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An improved potential for Ar-Kr

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An accurate intermolecular potential of the HFD-C form is proposed which appears to be the best representation of the Ar-Kr interaction. The potential, which possesses the correct long range behavior, predicts a wide variety of macroscopic and microscopic data. It is consistent with accurate second virial, viscosity, and diffusion coefficients. Differential scattering and low as well as high energy total cross section data are accurately predicted.

INTRODUCTION

The Ar-Kr interaction has been very extensively studied by a number of independent groups using scattering data and bulk properties in the dilute and condensed phases.

First of all, Lee *et al.*,¹ using the Barker-Henderson perturbation theory, calculated the excess free energy and excess volume for an equimolar liquid mixture at zero pressure and some specified temperatures. They adjusted parameters in a potential (LHB) of the Barker form expressed as a linear combination of the corresponding parameters for the pure systems until agreement with experiment was reached. Next, Gough *et al.*² and later Maitland and Wakeham³ used inversion procedures to obtain potentials (GMSM and MW, respectively) from dilute gas bulk properties and found slightly larger values for the energy and length parameters. By semiclassical inversion of high quality differential collision cross sections (dccc) data which exhibited both rainbow and rapid oscillations, Buck *et al.*⁴ determined a new potential (BHPS) of the Morse-Spline-Morse-Spline-van der Waals (MSMSV) form. The inversion procedure ensured that the attractive region was uniquely determined. The correctness of the well was confirmed by the ability of the potential to predict correctly the earlier Leiden total collision cross sections data (tccs) (Linse *et al.*⁵) and reliable second virial coefficient data.^{6,7} Transport data, however, are not predicted to within experimental error as a result of a potential wall which is too soft. The value of the length parameter determined by Buck *et al.*⁴ agrees with that found from condensed phase properties by Lee *et al.*¹ Subsequently, Aziz *et al.*⁸ presented a modified (APBS) version of the BHPS potential which satisfactorily predicts not only the differential and Linse integral cross sections but also the best transport and virial data. This latter compromise potential represented the best characterization of the Ar-Kr interaction, but certain unsatisfactory features remain. The piecewise nature of the potential is mathematically and esthetically displeasing. Disagreeable discontinuities exist in the potential derivatives, and matching of potential components is not always easy. More importantly, van den Biesen *et al.*⁹ found that the spline function worsened the predictive ability of the APBS and BHPS potentials for their new tccs data. Moreover, these potentials lie outside the Tang *et al.*¹⁰

upper bounds for the van der Waals tail. A potential of the HFD-C^{11,12} form could avoid these difficulties. In 1977, Aziz developed an unpublished potential of the HFD-C (HFD-C1) form which was subsequently cited as a private communication by Linse *et al.*,⁵ van den Biesen *et al.*,¹³ and van den Biesen *et al.*⁹ The potential predicts the dilute gas bulk properties as well as the APBS potential including the very precise diffusion data measured subsequently by Arora *et al.*¹⁴ In addition, it did an excellent job of predicting the various aspects of the very precise tccs data of van den Biesen *et al.*⁹ The HFD-C1 potential, while predicting many properties, did not possess a repulsive wall consistent with that determined by Rol and co-workers¹⁵ from high energy total cross sections. This HFD-C1 potential is presented in this paper to express the Ar-Kr interaction free from the difficulties associated with piecewise forms. A second potential (HFD-C2) is constructed which is not only

TABLE I. Parameters^a for HFD-C Ar-Kr potentials.

	HFD-C1	HFD-C2
A^*	0.333 806 3(8)	0.185 690 1(9)
σ^*	17.700 506	19.552 231
c_6	1.176 502 8	1.158 329 9
c_8	0.500 206 2	0.541 196 4
c_{10}	0.271 092	0.333 292 5
C_6 (a.u.)	96.998	95.500
C_8 (a.u.)	2 218.22	2 400.00
C_{10} (a.u.)	64 663.4	79 500.00
γ	2.90	4.260
D	1.38	1.490
$\epsilon/k(K)$	167.3	167.3
r_m (Å)	3.881	3.881
σ (Å)	3.468 ₂	3.468 ₄
B	3586.287 51	2 832.728
β	2.757 962 59	3.615 874 0
x_0	0.261 0	0.330 0

^aNote: Not all figures displayed are significant. We displayed them only to avoid round off errors.

