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Direct Determination of the Intermolecular Pair-Potential Energy Function of Methane from the Extended Principal of the Corresponding States

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The pair-potential energy function for methane has been determined using a direct inversion of the experimentally reduced viscosity collision integrals obtained from the corresponding-states correlation. The potential obtained in this way is in reasonable agreement with the potential independently known from the crossed molecular-beam technique.

The importance of intermolecular forces has been responsible for their extensive study for many decades. In the early 1970s most information concerning intermolecular forces was inferred from studies of the thermophysical properties.[1] Measurements of the viscosity of gases, for example, are used to estimate the intermolecular interaction that must produce this physical property. However, the direct determination of the intermolecular potential-energy function from this method has been proved to be extremely difficult. Despite many attempts, only in a few limited cases have been it proved possible. The functions resulting from this method do not appear to be unique.

On the other hand, a direct inversion of thermophysical data appears to be more successful, and yields a unique potential function.

In this paper we present a pair potential-energy function for methane which was calculated using the inversion method based on the experimental reduced-viscosity collision integral obtained from corresponding-states correlation.[2] Included are a comparison of our potential with two determined potentials.[3,4]

The coefficient of viscosity, η, of a dilute gas is[5]

$$\eta = \frac{5}{16}\frac{(\pi m K_B T)^{1/2}}{\overline{\Omega}^{(2,2)}} f_\eta, \tag{1}$$

where m is the molecular mass, T the temperature, K_B Boltzmann's constant, f_η a factor close to unity, and $\overline{\Omega}^{(2,2)}$ a so-called collision integral. It is convenient to reduce $\overline{\Omega}^{(2,2)}$ by dividing it by its corresponding rigid-sphere value. The unitless values are indicated by the notation $\Omega^{(2,2)*}$.

Inversion Procedure

The procedure is similar to that described in a previous paper[6] for Ar–Xe, Kr–Xe, and Ar–Kr, expect that here the temperature range is more restricted ($T^* \geq 1$, where $T^* = K_B T/\varepsilon$ and ε is the potential well-depth parameter). The same principle of corresponding states is utilized for the transport coefficients of molecular gases, as was used for the noble gases in the middle- and high-temperature ranges:[2]

$$1 \leq T^* \leq 10,$$
$$T^* \geq 10.$$

The results for the viscosity-collision integrals are

$$\begin{aligned} &1 \leq T^* \leq 10, \\ &\Omega^{(2,2)*} = \exp[0.46641 - 0.56991(\ln T^*) \\ &\qquad + 0.19591(\ln T^*)^2 - 0.03879(\ln T^*)^3 \\ &\qquad + 0.00259(\ln T^*)^4], \end{aligned} \tag{2a}$$

$$\begin{aligned} &T^* \geq 10, \\ &\Omega^{(2,2)*} = (\rho^*)^2\alpha^2[1.04 + a_1(\ln T^*)^{-1} \\ &\qquad + a_2(\ln T^*)^{-2} + a_3(\ln T^*)^{-3} + a_4(\ln T^*)^{-4}]. \end{aligned} \tag{2b}$$

where

$$\begin{aligned} &a_1 = 0, \\ &a_2 = -33.08338 + (\alpha_{10}\rho^*)^{-2}[20.0862 \\ &\qquad + (72.1059/\alpha_{10}) + (8.27648/\alpha_{10})^2], \\ &a_3 = 101.571 - (\alpha_{10}\rho^*)^{-2}[56.4472 \\ &\qquad + (286.393/\alpha_{10}) + (17.7610/\alpha_{10})^2], \\ &a_4 = -87.7036 + (\alpha_{10}\rho^*)^{-2}[46.3130 \\ &\qquad + (277.146/\alpha_{10}) + (19.0573/\alpha_{10})^2], \end{aligned}$$

in which $\alpha_{10} = \ln(V_0^*/10)$ is the value of $\alpha = \ln V_0^* - \ln T^*$ at the matching point of $T^* = 10$. The values of ρ^* and V_0^*, high-temperature dimensionless scaling parameters, are given in Ref. 2.

The direct inversion procedure for the viscosity is based on the idea that at a given T^* the value of $\Omega^{(2,2)*}$ is determined by the potential over only a small range of separation distances around a value r.[7] It is always possible to make this idea exact by defining a function G such that

$$U(r)=G_{\eta}\cdot T^{*}, \tag{3a}$$

and $\Omega^{(2,2)*}$ is approximately defined by

$$\Omega^{(2,2)*}=\left(\frac{r}{\sigma}\right)^{2}, \tag{3b}$$

where G_{η} is a temperature-dependent function changing from 0.72 at high temperatures to -0.561 at very low temperatures. However, despite this temperature variation, G_{η} is remarkably simialr for all reasonably realistic potential functions. Therefore, finding $U(r)$ from $\Omega^{(2,2)*}$ is straightforward when ε is equal to unity. Equations 2a and 2b can be inverted by the above method to yield $U(r)/\varepsilon$ as a function of r/σ. To do so, one inserts the value of G_{η}, given by Clancy and co-workers,[7] into Eq. 3a to obtain the potential-energy (U/ε); the corresponding value of r/σ may be obtained using the collision integral calculated from Eqs. 2a and 2b. This process may be repeated until convergence is obtained. At each step in the iteration process the percent deviation of the $\Omega^{(2,2)*}(T^{*})$ calculated from the potential and its correlated values $\Omega^{(2,2)^{*}}$ was determined. The convergence is usually obtained after only two iterations.[8,9] The values of the triple integral, ($\Omega^{(2,2)}$), are calculated using a computer program developed by O'Hara and Smith.[10,11] The value of σ turns out to be equal to the value σ_0, such that $U(\sigma_0)=0$; a precise value is $\sigma/\sigma_0=0.999$. We have obtained an accurate reduced potential by INVERT of the corresponding-states viscosity. This accurent potential can be used to obtain collision integrals needed to calculate the transport properties for methane. Three combinations of the collision integrals occur frequently enough in the expression for the transport coefficients of pure gases and mixtures to make it worth while giving them the following special symbols.

