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An improved intermolecular potential for sulfur hexafluoride

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Second virial coefficient data and viscosity were used to evaluate effective isotropic intermolecular potential functions proposed in the literature for sulfur hexafluoride. It was found that none of the potentials could predict the properties simultaneously. We have constructed a Morse–Morse–Spline–van der Waals (MMSV) potential which satisfactorily correlates second virial coefficient and viscosity data at the same time.

I. INTRODUCTION

This paper is concerned with the construction of an effective isotropic intermolecular potential for the pairwise interaction of SF₆. While it is true that the interaction could in principle be described best by an anisotropic potential, the data for this system, except for virials and viscosity, are rather sparse. For this reason, all the work done to date has involved isotropic potentials only. Such isotropic potentials nonetheless have provided good starting points in the search for anisotropic potentials (e.g., see Pack *et al.*¹ with respect to HeSF₆ and NeSF₆ interactions).

The development of an effective isotropic intermolecular potential has been more difficult than one might imagine. Several effective isotropic pair potential functions have been proposed to characterize the bulk properties of quasi-spherical molecules and, in particular, the hexafluorides, without much success. Generally these potentials have steeper repulsive walls than those which describe the rare gases. These include the Mie–Lennard–Jones (both 12–6 and 18–6), the 28–7 of Hamann and Lambert,² the hard-core potentials of Kihara³ and Dawe *et al.*,⁴ and the spherical shell model (SSM) of De Rocco and Hoover.⁵

The properties of viscosity and second virial coefficients for SF₆ were examined on the basis of these and other potential functions. None of the potential functions proposed in the literature could predict these properties simultaneously, but the 28–7 potential of Hamann and Lambert² showed some promise (e.g., McCoubrey and Singh⁶). In this potential, the individual 12–6 atomic interactions are summed for both central and shell atoms, and the resulting quantity is averaged for all orientations of the molecules. The expression for the resulting potential could be approximated by an n - m potential with n about 30 and m about 7. For mathematical convenience, they chose $n = 28$ and $m = 7$. The effect of increasing n and m is to narrow the well of the reduced curve, $V^*(x)$ vs x , where $x = r/r_m$ (Reed and Gubbins⁷). This behavior apparently compensates for the fact that the potential has an incorrect r^{-7} , rather than r^{-6} , asymptotic behavior. In spite of this serious deficiency, it was found that by adjusting the re-

pulsive exponent from 28 to 40, simultaneous predictions of viscosity and second virial coefficients could be significantly improved. Quite predictably, the potential, because of its incorrect long range behavior, predicts viscosities with deviations which increase in magnitude as the temperature decreases. Potential forms of the Hartree–Fock–dispersion type (HFD and HFD-B),^{8,9} which use an oversimplified damping function acting on all terms of the dispersion expansion together, were investigated and found not to provide a sufficiently repulsive wall to represent the experimental data when the accepted C_6 dispersion coefficient¹⁰ was used. A suitably repulsive potential form with some promise was found by using individual damping of the multipole expansion terms and by including a cubic term in the exponential function representing the repulsive component of the potential. However, this form is mathematically complex, and does not allow for easy adjustment of various parts of the potential. Hence we opted to use a piecewise potential of the Morse–Morse–Spline–van der Waals (MMSV) form employed previously as a convenient function by Lee and co-workers¹¹ and Pack and co-workers^{1,12} to represent the interactions of various spherical and roughly spherical molecules.

II. EXPERIMENTAL DATA

The only properties for which extensive data are available are those of viscosity and second virial coefficients. Viscosity data measured subsequent to 1970 appear to be self consistent. The most recent oscillating disc data of Strehlow and Vogel¹³ (298–673 K) appear to be the most accurate ($\pm 1\%$). These data are consistent with those of Timrot *et al.*¹⁴ (293–873 K). The capillary flow data of Harris *et al.*¹⁵ (218–302 K) and Dawe *et al.*⁴ (293–873 K) are somewhat less accurate, but these combined sets of data cover a broader temperature range. These data have an estimated error of about $\pm 1.5\%$, except for the data at lowest temperatures which are deemed by the authors to be less accurate. The most accurate value is expected to be the room temperature value of Strehlow and Vogel¹³ and this is the value to which the potential is fitted. Other data measured in the same period are those of Kestin *et al.*¹⁶

^{a)}EG&G Mound Applied Technologies is operated by EG&G Inc., for the U.S. Department of Energy, under Contract No. DE-AC04-88-DP43495.