TABLE II. Ar-Kr, rms deviations for various potentials.^a

Potential	Reference	Parameters					Bulk property ^a				
		ϵ/k (K)	r_m (Å)	σ (Å)	B^b cm ³ mol ⁻¹	B^c cm ³ mol ⁻¹	η^c μ P	η^b μ P	D^d cm ² s ⁻¹	D^e cm ² s ⁻¹	D^f cm ² s ⁻¹
HFD-C1	Present	167.3	3.881	3.4682	0.309	1.156	2.51(0.51)	4.16(0.61)	0.0422(3.12)	0.0011(0.51)	0.0001(0.04)
HFD-C2	Present	167.3	3.881	3.4684	0.404	1.173	2.58(0.55)	4.27(0.64)	0.0434(3.20)	0.0011(0.51)	0.0000(0.03)
APBS	Aziz <i>et al.</i> (Ref. 8)	167.5	3.88	3.476	0.373	1.186	3.82(0.79)	3.24(0.54)	0.0382(2.82)	0.0010(0.44)	0.0001(0.05)
BHPS	Buck <i>et al.</i> (Ref. 4)	167.1	3.88	3.460	0.541	1.301	3.20(0.75)	10.92(1.61)	0.0649(4.94)	0.0032(1.73)	0.0021(1.46)
LHB	Lee <i>et al.</i> (Ref. 1)	163.87	3.8807	3.4674	0.804	1.290	0.70(0.20)	8.35(1.14)	0.0657(4.83)	0.0024(1.13)	0.0011(0.80)
GMSM ($\gamma=9$)	Gough <i>et al.</i> (Ref. 2)	165.0	3.902	3.4766	2.638	2.155	1.73(0.39)	5.74(0.87)	0.0490(3.61)	0.0014(0.66)	0.0001(0.10)
MS ($\gamma=9$)	Maitland and Wakeham (Ref. 3)	165.0	3.934	3.489	4.681	2.915	8.80(2.00)	5.92(1.71)	0.0307(2.12)	0.0014(1.53)	0.0021(1.53)
$m-6-8$ ($m=11$; $\gamma=3$)	Arora <i>et al.</i> (Ref. 14)	177.5	3.8081	3.417	1.457	1.629	0.70(0.21)	4.22(0.60)	0.0271(2.20)	0.0010(0.46)	0.0001(0.04)
Morse-6	Konowalow and Zakheim (Ref. 22)	163.37	3.9285	3.4642	0.271	1.377	9.96(2.01)	22.96(3.32)	0.1064(7.97)	0.0048(2.47)	0.0032(2.23)
WMA	Watanabe <i>et al.</i> (Ref. 17)	163.541	3.8947	3.4719	0.196	1.259	0.37(0.14)	7.14(0.97)	0.0542(4.07)	0.0021(1.04)	0.0010(0.73)
MS-vdB ($\gamma=9$)	van den Biesen <i>et al.</i> (Ref. 13)	165.0	3.88	3.4570	1.183	1.667	3.27(0.75)	10.68(1.54)	0.0620(4.73)	0.0029(1.49)	0.0017(1.23)

^aQuantities refer to rms deviations and quantities in parentheses refer to rms percentage deviations.

^bBrewer (Ref. 6) virials. Estimated error ± 0.5 cm³ mol.

^cKestin *et al.* (Ref. 18) viscosity. Estimated error $\pm 1\%$.

^dHogernorst (Ref. 19) diffusion. Estimated error $\pm 1\%$.

^eVan Heijningen *et al.* (Ref. 21) diffusion. Estimated error $\pm 1\%$.

^fArora *et al.* (Ref. 14) diffusion. Estimated error $\pm 0.1\%$.

^gSchramm *et al.* (Ref. 7) virials.

^hViscosity of Maitland and Smith (Ref. 23) and Gough *et al.* (Ref. 24). Estimated error $\pm 1.5\%$.

