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Direct Determination of the Intermolecular Potential for Krypton

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In recent years a procedure has been developed for determining potential energy functions directly from measurements of gaseous transport properties, without assuming any particular functional form for the interaction potential. Previous applications of this procedure have required that the potential well depth be known independently. It is shown that this requirement is not necessary, and that the entire potential can be directly obtained with reasonable accuracy from the accurate viscosity data presently avilable. The interaction potential discussed is that for the inert gases.

Many attempts have been made to obtain the forces between molecules, as they are important in determining the physical and chemical properties of matter. Without direct ways of measuring the interaction potential energy function, it has become customary to postulate a parameterized functional form and adjust the parameters for best agreement between the calculated and experimental results. A method for accurately determining the potential energy function for the inert gases by fitting a number of measured quantities has been developed.[1] Here, we reexamine the problem of determining the potential energy function directly from measurements of a single property.

Our method for determining the neutral-neutral interaction potential is based on the method developed by Smith and others[2-6] and recently tested by Boushehri[7,8] in connection with the Extended Law of Corresponding State.[9] Previous applications of this inversion procedure required independent knowledge of the well depth ε. In this work the method used by Boushehri et al.,[10] to determine ε from viscosity data is adapted, so that the value of ε can be obtained from gas viscosities measurements alone. Here we use a unified formulation of viscosity, the ratio η/η_0 of the viscosity η to its value η_0 in the limit of zero temperature. This ratio first rises with increasing temperature to a maximum and then decreases, and the heigth of this maximum can be used to determine the well depth, and a method for its determination using the rate of iteration is described.

Recently a knowledge of the vibrational energy levels has been used to obtain the width of the potential energy well as a function of its depth, and that may be used to determine the shape of the internuclear potential energy function.[11] Lee and his co-workers have been able to obtain potential-energy functions for the inert gases from high-resolution measurements of the differential cross sections.[12] It is unlikely, other than for the simplest molecules, that an accurate potential can be developed from spectroscopic and high-resolution scattering cross section measurements. The method discussed in this paper is an attempt to estimate this quantity purely from viscosity data, which would be considered extremely valuable for substanes where other sources of data are unavailable.

The Kinetic Theory

Our starting point is the well-known equation[13] for the viscosity of an atomic gas

$$\eta = \frac{26.9654(MT)^{1/2} f_\eta^{(3)}}{r_m^2 \Omega^{(2,2)*}(T^*)} \tag{1}$$

where $T^*=KT/\varepsilon$ and where η is measured in micropoise. The function $f_\eta^{(3)}$, which is nearly unity, and the quantity $\Omega^{(2,2)*}(T^*)$ are functionals of the potential energy function. It is convenient to write viscosity in a different form. To do this we note that at low temperatures the interactions are dominated by an r^{-6} attractive term. Since $V\simeq C_6\, r^{-6}$, $\Omega^{(2,2)*}$ takes on the form.[14]

$$\Omega^{(2,2)*} \rightarrow 1.1943\ (C_6/K_BT)^{1/3}/r_m^2 \tag{2}$$

we can then introduce the viscosity limit η_0 defined by[15]

$$\eta_0 = 22.3903\ (MT)^{1/2}/(C_6/K_BT)^{1/2} \tag{3}$$

and rewrite Eq. 1 as

$$\eta/\eta_0 = 0.85167\ C_6^{1/3}\ \eta/M^{1/2}T^{5/6} \tag{4}$$

where η is in micropoise and C_6 is in atomic units.

We are now in a position to consider Eq. 4 as a unified formulation of the viscosity for all gases. The estimate of well depth is obtained conveniently from the observation of the maximum η/η_0 only.

Inversion Procedure

The experimental collision integral may be used to define the intermolecular potential energy function from which they arise, $V(r)$. A separation distance r_0, for a given temperature, may be defined such that

$$\overline{\Omega}^{(2,2)} = \pi r_0^2 \tag{5}$$

where r_0 represents the collision diameter for hard-sphere molecules which would have the same viscosity as the real molecule and where $\overline{\Omega}^{(2,2)}/\pi r_m^2 = \Omega^{(2,2)*}$. The potential $V(r_0)$ is given by the relation.

$$V(r_0) = G\ K_BT \tag{6}$$

where G is a temperature dependent function that may be calculated using a model system whose intermolecular potential energy function is known. This process may be repeated to refine the $G(T^*)$ values and hence to obtain an improved $V(r)$ that precisely represent the intermolecular potential energy function. Thus knowing the well depth, the values of viscosity as a function of T can be converted to the potential V as a function of r_0.

In order to obtain a collision integral $\Omega(2,2)$, three successive numerical integrations are needed. Estimation of the triple integral is made by employment of Gatland version of the Computer Program developed by O'Hara and Smith.[16)]

To establish the value of the well depth, one may carry out a search procedure. That is, at each stage in the iteration process the values η/η_0 are back calculated from the improved $V(r)$ using an assumed well depth. Several iteration may be used until agreement with the previous iteration is achieved. For findig $V(r)$ directly from measurement of viscosity, one may estimate an initial value of the well depth ε. This estimate value of well depth is obtained conveniently from the observation of the maximum η/η_0, if the maximum η/η_0 is too large, the estimated ε needs to be increased and vice versa, so that a different value of ε is chosen, and the process repeated until agreement with experiment is reached.