(296–474 K), Ueda and Kigoshi¹⁷ (273–346 K), and Hoggland *et al.*¹⁸ (298–333 K).

According to Dymond and Smith¹⁹ the second virial coefficients for SF₆ are generally in good agreement. They have provided recommended values over the temperature range from 200–525 K, which were obtained by drawing a smooth curve through all the points. The error bars assigned to these values range from 15 mℓ/mol at 200 K to 2 mℓ/mol at 525 K. The data include those of MacCormack and Schneider²⁰ (273–523 K), Hamann *et al.*^{21,22} (293–448 K), Clegg *et al.*²³ (307–405 K), Mears *et al.*²⁴ (273–523 K), Bellm *et al.*²⁵ (300–550 K), Hahn *et al.*²⁶ (200–472 K), Sigmund *et al.*²⁷ (272–423), Hosticka and Bose²⁸ (323–374 K), Santafe *et al.*²⁹ (273–323 K), Hajjar and MacWood³⁰ (343–373 K), Nelson and Cole³¹ (323 K), Dymond and Smith¹⁹ (273–323), and Rigby¹⁹ (298–323 K).

For temperatures below 325 K (that is for reduced temperatures below T^* about 0.7) the Dymond–Smith correlation depends heavily on the data of Hahn *et al.*²⁶ (200–472 K). The values of this correlation function seem to drop off too rapidly below 325 K. That is, they become too negative. This is an often observed characteristic for low temperature measurements of the second virial coefficients. For example, in the case of argon where there is an abundance of data and where the potential well is accurately known, calculated values of the second virials are less negative than experimental ones.^{32,33} This behavior is even more evident in the case of krypton.³⁴ The data of Malyshch³⁵ (253–475 K), which incidentally contain a fair amount of scatter, seem to take a more reasonable trend before they, too, drop off too rapidly below 250 K. Because of the scatter in the data, we fitted all of the virial data above 250 K by the method of least squares to an empirical correlation function. The form of this relation was

$$B(T) = A + B/T + C/T^2 + D/T^3. \quad (1)$$

We also fitted the viscosity data measured after 1970 to the function

$$\ln \eta = A \ln T + B/T + C/T^2 + D. \quad (2)$$

The parameters for these functions are presented in Table I.

In our fitting procedure, we chose C_6 (= 597.5 a.u.) to be within 2% of the accurate dispersion coefficient calculated by Kumar *et al.*¹⁰ The other parameters of the potential were adjusted to provide the best fit to the viscosity values of Strehlow and Vogel¹³ and Smith and co-workers,^{4,15} the lower temperature second virials as given by Eq. (1), and the virial correlation of Dymond and Smith¹⁹ above 325 K.

III. THE POTENTIAL

The Morse–Morse–Spline–van der Waals (MMSV) functional form¹¹ is given by

$$V(r) = \epsilon V^*(x),$$

where

$$\begin{aligned} V^*(x) &= \exp\{-2\beta_1(x-1)\} \\ &\quad - 2 \exp\{-\beta_1(x-1)\}, \quad 0 < x \leq 1 \\ &= \exp\{-2\beta_2(x-1)\} \\ &\quad - 2 \exp\{-\beta_2(x-1)\}, \quad 1 < x \leq x_1 \\ &= a_1 + (x-x_1)\{a_2 + (x-x_2) \\ &\quad \times [a_3 + (x-x_1)a_4]\}, \quad x_1 < x \leq x_2 \\ &= -(c_6/x^6 + c_8/x^8 + c_{10}/x^{10}), \quad x > x_2. \end{aligned}$$

The parameters of the potential are given in Table II.