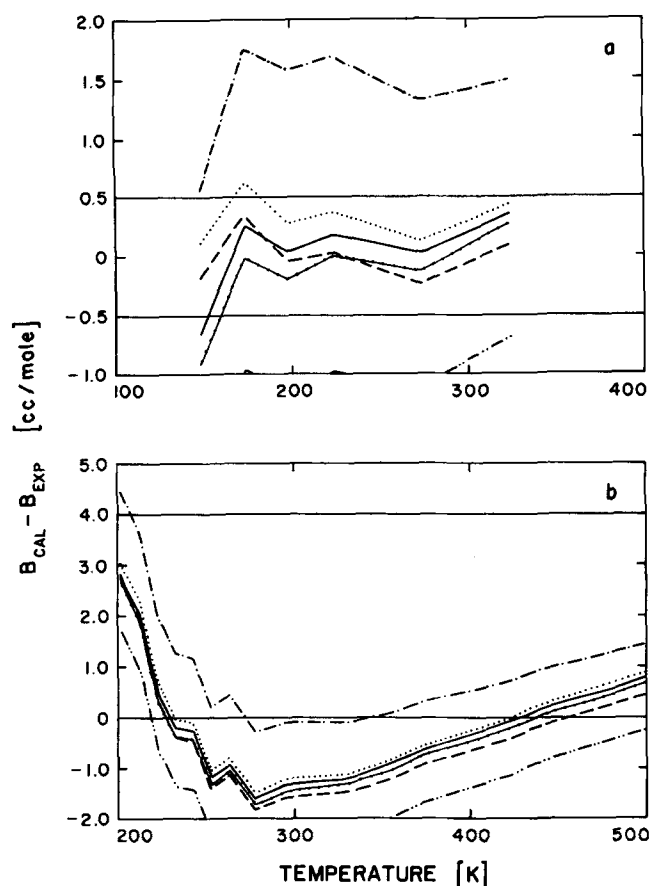


FIG. 1. Deviation curves for the interaction second virial coefficient. (a) Data of Brewer (Ref. 6) (error bars ± 0.5 cc/mol). (b) Data of Schramm *et al.* (Ref. 7) (error bars ± 4 cc/mol). Potentials: Present (HFD-C1) — and (HFD-C2) — —; APBS...; Arora *et al.* - - - -; WMA - -; MS-vdB - - - - -.

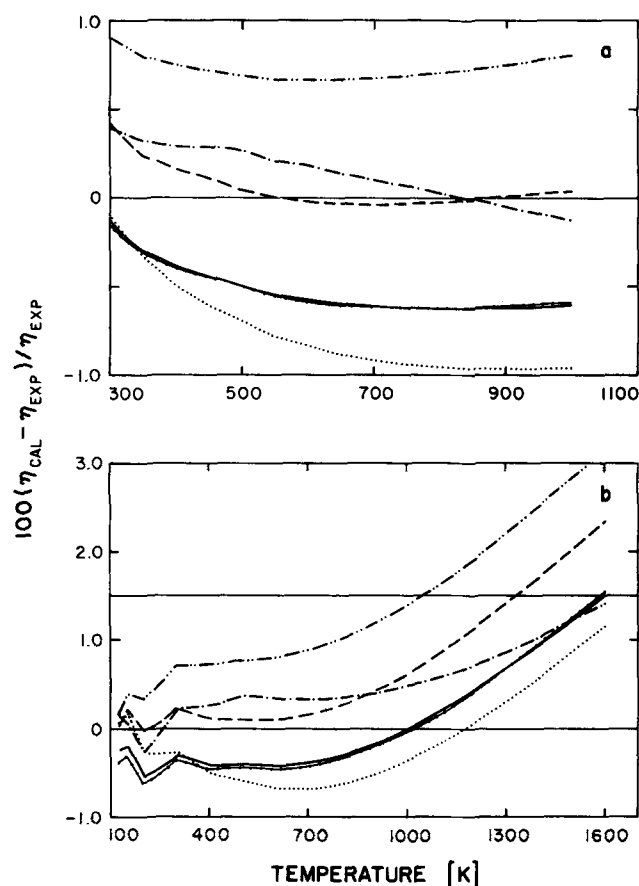


FIG. 2. Deviation curves for the interaction viscosity. (a) Data of Kestin and co-workers (Ref. 18) (error bars $\pm 1\%$). (b) Data of Smith and co-workers (Refs. 23 and 24) (error bars $\pm 1.5\%$). Legend as in Fig. 1.

TABLE III. Ar-Kr, rms deviations for various potentials.

