

## INTERMOLECULAR POTENTIALS AND THERMOPHYSICAL PROPERTIES OF LARGE GLOBULAR MOLECULES

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**Abstract.** The goal of this work is to prove the applicability of the isotropic temperature-dependent potential (ITDP) to some polyatomic globular molecules and to obtain reliable data for their transport and equilibrium properties. The four parameters of this effective Lennard-Jones type potential are determined by minimization of the weighted sum of squared deviations between experimental and calculated viscosity and second virial coefficient data.

First results are obtained for the molecules tetramethylmethane,  $C(CH_3)_4$ , and tetramethylsilane,  $Si(CH_3)_4$ . The intermolecular potentials (IP) obtained are used to calculate reliable data for viscosity, self-diffusion and second virial coefficients in the temperature range between 250 and 800 K. These data might be useful for modeling mass transport relevant in chemical-vapor deposition (CVD). Consequences for the IP of the higher homologues  $Ge(CH_3)_4$ ,  $Sn(CH_3)_4$ , and  $Pb(CH_3)_4$  are discussed.

**1. Introduction.** Polyatomic molecules of the type  $X(CH_3)_4$ , ( $X = C, Si, Ge, Sn$  or  $Pb$ ), recently have attracted much interest because all of them find an important impact on the quality and/or the price of the life. Some of them like  $Ge(CH_3)_4$  [1] and  $Si(CH_3)_4$  [2,3] find applications in semiconductor industries and chemical vapor deposition (CVD) technologies. Others like  $Pb(CH_3)_4$  have been important additives in fuels [4] and are therefore relevant to flame-combustion processes. Moreover, especially  $Pb(CH_3)_4$  contributes to the increase of heavy metals and harmful radicals in the atmosphere and the environment. Understandably there is a need for having reliable data on thermophysical properties (TP) of these gases.

We will concentrate on only two gases, tetramethylmethane (TMM),  $C(CH_3)_4$ , and tetramethylsilane (TMS),  $Si(CH_3)_4$ . There is an appreciable amount of TP data available for TMM. These include measurements on the gas-phase viscosity  $\eta$ , and on the second  $pVT$  ( $B$ )- and acoustic ( $\beta$ ) virial coefficients. For TMS, only few experimental data on  $\eta$  and  $B$  are given in the literature. For both gases the IP obtained with different methods and different input data are not able to reproduce all measured values. In the case of the other tetramethyl compounds no experimentally determined gas-phase TP data are available. Of course, these data can be estimated from suitable IP. At the moment, however, reliable potentials do not exist.

The goal of our study is to fit simultaneously all available experimental TP data for a given compound by means of an ITDP. The potential parameters achieved can be used for e.g. prediction of temperature-dependent equilibrium and transport properties in a temperature range that exceeds the range of the existing experimental data.

**2. Procedure of defining the ITDP parameters.** The isotropic temperature-dependent potential  $U(r,T)$  is a LJ (n-6) potential can be written as

$$U(r,T) = \frac{\varepsilon(T)}{n-6} \left\{ 6 \left[ \frac{r_m(T)}{r} \right]^n - n \left[ \frac{r_m(T)}{r} \right]^6 \right\}, \quad (1)$$

where  $r_m(T)$  is a temperature-dependent distance between two interacting molecules at which  $U=\varepsilon$ . It is defined as  $r_m(T) = r_m(T=0) + \delta(T)$  - Here  $\delta(T)$  is an effective enlargement of the molecule which can be calculated with the aid of the vibrational partition function. The effective temperature-dependent well-depth  $\varepsilon(T)$  is subsequently calculated via

$$\varepsilon(T) = \varepsilon(T=0) \left[ \frac{r_m(T=0)}{r_m(T)} \right]^6. \quad (2)$$

Therefore, the ITDP is an effective potential with slightly temperature dependent parameters  $r_m$  and  $\varepsilon$  reflecting the vibrational excitation of the molecule. In brief, we calculate this dependence via the vibrational partition function. In general the four parameters  $n$  (repulsive parameter),  $r_m$ , (equilibrium distance at  $T=0$  K),  $\varepsilon$  (potential well depth at  $T=0$  K), and  $\delta$  (the enlargement of the molecule when excited from the ground state to the first vibrationally excited level) are obtained by minimizing the sum  $P$  of the weighted squared deviations between the experimental and calculated thermophysical ( $B, \beta, \eta$ ) input data.

Following the model described above we have built up an efficient computational code that enables us to make different kind of calculations. The only input data needed are the molecular mass, the normal vibrational frequencies, and the experimental data with their relative experimental errors.

The universality and the reliability of the model and the computational procedure have been proved in our recently published results for a number of globular molecules ([5-7]).

**3. Results.** The potential parameters ( $\varepsilon$  in K,  $r_m$  in  $10^{-8}$  cm and  $\delta$  in  $10^{-10}$  cm) obtained in this work for TMM and TMS are given in Table 1. In Fig. 1 an example of the ITDP is given for both gases at different temperatures.

