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Direct Calculation of CH_4–He Interaction Potential from the Extended Principle of Corresponding States

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The interaction potential energy between CH_4 and He has been determined from the extended law of corresponding states for viscosity using the inversion technique. Lennard–Jones (12-6) and BBMS potential functions have been checked as the initial model potentials required by the technique. The resulting potential energy from L–J potential is in excellent agreement with the one obtained from crossed molecular beam experimental results. The interaction potential energies from inversion reproduce the viscosity within 1%, the binary diffusion coefficient within 5%, and the thermal diffusion within 25%.

Intermolecular potential energy, in general, plays an important role in the determination of physical and chemical properties of matter. The direct measurement of the potential energy between molecules is impossible, so it seems reasonable to apply indirect methods. In recent years a considerable advancement in our knowledge about the forces between atoms and molecules has taken place. In this respect, there are many data available for extraction of information about the forces between molecules. They may be categorized as: 1) spectroscopic observations, 2) second virial coefficient, 3) transport properties, and 4) molecular beam scattering.

The traditional procedure for the determination of the potential function assumes a function with adjustable parameters that allow making agreement with experimental observations.[1] The main limitation here is that the resulting potential function is not unique. Such limitation of this approach is the encouragement for inversion of experimental equilibrium and transport data to obtain the potential energy as proposed by E. B. Smith.[2—7] Researchers have already inverted the vibrational and rotational fine structure of IR and UV absorption spectra of diatomic molecules.[8] The Gough method of direct inversion of transport properties[2] has recently been applied to experimental second virial coefficients, viscosity, and diffusion; the inversions of the mentioned data from corresponding states correlations have been given a wide applicability by Boushehri et al.[9—15] It should be noted that the accuracy is not necessarily enhanced by greater complexity.

In the present paper the direct inversion of the viscosity functional obtained from the extended law of corresponding states[16—18] for collision integral is used to produce the interaction potential energy of the CH_4–He system. The results are in excellent agreement with the potential function obtained from experimental data on crossed atomic beam scattering.[19]

Collision Integral. In this section we will give an introduction to the collision integral. The role of the collision integrals in the inversion procedure will be seen in the next section.

The collision integral $\Omega^{(l,s)}$ is the first of a family of integrals that arise in the kinetic theory derivations,[20)]

$$\Omega^{(l,s)}(T)=\left[(s+1)!(kT)^{s+2}\right]^{-1}\int_0^{\infty}(Q^{(l)}(E))\mathrm{e}^{-E/kT}E^{s+1}\mathrm{d}E, \quad (1)$$

where E is the relative energy of the colliding partner, and $Q^{(l)}(E)$ is a transport cross section that classically is given by the equation

$$Q^{(l)}(E)=2\pi\left[1-\frac{1+(-1)^l}{2(1+l)}\right]^{-1}\int_0^{\infty}(1-\cos^l\theta)b\,\mathrm{d}b, \quad (2)$$

in which θ is the relative deflection angle between two colliding partners of energy E and impact parameter b at the gas temperature. The normalization factors in Eqs. 1 and 2 are chosen so that all of the $\Omega^{(l,s)}$ and $Q^{(l)}$ are equal to πd^2 for the collision of rigid spheres of diameter d. The deflection angle θ is calculated as a function of b and E from the classical equation of motion

$$\theta(b,E)=\pi-2b\int_0^{\infty}\left[1-\frac{b^2}{r^2}-\frac{U(r)}{E}\right]^{-1/2}\frac{\mathrm{d}r}{r^2}, \quad (3)$$

where the distance of the closest approach r_0 is the outermost root of

$$1-\frac{b^2}{r_0^2}-\frac{U(r_0)}{E}=0. \quad (4)$$

Inversion Procedure. It has been shown that for molecules that interact with an inverse power law like $U(r)=A/r^m$, where A is a constant with both positive and negative values, and r is the internuclear distance, there is a relation between temperature and potential energy:

$$\bar{r}=\left(\frac{kT}{A}\right)^{-1/m}F(m), \quad (5)$$

where $F(m)$ is a function of m only, and kT has its usual meaning. Then, the interaction potential energy at the separation of $\bar{r}$ would be in the form of

$$U(\bar{r}) = kT\,[F(m)]^{-m}\,. \tag{6}$$

Practically, $G(m)$ is chosen such that

$$U(\bar{r}) = kT\,[G(m)]\,. \tag{7}$$

$G(m)$ is a function that depends on the collision integral, potential energy, and temperature. Earlier, Hirschfelder and Eliason have used relationships Eqs. 5, 6, and 7 to calculate the transport properties of molecules with an inverse power law.[21)]