		Microscopic property		
Potential	References	$I(\theta)^a$	$Q(\bar{g})^b$	$Q(\bar{g})^c$
		$T = 753, 13 \text{ K}$	Ar-Kr	Kr-Ar
HFD-C1	Present	0.104	0.004 99	0.006 15
HFD-C2	Present	0.107	0.003 98	0.004 08
APBS	Aziz <i>et al.</i> (Ref. 8)	0.091	0.009 27	0.008 21
BHPS	Buck <i>et al.</i> (Ref. 4)	standard	0.008 48	0.009 03
LHB	Lee <i>et al.</i> (Ref. 1)	0.127	0.013 21	0.012 97
GMSM ($\gamma=9$)	Gough <i>et al.</i> (Ref. 2)	0.180	0.004 23	0.004 81
MS ($\gamma=9$)	Maitland and Wakeham (Ref. 3)	0.290	0.006 59	0.007 27
$m-6-8(m=11; \gamma=3)$	Arora <i>et al.</i> (Ref. 14)	0.312
Morse-6	Konowalow and Zakheim (Ref. 22)	0.203
WMA	Watanabe <i>et al.</i> (Ref. 17)	0.073	0.007 52	0.008 38
MS-vdB ($\gamma=9$)	van den Biesen <i>et al.</i> (Ref. 13)	0.079	0.004 39	0.004 84

^aBuck *et al.* (Ref. 4) differential cross sections.

^bvan den Biesen *et al.* (Ref. 9) total cross sections (Ar-Kr).

^cvan den Biesen *et al.* (Ref. 9) total cross sections (Kr-Ar).

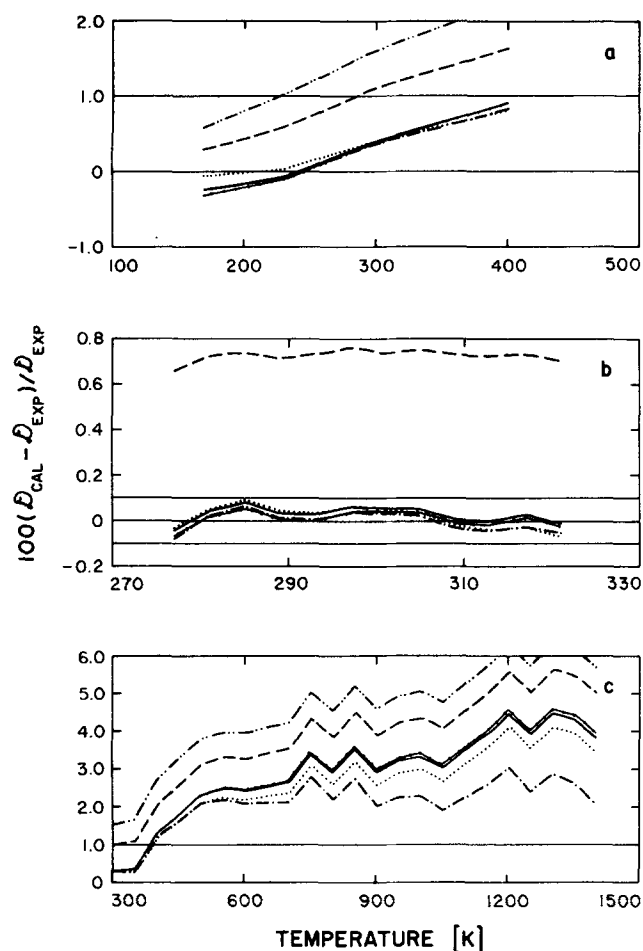


FIG. 3. Deviation curves for the diffusion coefficient. (a) Data of van Heijningen *et al.* (Ref. 21) (error bars $\pm 1\%$). (b) Data of Arora *et al.* (Ref. 14) (error bars $\pm 0.1\%$). (c) Data of Hogervorst (Ref. 19). Legend as in Fig. 1.

more consistent with the high energy scattering wall but even agrees more closely with latest Leiden tccs data. These potentials are compared with other recent potentials with respect to their predictive abilities for various macroscopic and microscopic properties. The recommended potential is the HFD-C2.

