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DIFFERENTIAL COLLISION CROSS SECTIONS AND THE INTERMOLECULAR POTENTIAL OF NEON*

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The differential collision cross section of neon has been measured and the data used to obtain the intermolecular potential. Calculations of the macroscopic properties made using this potential are in reasonable accord with experiment.

The first measurements of the differential cross sections of the rare gases were previously reported by this laboratory.¹ These measurements were made with the modulated molecular beam technique using highly selective preamplification and long integration times on the output of a lock-in amplifier. Through an increase in selectivity and the use of an Enhancetron as a signal averager to recover the scattered-beam waveform, the signal-to-noise ratio was greatly improved.

In these experiments, beam stops were used on both beams to eliminate background. This background comes largely from scattering of the beam in the collimating region and varies from 10^{-3} to 10^{-5} times the total beam intensity with the Enhancetron as a signal averager. At 6 deg in the center-of-mass system the scattering signal is 50% of this background using four stages of tuned amplification with the Enhancetron. In previous experiments using the lock-in technique the scattering signal was only 10% of the background. Since this background was in phase it was interpreted as a scattered beam originating in the collimation region and an analysis must include the attenuation of this beam, as it passed through the main scattering region. In the Enhancetron this background was reduced fivefold and the correc-

tion also reduced fivefold. Even if this factor were disregarded, it would only change our results by 20%. The reduction in this correction accounts for most of the discrepancy with results obtained using lower selectivity with a lock-in amplifier, and simultaneously improved the consistency between measured total cross sections and integrated differential cross sections. Direct subtraction of signals on the Enhancetron also eliminated phase shifts found at very low signal levels.

The differential cross sections which are reported here are absolute measurements without correction for finite geometry. The geometrical corrections were included in the theoretical analysis and so the calculated differential cross sections were for an apparatus having our geometry.² These corrections would lower all experimental cross sections at scattering angles of 3 deg or higher by 20-25% and raise the first two measurements by the same amount, with little effect on the other points. Almost all of this correction came from the finite beam and detector widths. These corrections can probably be made with a net error of less than 5% of the experimental value.

The scattered beam intensities which must be measured were a factor of several hundred to

100 000 below the intensity of the unscattered molecular beam. While the beams were detected mass spectrometrically, mass selection served only to reduce ion-source noise. The integrated differential cross sections from lock-in measurements gave total cross sections about 60% higher than those from direct measurement. The integrated differential cross sections from Enhancetron signal averaging are within 10-15% of the experimental total cross sections for neon, argon, and methane. Both types of differential cross-section measurements were in good agreement at low angles but the lock-in measurements were too high at larger angles for both argon and neon.

After elimination of inconsistencies in the two types of scattering measurements, the next test is whether the intermolecular potentials obtained from the experimental differential cross sections give realistic values of the macroscopic properties.

The measured differential cross sections of neon are shown in Fig. 1, where a comparison is made with calculations from the Lennard-Jones potential. The measurements were made with perpendicular beams at 300°K and were reduced to the center-of-mass system using the methods of Berkling³ and Bernstein.⁴ The general proce-

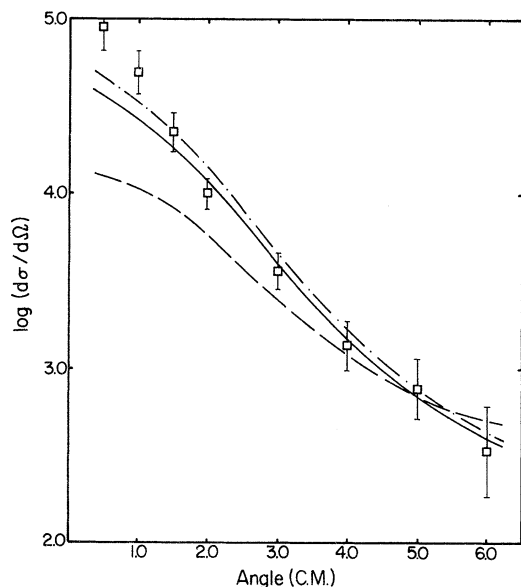


FIG. 1. Log of the differential cross section for neon versus angle (deg). Experiments points are indicated by squares. The error bars indicate average deviations. The results calculated from the Lennard-Jones potential are indicated by a dashed line, from potential A by a dot-dashed line, from potential B by a solid line.

cedure for the Berkling corrections was outlined in Ref. 2. These corrections appear to be largely independent of an assumed potential as long as the cross section is calculated for relative velocities. With a Boltzmann distribution, resultant errors are probably less than 5%. We believe we have an accurate value of molecular number density in the scattering beam. The only cross check is with other total cross-section measurements. Our value of 340 \AA^2 for argon is just within the experimental limits of the best experimental value of $319 \pm 7\%$.⁵ The largest errors in these experiments are statistical scatter and unknown systematic errors. Enough experiments have been done at each point so that the most probable statistical error is less than 25%, even at large angles. A very tentative total error estimate might be from 20% in the best case to 40% in the higher angle measurements. From the calculations of macroscopic properties which follow, it does not appear that the errors were this large nor does it appear that there were any large systematic errors. The deviations from the predictions of the Lennard-Jones potential are greatest at small angles where the lock-in technique and the results from Enhancetron averaging were in good agreement.