Accordingly, the inversion technique is based on the transformation of a data point $[\Omega_i{}^{*(2,2)}, T_i{}^*]$ to an equivalent point $[U(r_i{}^*), r_i{}^*]$ by the following equations:

$$r^* = \left(\Omega^{*(2,2)}\right)^{1/2}, \tag{8}$$

$$U^*(r^*) = U(r^*)/\varepsilon = T^*\,[G(T^*)]\,, \tag{9}$$

where $T^* = T/(\varepsilon/k)$ and ε is the potential well depth. The reduced collision integral, $\Omega^{*(l,s)}$, is a function of T^* and may be defined as

$$\Omega^{*(l,s)}(T^*) = \frac{\Omega^{(l,s)}}{\pi\sigma^2} \tag{10}$$

where σ is a scaling parameter such that $U(\sigma) = 0$. The collision integral $\Omega^{(l,s)}$ is characterized by l and s. According to the Chapman–Enskog solution of the Boltzman equation for the transport properties, it can be calculated by the numerical integration of the corresponding triple integrals typically in three successive iterations. We have used the Gatland version of the computer program developed by O'Hara and Smith for the calculation of the triple integrals.[22)]

The procedure involves the choice of an approximate potential model and thus determination of an initial estimate for $G(T^*)$ at a given T^* as the inversion function. Then, the calculation is followed by the determination of a corresponding r^* according to Eq. 8, using reduced viscosity collision integrals that are available in the form of corresponding states correlation.[16—18)] This allows determination of $U(r)/\varepsilon$ in terms of r/σ. Since $U(r)$ is defined such that $U(\sigma_0) = 0$, it turns out that, the value of σ is nearly equal to σ_0; precisely, $\sigma/\sigma_0 = 0.998$. The above procedure is repeated until the convergence occurs. The converged value of $U(r)$ at the corresponding r would be closer to the true potential function of the system and the value of $G(T^*)$ is refined. The convergence condition is the degree to which the collision integral, around an iteration, corresponds to the experimental data.[2)] The present potential energies are the results obtained after two iterations (see below).

Results and Discussion

Viscosity collision integrals for a molecular gas at low temperature are not available and therefore our effort was just devoted to the calculation for which $T^* \geq 1.0$. The reason for this may be stated as the existence of those long range contributions that can neither be calculated nor separated. These are the dispersion interaction energy with the power law of r^{-6}, the quadrupole–quadrupole interaction energy, r^{-5}; the dipole–quadrupole, r^{-4}; and the dipole–dipole interaction energy, r^{-3}.[18)] Therefore, this requires the extrapolation of the potential energy at long ranges. The extrapolation function that has been used is $U^* = -C_6 u^6$ where, C_6 is the dispersion coefficient and u is the reciprocal of the reduced intermolecular separation, both in atomic units. Noticeably, the extrapolation is insensitive to the extrapolation potential function.[2)] The results are shown in Fig. 1 and compared with the potential function calculated by Buck et al. that has been claimed to be highly reliable.[19)] A close look at the plot indicates that the inversion procedure, using Lennard–Jones (12-6) as the initial potential model required by the procedure, would produce a unique potential energy function for the mixture CH_4 and He, whereas the procedure converges after the second iteration. This is like our inversion procedure by the BBMS potential function[8)] which converges after the third iteration.

It should be mentioned that no data points for the potential function from the inversion procedure are seen beyond $r=$

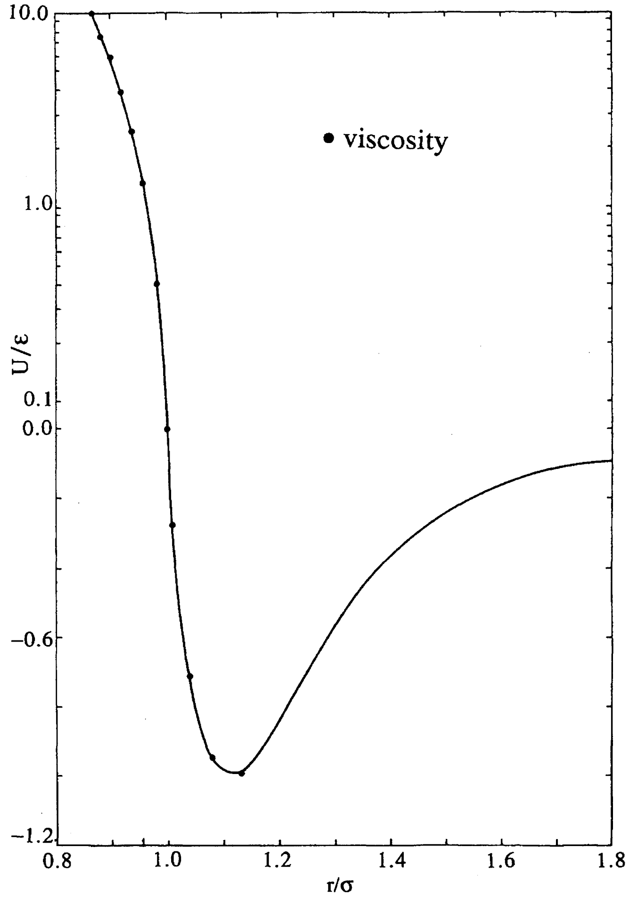

Fig. 1. The potential energy for CH_4–He system. The results of inversion of viscosity data shown by •. The solid line, shown for comparison, is the potential function obtained from scattering data (Ref. 19).