IV. RESULTS AND DISCUSSION

In Fig. 1, we present a “reverse” deviation plot where the points indicate the percentage deviations of the experimental data from the predictions of the potential represented by the reference line. The potential reproduces the room temperature result of Strehlow and Vogel to within $\pm 0.1\%$ and the rest of their data which go up to 673 K to within 1%. The data of Timrot *et al.* are also predicted to within $\pm 1\%$. The data of Dawe *et al.* from 550–900 K and Harris *et al.* from 233–300 K are also predicted to within 1%. In other words, all the reliable viscosity data are predicted by the potential.

In Fig. 2(a) we present the corresponding reverse deviation plot for virials showing the Dymond–Smith correlation and the data of Mears *et al.*²⁴ and MacCormack and Schneider.²⁰ The points represent the deviations of the experimental data from the predictions of the potential represented by the reference line. In Fig. 2(b) we present all the virial data to indicate that the scatter of the data is roughly symmetrically distributed about the reference line above 320 K and then the data points fall off in an increasing manner as T decreases. It is interesting to note from Fig. 2(a) that the potential almost perfectly predicts the virials of Mears *et al.*²⁴ above 307 K (solid squares). Below this temperature, their data appear to be too negative as indicated by the value of MacCormack and Schneider²⁰ (triangles) at 273 K. The tendency for experimental values to be too negative at low T^* values appears to be a common occurrence, as mentioned above.

In Table III we present rms deviations [for $B(T)$] and rms percentage deviations [for $\eta(T)$] from the experimental data for the present potential as well as for various literature potentials proposed for SF₆. Two columns are

TABLE I. Parameters for the least squares fitting functions.^a

	$B(T)$ [Eq. (1)]	$\eta(T)$ [Eq. (2)]
A	$+0.908\ 85 \times 10^2$	$+0.422\ 81$
B	$-0.338\ 31 \times 10^5$	$-0.284\ 60 \times 10^3$
C	$-0.220\ 67 \times 10^8$	$+0.211\ 36 \times 10^5$
D	$-0.122\ 24 \times 10^9$	$+3.333\ 0$
rms % deviation	2.5%	0.2%
Range of data	250–550 K	220–875 K

^aUnits are mℓ·mol⁻¹ for virials and μP for viscosity.