In summary, values of collision integral $\Omega(2,2)$ must be obtained from Eq. 1 using highly accurate data. Three interation may be used, if agreement with the previous iteration is not achieved, then a different value of ε is chosen and the process repeated until agreement with experiment is reached. An inital value for the well depth $\varepsilon/k=184$ K is used. The inversion function from Ref. 17 used for an initial estimate of $G(T^*)$. Following the inversion procedure, we obtain calculated values (η/η_0, T) shown as curve 1 in Fig. 1 and compared with the "Smoothed" data shown as Exp. The difference between maximum values, η/η_0 of the two curves is about 1.5%. The (η/η_0, T) values in second iteration are virtually indistinguishable from curve 1 in Fig. 1 and hence is not shown. Thus three steps may be followed in the inversion scheme:

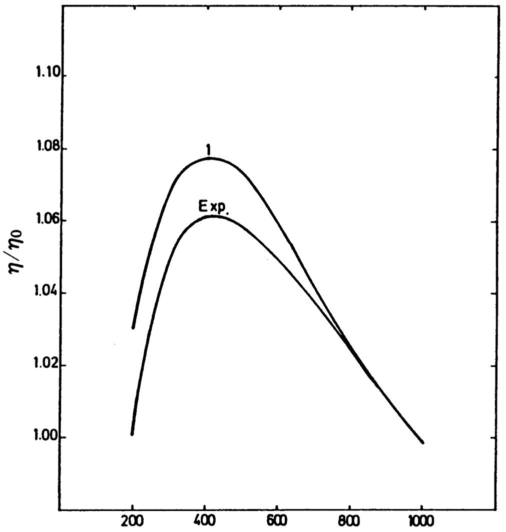

Fig. 1. The ratio η/η_0 as a function of T. Values of η/η_0 in the range $140<T<200$ and $1000<T<2000$ have been omitted for the sake of clarity. The lower curve (Exp.) represents the smoothed viscosity data (Ref. 19). The other curve 1 assuming a well depth $\varepsilon/k=184$. The results in 2nd iteration are nearly identical with those obtained in the first iteration, and are therefore not shown separately.

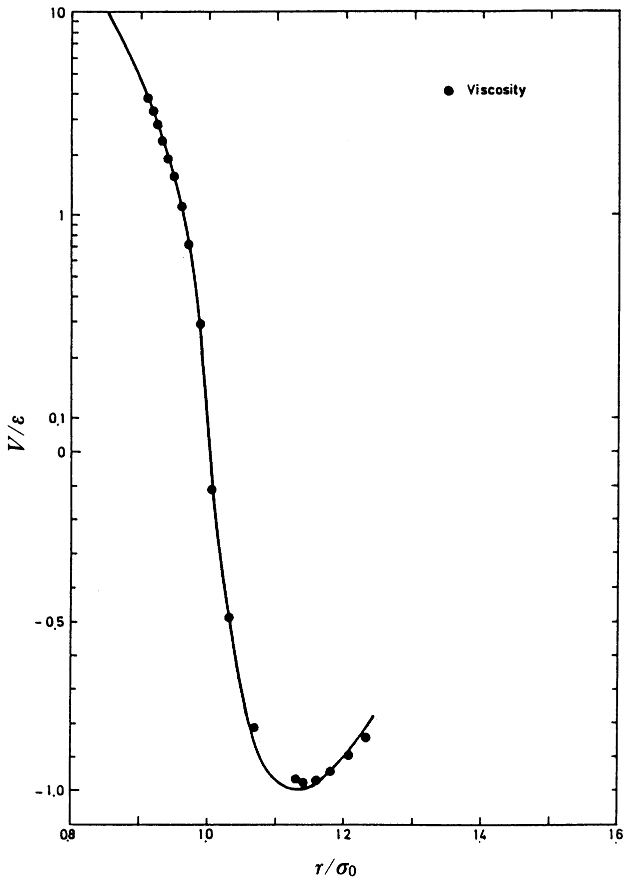

Fig. 2. Reduced pair potential obtained by direct inversion based on the smoothed viscosity data compiled by Smith for krypton (●), $\varepsilon/k=184$ K. Also shown for comparison is a typical curve obtained primarily from thermal scattering data (Kr–Kr, Ref. 18), $\varepsilon/k=198$ K. Note that the scale changes from linear to logrithm at $V/\varepsilon=0.1$.

1) Two iteration may be performed to find $V(r)$ for a given ε and a given set of highly accurate data.

2) If the calculated and experimental (η/η_0, T) does not agree within some limit then estimated ε needs to be increased for large value of η/η_0 and vice versa.

3) Return to step 1 and continue until the correct value of ε is obtained.

These three steps should provide a useful technique for the determination of ε values for substances where other source of data are unavailable.

It is of interest to note that the potential obtained for Krypton when plotted in reduced form, using σ and ε/k

determined in this work, is in good agreement with Lee Potential[18] (see Fig. 2).

Conclusion

The present work indicates an application of the concept in Ref. 10 to the smoothed viscosity data. Other than the simplest molecules, it is unlikely to obtain accurate well depth from spectroscopic measurements. The availability of highly accurate viscosity data over a reasonable range of temperature opens up the possibility of obtaining the well depth ε from measure of this single property without the use of additional experimental information or assumption of any mathematical form for the interaction energy function. This method would be considered extremely valuable for substances where other sources of data are unavailable.

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