Table 1. ITDP Parameters.

Gas	$\varepsilon$	$r_m$	$n$	$\delta$	$m_B$	$m_\eta$	$m_\beta$	rms
TMM	586.3	5.779	28.02	1.41	74	29	8	1.20
TMS	674.8	5.905	20.79	1.88	38	17	-	0.74

( $m_B, m_\eta, m_\beta$  - number of the measured values of  $B, \eta$  or  $\beta$  taken into consideration, respectively; rms

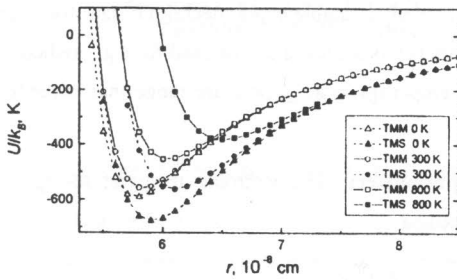


Fig. 1. Inter-molecular potentials for TMM and TMS  
Calculated at different temperatures

The TP of both TMM and TMS vapors have been calculated using the corresponding ITDP parameters (Table 1). Our calculations are compared with the experimental ones on figures 2a, 2b and 2c ( $B$ ,  $\eta$ ,  $\beta$  of TMM, correspondingly) and 3a, 3b ( $B$ ,  $\eta$  of TMS). In general, all experimental data for both substances are fitted with good accuracy with respect to the experimental error. This observation allows for a reliable prediction of recommended  $B$ ,  $\eta$ , and  $\rho D$  ( $\rho$  – density,  $D$  – diffusion coefficient) in an extended temperature range between 250 and 800 K. Tabulated temperature dependencies can be re-approximated by convenient algorithms and used for easy estimations. One can make calculations by means of ITDP at fixed temperatures as easy as with a LJ (n-6) potential using the repulsive parameter  $n$  (Table 1) and tabulated temperature dependencies of the effective potential parameters  $r_m(T)$  and  $\varepsilon(T)$ .

**4. Conclusion.** The observed convergence of the simultaneous fit of different available transport and equilibrium data proved the validity of the ITDP approach to the gases TMM and TMS. The so defined IP can be used for calculations of different potential-dependent properties. Tabulated  $B(T)$ ,  $\eta(T)$ ,  $\rho D(T)$  are convenient for interpolation and may be useful for estimations at temperatures out of the experimental temperature range. Our future projects are concerned with the possibility of finding a way to determine the IP of the tetramethyl compounds of Ge, Sn, and Pb, for which gas-phase TP are not yet investigated.

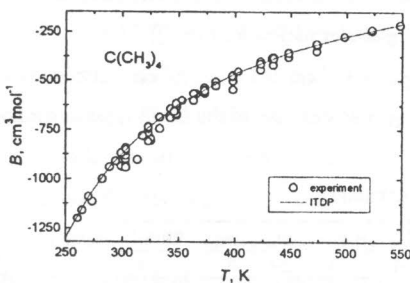


Figure 2a. Second virial coefficient of TMM

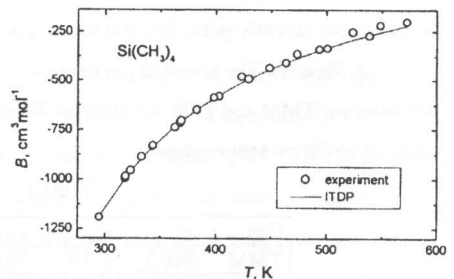


Figure 3a. Second virial coefficient of TMS

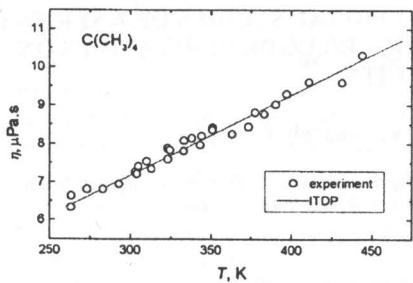


Figure 2b. Viscosity of TMM

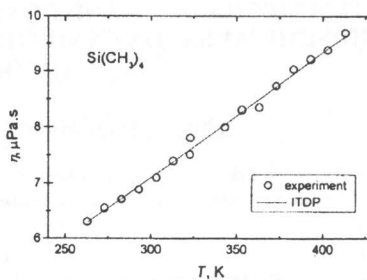


Figure 3b. Viscosity of TMS

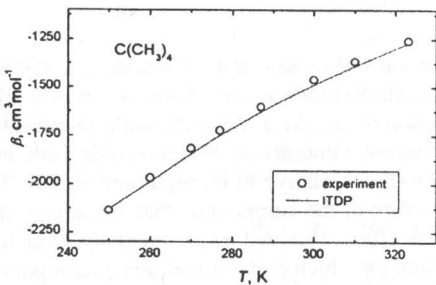


Figure 2c. Second acoustic virial coefficient of TMM

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