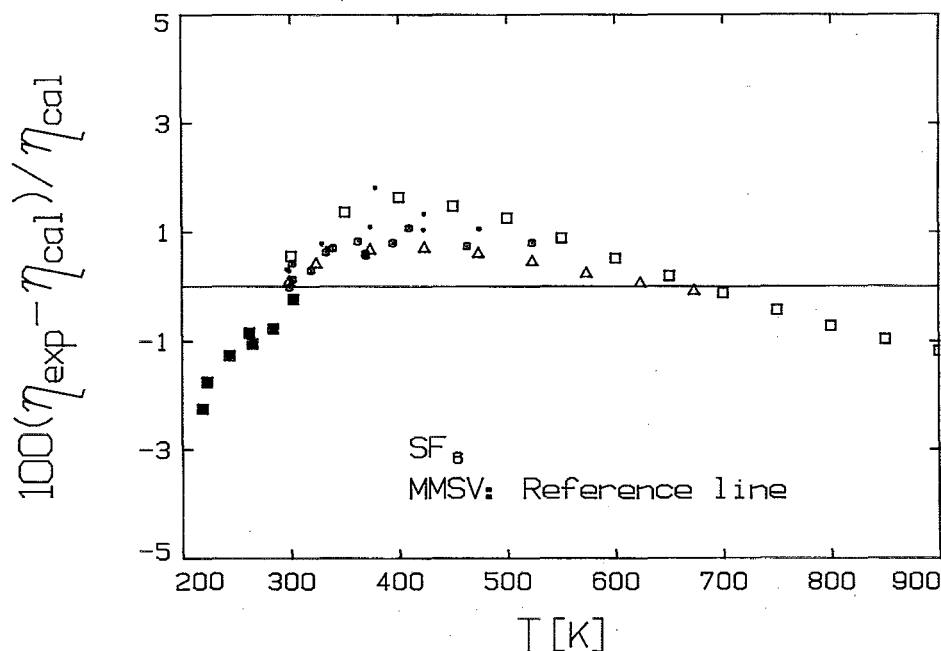


FIG. 1. Percentage deviations of the primary viscosity data from the predictions of the MMSV potential: (Δ) Strehlow and Vogel (Ref. 13); (\blacksquare) Harris *et al.* (Ref. 15); (\circ) Timrot *et al.* (Ref. 14); (\square) Dawe *et al.* (Ref. 4), and (\bullet) Kestin and Ro (Ref. 37).

shown for each property, B and η . For each of these properties the first column shows deviations of the potentials from selected experimental data, while the second column shows deviations of the potentials from the correlation functions of Eq. (1) (virials) and Eq. (2) (viscosity). These functions, as described above, were determined by a least-square fit to a large assortment of literature data. From an examination of the table, it is evident that the present MMSV potential provides the best overall reproduction of both viscosity and virial data.

V. CONCLUSION

In conclusion, we present an improved effective isotropic potential of the MMSV form for SF₆. The new potential incorporates the recent determination of the C_6 dispersion coefficient and it predicts the best viscosity and second virial data simultaneously in a manner better than any other literature potential.

TABLE II. Parameters for MMSV SF₆ potential. Not all figures displayed are significant. Some are shown only to avoid round off errors.

ϵ/k	[a.u.]	$= 1.431\,407 \times 10^{-3}$	ϵ/k	[K]	$= 452.0$
r_m	[a.u.]	$= 8.891\,16$	r_m	[Å]	$= 4.705$
σ	[a.u.]	$= 8.669\,552$	σ	[Å]	$= 4.5877$
C_6	[a.u.]	$= 597.5$	c_6		$= 0.844\,936\,426$
C_8	[a.u.]	$= 30\,000$	c_8		$= 0.536\,649\,157$
C_{10}	[a.u.]	$= 1\,500\,000$	c_{10}		$= 0.339\,424\,767$
r_1	[a.u.]	$= 9.918\,307\,946$	r_1	[Å]	$= 5.248\,542\,914$
r_2	[a.u.]	$= 13.114\,462\,14$	r_2	[Å]	$= 6.939\,875$
			x_1		$= 1.115\,524\,53$
			x_2		$= 1.475$
			β_1		$= 52.0$
			β_2		$= 6.00$
			a_1		$= -0.75$
			a_2		$= 1.772\,124\,09$
			a_3		$= -3.415\,743\,25$
			a_4		$= -0.258\,221\,01$