THE POTENTIAL

Aziz and Chen¹¹ presented an accurate empirical potential for the argon interaction in modified HFD¹⁶ form currently referred to as HFD-C. Later, Aziz¹² developed an accurate potential for the krypton interaction using the same model. The potential has the following form

$$V(r) = \epsilon V^*(x),$$

where

$$V^*(x) = A^* x^\gamma \exp(-\alpha^* x) - F(x) \sum_{j=0}^2 c_{2j+6} / x^{2j+6},$$

with

$$F(x) = \exp\{-(D/x - 1)^2\}, \quad x < D, \\ = 1, \quad x > D.$$

Potentials of the HFD-C form tend to "turn over" for large values of the γ parameter. To ensure that the repulsive wall possesses a negative slope to very small separations, a function of the form

$$B \exp(-\beta x)/x$$

is smoothly connected to $V^*(x)$ at x_0 for the region $x \leq x_0$. This should not pose a serious problem since no physical observable senses the potential at separation of the order x_0 or less.

While the original HFD potential had no adjustable

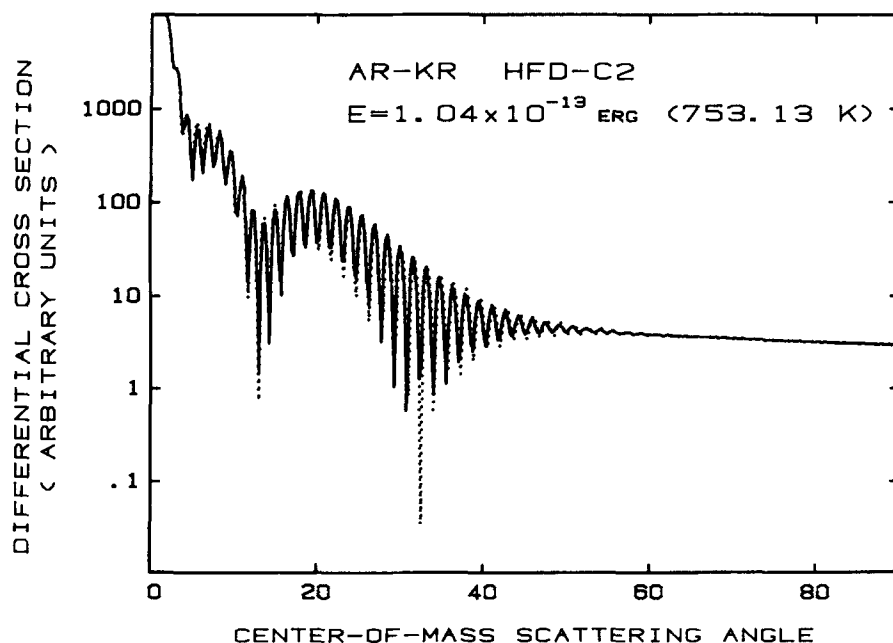


FIG. 4. Differential cross sections for the energy of $E = 753.13$ K in the center-of-mass frame of reference calculated for the HFD-C2 potential (solid line) compared with that calculated for the BHPS potential (dots).

