient and the viscosity are calculated by means of these potentials. The experimental $B(T)$ data can clearly be reproduced only with the ITDP proposed in this
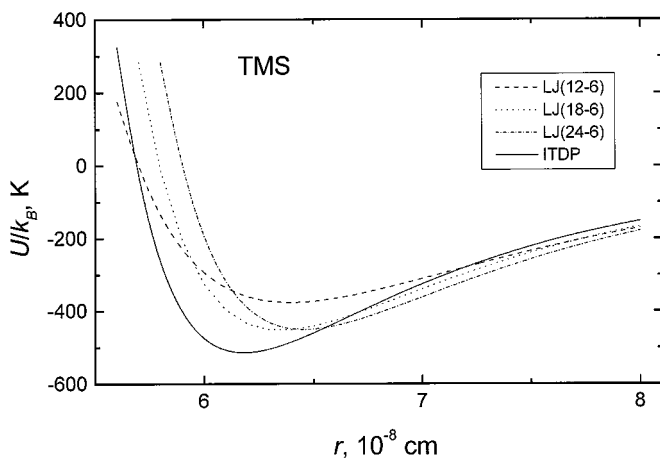

Fig. 5. Comparison of ITDP of TMS at $T = 400$ K with the isotropic potentials proposed in Ref. 11. Calculations performed with both LJ(24–6) potentials given in Ref. 11 practically coincide.

work. However, in the case of the viscosity of TMS, the L–J (18–6) potential gives an equally good fit to the experimental data compared to our ITDP.

6.2. Mixtures

A relatively systematic study of CH_4–$C(CH_3)_4$ mixture second (pVT)-virial coefficients is presented in Ref. 25. We calculated all 48 values of B_{mix} measured at eight temperatures and six mole fractions of CH_4 using our previously obtained parameters of methane ($n = 22.8$, $\varepsilon/k_B = 226.8$ K, $r_m = 3.815 \times 10^{-10}$ m, $\delta = 0$) [5]. The agreement between experimental values and our calculations is quite good in the frame of the accepted experimental error of 10%. As is apparent from the deviation plot given in Fig. 6, the coincidence is less than $-0.5a_{exp}$ (e.g., about 5–7%) for pure CH_4 (mole fraction $x = 0$) and close to zero in the case of pure $C(CH_3)_4$ ($x = 1$), which confirms the correctness of the potential parameters for both constituents [5]. For $x = 0.608$ and 0.696, the deviations are $(0.5$–$0.6)$ a_{exp}. The deviations are only slightly larger than $1a_{exp}$ for the two $x = 0.180$ and 0.357 mole fractions. Perhaps this fact can be explained by the lower accuracy in the determination of the corresponding mole fractions.

The discrepancy between our ITDP calculations and the published second virial coefficients B_{12} of unequal molecules [25, 40] is rather large ($> 2a_{exp}$). The only exception concerns $C(CH_3)_4$–CF_4 [40]. The single reported $B_{12} = -234.0$ cm$^3 \cdot$ mol^{-1} calculated at $T = 323.15$ K agrees fairly well with our calculation ($B_{12} = -247.0$ cm$^3 \cdot$ mol^{-1}). Even the calculations of Hamann et al. [25] derived from B_{mix}, which is well approximated
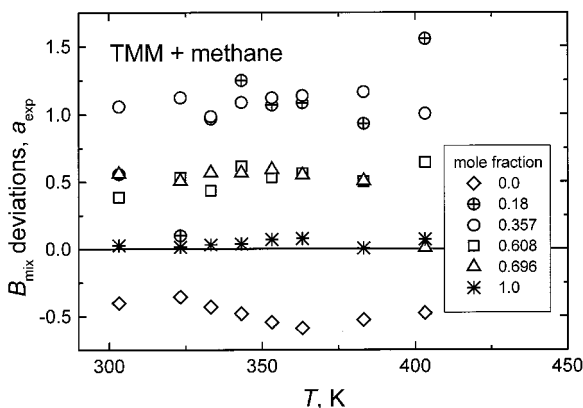

Fig. 6. Deviation plot of second mixture (pVT)-virial coefficients B_m of $C(CH_3)_4$–CH_4 mixtures [25].

by our ITDP, differ essentially from ours. These calculations involve potential parameters of the second constituent (CH_4, CF_4, or SF_6). Their choice is rather subjective and is not analyzed in this study.

7. CONCLUSION

We have determined isotropic temperature-dependent potentials (ITDP) for $C(CH_3)_4$–$C(CH_3)_4$ and $Si(CH_3)_4$–$Si(CH_3)_4$ interactions. In the case of $C(CH_3)_4$, the parameters are extracted from experimental sets of B, η, and β data, whereas in the case of TMS, only B and η data are available. For the first time, measurements of the second acoustic virial coefficient are included in the minimization procedure for the determination of the ITDP. We are confident that additional measurements of other potential-dependent properties will help us to validate the proposed potential parameters. Therefore, we continue to perform collision-induced light scattering measurements in our laboratory. Preliminary results already indicate that the ITDP of TMM gives a good fit of these experimental data, too.

It is essential to point out that the $Ge(CH_3)_4$, $Sn(CH_3)_4$, and $Pb(CH_3)_4$ thermophysical properties could also be predicted by means of ITDP defined on the basis of the results for TMM and TMS using the as yet unpublished sets of normal vibrational frequencies.

In this paper we have not explored the suitability of other potential models. Although the ITDP fits the available experimental data with an exceptional high accuracy, our studies do not exclude the possibility that other potential models (e.g., anisotropic or multicenter potentials) give at least an equally good representation of the experimental data. These studies, however, are outside the scope of this work.

ACKNOWLEDGMENT

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