$$A^{*}=\Omega^{(2,2)*}/\Omega^{(1,1)*}, \tag{4a}$$

$$B^{*}=[5\Omega^{(1,2)*}-4\Omega^{(1,3)*}]/\Omega^{(1,1)*}, \tag{4b}$$

$$C^{*}=\Omega^{(1,2)*}/\Omega^{(1,1)*}. \tag{4c}$$

These three quantities are all very nearly unity. The most commonly needed collision integrals and their ratios are given in Table 1.

Table 1. Dimensionless Collision Integrals $\Omega^{(\ell,s)*}=\overline{\Omega}^{(\ell,s)}/\pi\sigma^{2}$ and the Related Ratios for CH_4–CH_4

$\log_{10} T^{*}$	$\Omega^{(1,1)*}$	$\Omega^{(2,2)*}$	A^{*}	B^{*}	C^{*}
0.0	1.4051	1.5622	1.1118	1.1931	0.8449
0.1	1.2673	1.4025	1.1067	1.1655	0.8571
0.2	1.1538	1.2714	1.1092	1.1418	0.8717
0.3	1.0614	1.1664	1.0989	1.1242	0.8868
0.4	0.9863	1.0832	1.0982	1.1128	0.9007
0.5	0.9248	1.0173	1.1000	1.1067	0.9125
0.6	0.8734	0.9641	1.1038	1.1041	0.9218
0.7	0.8294	0.9200	1.1092	1.1039	0.9284
0.8	0.7907	0.8819	1.1153	1.1059	0.9328
0.9	0.7556	0.8475	1.1216	1.1076	0.9355
1.0	0.7231	0.8152	1.1274	1.1086	0.9371
1.1	0.6926	0.7840	1.1320	1.1090	0.9381
1.2	0.6638	0.7535	1.1351	1.1082	0.9388
1.3	0.6365	0.7234	1.1365	1.1045	0.9398
1.4	0.6109	0.6934	1.1350	1.0979	0.9414
1.5	0.5871	0.6635	1.1301	1.0869	0.9445
1.6	0.5658	0.6338	1.1202	1.0698	0.9489
1.7	0.5474	0.6052	1.1056	1.0517	0.9552
1.8	0.5321	0.5790	1.0881	1.0755	0.9632
1.9	0.5202	0.5563	1.0694	1.0184	0.9715
2.0	0.5115	0.5379	1.0516	1.0061	0.9795

Results and Discussion

The intermolecular pair-potential for methane has been determined from the corresponding-states viscosity. We have inverted $\Omega^{(2,2)*}$, which gives mainly the repulsive part of the potential ($T^{*}\geq1$). Our potential was compared with two previously determined potentials. Figure 1 shows our potential, E. B. Smith potential, and the potential obtained from the molecular-beam scattering technique for methane. The new potential obtained in this work is in reasonable accord with the molecular-beam scattering potential, while the E. B. Smith potential shows poor agreement and it is clearly inadequate.

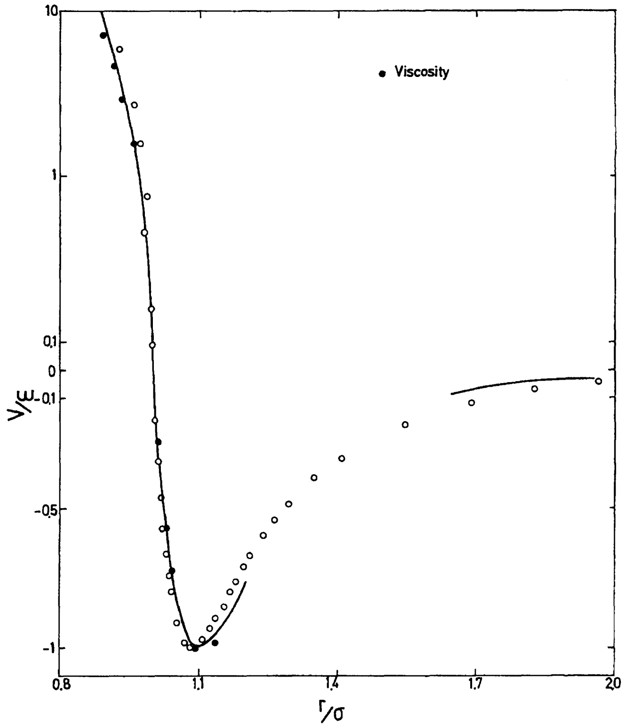

Fig. 1. Intermolecular potential for CH_4–CH_4. (●), our potential; (○) E. B. Smith potential.[4] The solid curve follows the molecular beam scattering data.[3]

Since we have used the corresponding-states correlation, and this correlation was obtained from more accurate data, it can be claimed that our potential is superior to the E. B. Smith potential.

Therefore, the inversion procedure used in this work indicates that the application of such procedure to the methane–methane system would be relatively reasonable, and produces a useful methane–methane potential. This technique also largely eliminates the need for the unsatisfactory trial-and-error methods which have been used to obtain potential-energy functions from thermophysical data.

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