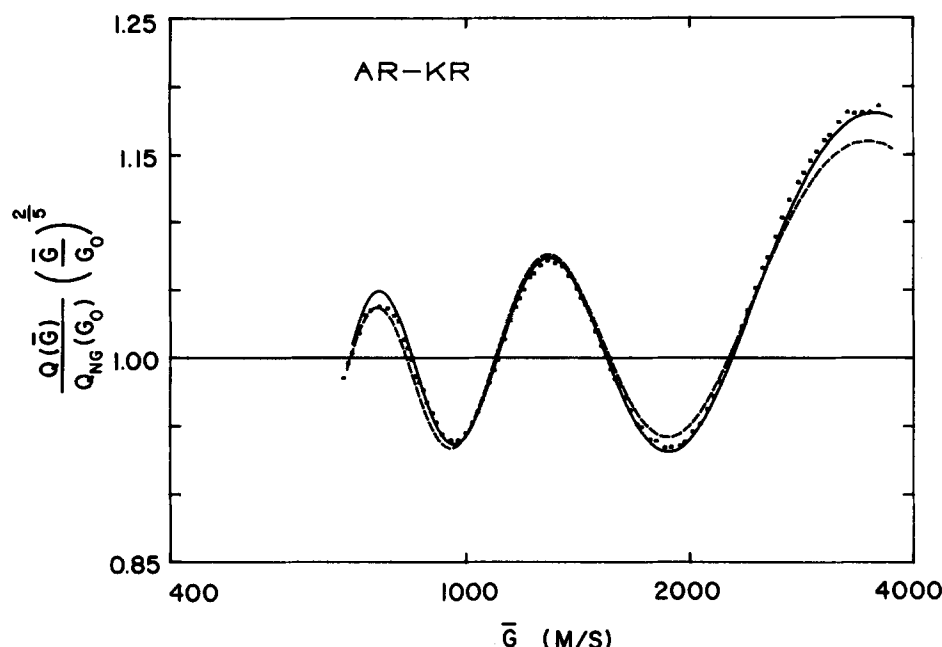


FIG. 5. Comparison of the experimental total cross section data of van den Biesen *et al.* (Ref. 9) (dots) with the total cross sections calculated on the basis of the present (HFD-C2) potential (solid line); APBS (dashed line); Ar (primary beam)-Kr (secondary beam).

parameters, we allow ϵ , r_m , D , and γ to vary while keeping the dispersion coefficients within the bounds given by Tang *et al.*¹⁰ Considerable flexibility is achieved under the circumstances. The parameters for the HFD-C1 and HFD-C2 potentials are given in Table I.

Intercomparisons of various recent potentials for Ar-Kr are summarized in Table II. These include the APBS, BHPS, and LHB potentials mentioned above. Also included in the analysis are the inversion potentials of Gough *et al.*² (GSMS) and Maitland and Wakeham,³ the m -6-8 potential of Arora *et al.*,¹⁴ the WMA potential of Watanabe *et al.*,¹⁷ and the tccs-fit potential (MS-vdB) of van den Biesen *et al.*¹³ The WMA potential is based on a knowledge of the first Coulomb interaction

energy, a suitable damped three term long range asymptotic expansion of the second order Coulomb energy and a semiempirical representation of the exchange interaction energy which contains one adjustable parameter. The single parameter was fixed by fitting the second virial coefficients while constraining the dispersion coefficients to within the bounds given by Tang *et al.*¹⁰

Deviation plots are presented in Figs. 1-3 for the HFD-C1, HFD-C2, APBS, WMA, m -6-8, and MS-vdB potentials. For deviation plots of other potentials, the reader is referred to Aziz *et al.*⁸ except that, in the present analysis, the interaction viscosity data Kestin *et al.*¹⁸ are used. From Table II and Figs. 1-3, it is seen that HFD-C1 and HFD-C2 potentials predict sec-

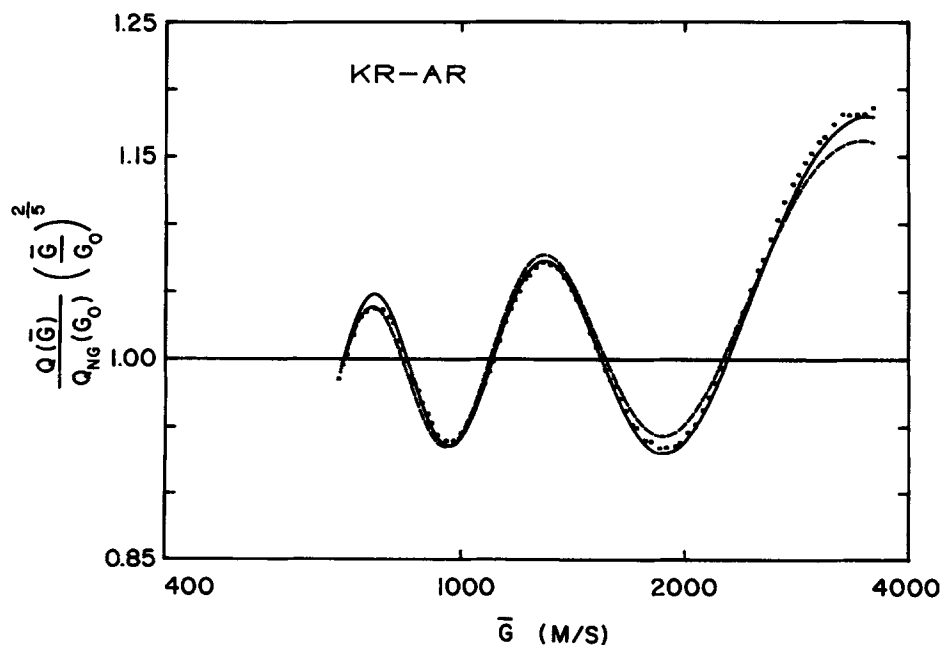


FIG. 6. Comparison of the experimental total cross section data of van den Biesen *et al.* (Ref. 9) (dots) with the total cross sections calculated on the basis of the present (HFD-C2) potential (solid line); APBS (dashed line); Kr (primary beam)-Ar (secondary beam).