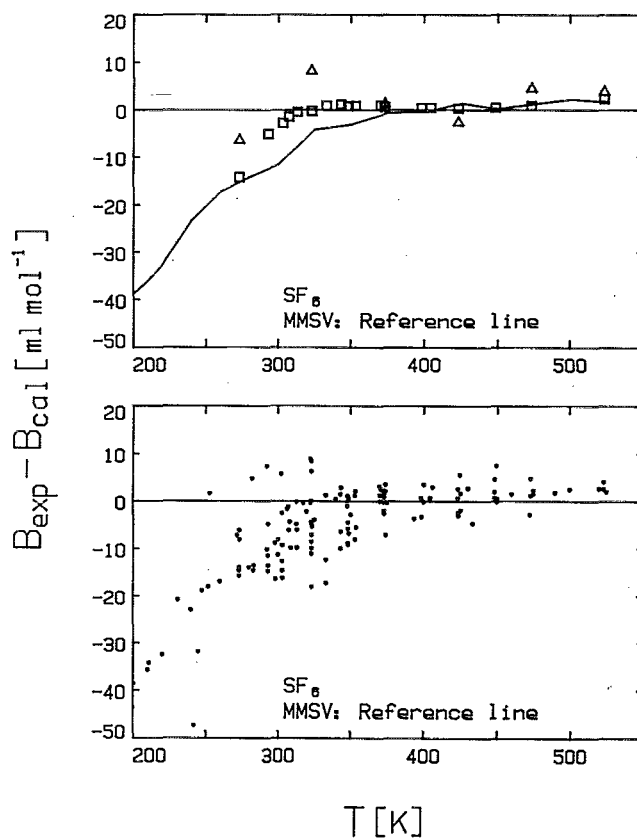


FIG. 2.(a) Deviations of the second virial correlation of Dymond and Smith (solid line) from the predictions of the MMSV potential. The deviations of the primary second virial coefficients from the predictions of the MMSV potential: (\square) Mears *et al.* (Ref. 24); (Δ) MacCormack and Schneider (Ref. 20). (b) Deviations of all second virial coefficient data (Refs. 19–31) from the predictions of the MMSV potential.

TABLE III. Rms deviations of SF₆ potentials from experimental data.

Potential	Reference	ϵ/k [K]	σ [Å]	r_m [Å]	$B(T)^a$	$B(T)^b$ [m ³ /mol ⁻¹]	$\eta(T)^c$	$\eta(T)^d$
MMSV	Present	452	4.5877	4.705	3.91	4.59	0.90	0.87
LJ 12-6	McCoubrey and Singh (Ref. 36)	155	5.46		98.90	103.54	2.14	2.06
LJ 12-6	Malyshev (Ref. 35)	170	6.5		18.28	19.33	30.72	31.39
LJ 12-6	Sigmund <i>et al.</i> (Ref. 27)	182	6.031		6.83	7.19	21.33	21.84
LJ 12-6	De Rocco and Hoover (Ref. 5)	186		6.72	9.70	6.49	20.74	21.18
LJ 12-6	Hamann <i>et al.</i> (Ref. 22)	188.7	5.91		8.43	5.51	19.07	19.47
LJ 12-6	McCoubrey and Singh (Ref. 36)	192	5.18		53.65	59.84	4.76	4.34
LJ 12-6	McCoubrey and Singh (Ref. 36)	195	5.71		6.10	7.96	14.30	14.57
LJ 12-6	De Rocco and Hoover (Ref. 5)	196		6.35	6.57	10.39	12.85	13.11
LJ 12-6	MacCormack and Schneider (Ref. 20)	200.9	5.51		9.88	15.50	8.94	9.09
LJ 12-6	Ueda and Kigoshi (Ref. 17)	225	5.15		11.87	17.62	1.15	1.11
LJ 12-6	Kestin and Ro (Ref. 37)	225.36	5.16		12.04	17.10	1.25	1.06
LJ 12-6	Ratzsch and Wohlfarth (Ref. 38)	252.06	4.80		15.99	22.65	10.23	11.33
LJ 12-6	Ratzsch and Wohlfarth (Ref. 38)	253.05	4.80		16.40	22.57	10.06	11.18
LJ 12-6	Ellis and Raw (Ref. 39)	259	5.01		44.17	41.32	2.14	2.43
LJ 28-7	Hamann and Lambert (Ref. 2)	414		5.37	9.16	7.35	10.04	10.03
LJ 28-7	McCoubrey and Singh (Ref. 6)	439	4.68		7.56	9.18	2.04	2.16
LJ 40-7	Aziz and Taylor (Ref. 40)	494.7		4.9437	5.10	4.24	1.60	1.47
SSM1	Sigmund <i>et al.</i> (Ref. 27)	423.4		5.326	3.65	2.57	8.56	8.82
SSM2	Sigmund <i>et al.</i> (Ref. 27)	425		5.327	4.01	2.29	8.71	8.96
SSM1	De Rocco and Hoover (Ref. 5)	335		5.78	8.08	5.43
SSM2	De Rocco and Hoover (Ref. 5)	434		5.18	3.22	1.74	4.27	4.42

^aRms deviations from the data of Refs. 20 and 24.^crms % deviations from data of Refs. 4 and 13–16.^brms deviations from correlation Eq. (1).^drms % deviations from correlation Eq. (2).

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