Qualitatively the data require a substantial increase in intermediate- and long-range forces coupled with some reduction of the potential bowl depth. Intermolecular potentials were obtained by fitting the data⁶ and Fig. 1 illustrates two such fits. The corresponding intermolecular potentials are illustrated in Fig. 2 along with the Lennard-Jones potential.

The two potentials give very similar differential cross sections and are almost equally valid

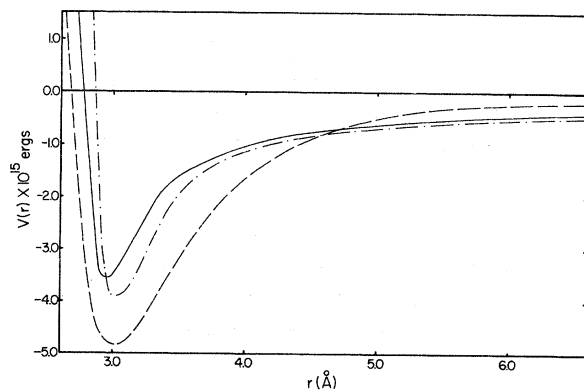


FIG. 2. Intermolecular potentials. The Lennard-Jones potential is indicated by the dashed curve. Notation for the scattering potentials is given in the caption for Fig. 1.

by the least-squares criteria. The experimental value of the total cross section is 195 \AA^2 . Potential A gives a total cross section of 210 \AA^2 and potential B gives a total cross section of 187 \AA^2 . At best, there can be only a slight preference for potential B against A on the basis of scattering data. On the other hand the Lennard-Jones potential is incompatible with the scattering data, especially beyond 5.0 \AA and probably beyond 3.0 \AA .

The primary purpose of these scattering measurements was to provide intermolecular potentials which could be used in the calculation of macroscopic properties and inversely provide a cross check on the validity of the scattering measurements. When we proceed to the calculation of virial, viscosity, and diffusion coefficients, potential B is decisively better than A . The differential cross section and the virial coefficient provide different kinds of information, the latter being more sensitive to the repulsive parts of the potential. The fit of potential B to the virial data⁷ is illustrated in Fig. 3 and is typical of the results for this potential in calculations of viscosity and diffusion coefficients. There are systematic high-temperature deviations which can be lessened by altering the potential inside of 2.55 \AA (0.04 eV). Thermal-energy beams probe this region very feebly.

The cohesive energy of the neon crystal has also been calculated at 0°K . The most stable static crystal structure was found to be face-centered cubic. This was apparently due to the rather slower decrease of attractive forces between 4 and 6 \AA which is in contrast to the behavior of the Lennard-Jones potential. Calculations of the cohesive energy for the crystal are quite involved because of the magnitude of the vibratory oscillations. The usual approximation of having neighboring atoms fixed on lattice sites leads to large errors in calculations of lattice energies and crystal spacing. Since the cell potential is a function of vibrational amplitude of neighboring atoms and the lattice parameters, an iteration is carried out until self-consistent results are obtained. For potential B the cohesive energy is 566 cal/mole . The experimental value is 602 cal/mole . The Lennard-Jones potential gives 508 cal/mole . On the other hand, the zero-point energy for the Lennard-Jones potential (153 cal/mole) is better than for the scattering potential (185 cal/mole). The sublimation energy for the scattering potential is only slightly better (15%

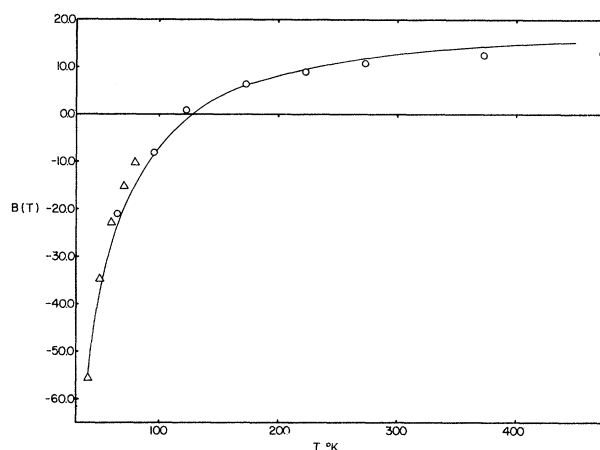


FIG. 3. Quantum mechanical virial coefficient. The triangles refer to the data of Keesom and Lammeren (Ref. 7) and the circles to the data of Otto (Ref. 7). The solid curve was calculated using potential B .

low) than that for the Lennard-Jones potential (21%). Both potentials give correct nearest-neighbor distances (3.16 \AA).

In summary, the scattering data indicated rather strong attractive forces at intermediate distances. If we grant this point, a reduction of the bowl area as found in potentials A and B is necessary to give reasonable fits of low-temperature virial coefficients. In the case of neon the potentials which can be obtained appear to be consistent with the macroscopic properties within the limits of these errors. On the other hand, the Lennard-Jones potential is inconsistent with the scattering data.

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