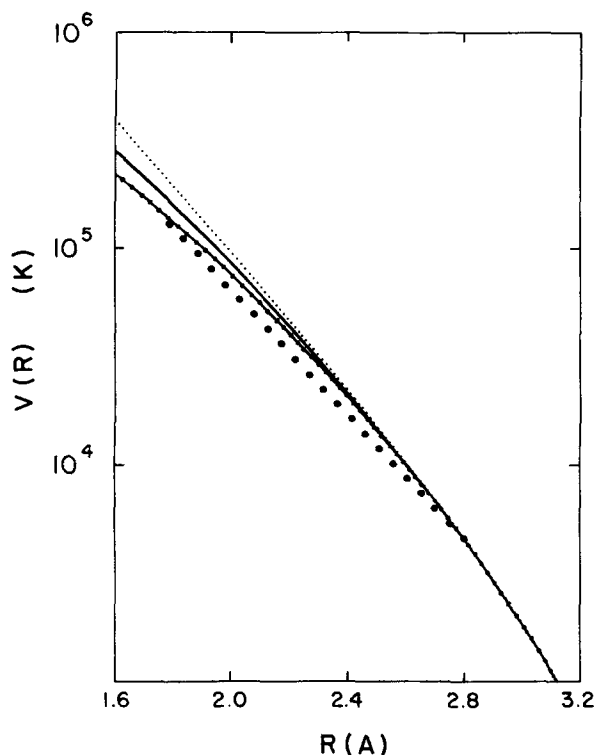


FIG. 7. Repulsive walls of the HFD-C1 (—), HFD-C2 (—○—), and APBS (···) potentials compared with the repulsive wall of the potential determined by Rol and co-workers (Ref. 15) (●) from high energy total cross sections.

ond virial coefficients and transport data to within experimental error²⁵ except for the diffusion data of Hogervorst¹⁹ which is predicted by no potential. The values of diffusion are considered to err on the low side by Taylor.²⁰ This trend is consistent with the predictions of all of the potentials.

Insofar as assessing the ability of the HFD-C potentials to predict dccc data the following approach is taken. The BHPS potential to which the original data was fitted was used to generate pseudo dccc in the center-of-mass frame of reference. These data generated in this way are considered as standard data with which the predictions based on the HFD-C potentials may be compared. "Experimental" resolution of these pseudodata is "infinite" and, consequently, substantial structure in the cross sections is evident. The results are presented in Fig. 4 where the dots represent the BHPS pseudodata and the continuous line is the prediction of the HFD-C2 potential. The agreement is seen to be quite satisfactory. In fact, the prediction of slightly lower amplitudes at small angles is more in keeping with original data than is the BHPS or APBS potential. The rms deviation between the logarithms of the theoretical and pseudodata calculated at intervals of 0.25° from 0° to 90° in the center-of-mass frame of reference is taken as a measure of the goodness-of-fit. These deviations are presented in Table III. Also presented in Table III are the rms deviations between experimental⁹ and theoretical tccc on the basis of the various potentials for both Ar (primary beam)-Kr

(secondary beam) and Kr (primary beam)-Ar (secondary beam) cases. The results for the present HFD-C2 and APBS potentials are displayed in Figs. 5 and 6.

In Fig. 7, the repulsive walls of the HFD-C1, HFD-C2, and APBS potentials are shown along with the high repulsive wall of the potential determined by Rol and co-workers¹⁵ from high energy cross sections. The HFD-C1 and APBS potentials are seen to lie above that of Rol but the HFD-C2 potential is in closest agreement with it.

In conclusion, the HFD-C2 potential is a simple and accurate potential which appears to be the best representation of the Ar-Kr interaction insofar as its ability to predict a wide variety of dilute gas bulk and microscopic properties.

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²⁵From the trend of the deviation plots for the second virial coefficients, it is probable that the data point at 148.15 K should have associated with it error bounds of ± 1 cc/mol.