1.2σ (See Fig. 1). This is because the corresponding states correlation for the collision integral is available only for $T^* > 1$, that corresponds to $r < 1.2\sigma$.

We have noticed discrepancies between the potential energy from the inversion procedure and the experimental potential function by Slankas et al.[23] However the potential function that we have used for comparison[19] (solid line in Fig. 1) has been confirmed recently.[24]

Conclusion

The intermolecular energy function of the CH_4 and He mixture has been calculated by the inversion technique. It is assumed to be unique and well compares with that of Buck et al.[19] It also can be used to calculate the reduced collision integrals A^*, B^*, and C^*. Table 1 contains the output of the inversion of viscosity data. These reduced collision integrals are used in the formulas for the transport properties and are defined as

$$A^* = \Omega^{*(2,2)} / \Omega^{*(1,1)}, \tag{11}$$

$$B^* = \left(5\Omega^{*(1,2)} - 4\Omega^{*(1,3)}\right) / \Omega^{*(1,1)}, \tag{12}$$

$$C^* = \Omega^{*(1,2)} / \Omega^{*(1,1)}. \tag{13}$$

These plus similar results substantiate the usefulness of the viscosity data in the inversion technique.[13]

It is expedient to see whether the potential energies we obtained by this inversion procedure could produce the viscosity data back. We did follow a procedure for viscosity and diffusion coefficient. The results are tabulated in Table 2. For the temperature range we considered here, we are able (within the precision of the experimental data) to neglect the quantum effects for the present gaseous mixtures. Our estimated accuracies are about 1% for η (viscosity), 5% for D_{12} (binary diffusion) coefficient. Of course thermal diffusion factor can also be estimated, but only within 25%.

F_η higher-order correction term for viscosity, and Δ_{ij} higher-order correction term for binary diffusion coefficient were applied using Eqs. (C1a) and (5) from Ref. 17.

Table 1. The Output Values of the Inversion of Viscosity Data for the Case that Lennard–Jones (12-6) Were Used as the Initial Potential Model

$\log T^*$	$\Omega^{*(1,1)}$	$\Omega^{*(2,2)}$	A^*	B^*	C^*
0	1.39767	1.55939	1.1157	1.1952	0.8489
0.1	1.26353	1.40187	1.1095	1.1680	0.8597
0.2	1.15195	1.27138	1.1037	1.1445	0.8730
0.3	1.06037	1.16620	1.0998	1.1264	0.8872
0.4	0.98554	1.08250	1.0983	1.1135	0.9007
0.5	0.92408	1.01557	1.0990	1.1051	0.9126
0.6	0.87294	0.96126	1.1012	1.1000	0.9223
0.7	0.82956	0.91600	1.1042	1.0971	0.9299
0.8	0.79193	0.87713	1.1076	1.0956	0.9356
0.9	0.75856	0.84278	1.1110	1.0951	0.9397
1.0	0.72833	0.81176	1.1146	1.0958	0.9424
1.1	0.70035	0.78338	1.1186	1.0982	0.9440
1.2	0.67393	0.75705	1.1233	1.1020	0.9445
1.3	0.64851	0.73194	1.1734	1.1055	0.9441
1.4	0.62378	0.70677	1.1330	1.1056	0.9434
1.5	0.59985	0.68028	1.1341	1.0995	0.9436
1.6	0.57722	0.65200	1.1296	1.0863	0.9455
1.7	0.55667	0.62272	1.1186	1.0679	0.9500
1.8	0.53895	0.59407	1.1023	1.0476	0.9567
1.9	0.52454	0.56799	1.0828	1.0288	0.9650
2.0	0.51354	0.54595	1.0631	1.0136	0.9737

Table 2. Properties of an Equimolar Mixture of Methane and He-4 (CH_4–He)

T / K	η / μPa s	D (1.013 bar) / 10^{-4} m^2 s^{-1}
200	10.44	0.3550
250	12.42	0.5170
300	14.24	0.7020
273.15	13.28	0.6000
293.15	14.00	0.6750
313.15	14.71	0.7540
333.15	15.40	0.8360
353.15	16.07	0.9220
373.15	16.72	1.0110
423.15	18.31	1.2470
473.15	19.82	1.5020
523.15	21.29	1.7740
573.15	22.68	2.0670
623.15	24.04	2.3770

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