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Accurate Thermal Conductivity Coefficients for Argon Based on a State-of-the-Art Interatomic Potential

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An accurate interatomic potential was constructed by fitting a realistic function, constrained by theory, to a set of judiciously selected macroscopic and microscopic properties but not including thermal conductivity. Using this potential, accurate values of thermal conductivity of argon are obtained for the temperature range 100 to 6600 K. These are presented in tabular form as well as in terms of a correlation function.

KEY WORDS: argon; Hartree–Fock dispersion (HFD) potential; interatomic potential; shock-tube conductivity; thermal conductivity.

1. INTRODUCTION

The behavior of an atomic system is implicitly described by its associated interatomic potential. Given an accurate potential and the theories connecting it to the various properties of the system, one can calculate these with a great deal of precision. In this sense, the interatomic potential contains an enormous amount of information in condensed form.

An accurate potential for argon was constructed [1] by fitting a realistic function, constrained by theory, to a set of judiciously selected macro- and microscopic properties but *not including* thermal conductivity. The nature of the potential function required and the fitting procedure used are described and the many different properties that the potential is able to predict are indicated. The potential which accurately reproduces precise viscosity data should, of necessity, predict the thermal conductivity, which in first-order kinetic theory, depends on the same collision integral $\Omega^{(2,2)}$ [2]. Using this potential, accurate values of conductivity are calculated in

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the third-order Chapman–Cowling approximation [2] for the temperature range 100 to 6600 K. The values compare favorably with most of the primary conductivity data including the high-temperature shock-tube data of Cavers et al. [3] and Collins and Menard [4] but differ substantially from those presented by Hoshino et al. [5],

2. CONSTRUCTION OF THE POTENTIAL

In recent years, substantial advances have been made in the determination of accurate potentials for the monatomic gas pairs [6]. These advances have been achieved through the availability of precise experimental and theoretical information and new techniques for their analysis. A wide variety of information is available: precise dispersion coefficients, differential (dccs) and total (tccs) collision cross sections, vibrational–rotational spectra, and dilute-gas transport properties.

Some general comments should be made about the construction of an accurate potential and the mathematical function chosen to represent it. Accurate theoretical calculations have been made for the long-range and, additionally, in the case of argon, for the short-range. The attractive minimum which occurs from a balance of long- and short-range forces is difficult, if not impossible, to determine theoretically. This intermediate portion can be obtained by a fit of a potential function to a variety of carefully selected experimental data. The function must be realistic at short and long range and should lend itself readily to the inclusion of theoretical values if available. In addition, the potential function should be simple yet possess just enough flexibility to accommodate all the properties of interest. Potentials of the Lennard–Jones, m-6-8 [7], or exp-6 are not suitable candidates because they do not satisfy all of the above requirements. One potential that does is a modification [8] of the so-called HFD (Hartree–Fock dispersion) potential [9] and is now dubbed HFD-B. The HFD-B potential function has the following form:

$$V(r) = \varepsilon V^*(x) \tag{1}$$

where

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

with

$$F(x) = \begin{cases} \exp\left[-\left(\dfrac{D}{x} - 1\right)^2\right], & x < D \\ = 1, & x \geqslant D \end{cases} \tag{3}$$

Table I. Region of Potential Sensed by Various Properties

Property	Potential region sensed
Bulk property[a]	
Second virial coefficient	Area of potential well
LT second virial coefficients	Long-range tail
HT self-diffusion	Slope of repulsive wall
HT thermal diffusion	Slope of high repulsive wall
LT viscosity	Long-range tail
RT viscosity	Location of potential crossing point
LT thermal diffusion	Shape of potential well
Equilibrium condensed phase properties	Potential minimum
Molecular beam data	
High-energy tccs	Repulsive wall at small separations
Low-energy tccs (glory structure)	Potential well from minimum to long range; constrains product of ε and r_m
Dccs	Depending on relative energy of beams; low repulsive wall to inflection point in outer attractive wall
Spectroscopic data (uv absorption data)	
Vibrational spacings	Well depth, width of potential well as function of depth
Vibration–rotation band system	Shape and magnitude of potential well

[a] HT, high temperature; RT, room temperature; LT, low temperature.

Table II. Parameters for HFD-B Ar–Ar Potential[a]

A^*	2.26210716×10^5
α^*	10.77874743
c_6^*	1.10785136
c_8^*	0.56072459
c_{10}^*	0.34602794
C_6 (au)	64.3
C_8 (au)	1640
C_{10} (au)	51000
β^*	−1.8122004
β	−0.128422
D	1.36
ε/k (K)	143.224
r_m (Å)	3.7565
σ (Å)	3.3527_9

[a] Not all figures displayed are significant. We displayed them only to avoid round-off errors. C_6, C_8, and C_{10} are expressed as atomic units (au).

Table III. Primary Data Predicted by HFD-B Potential to Within Experimental Error

	Temperature range (K)	Error bars	rms deviation^a
Bulk Properties			
Second virial coefficients (ml · mol^{-1})			
Michels et al. (3-term fit) [14]	273–423	±0.3	0.09
Michels et al. (3-term fit) [15]	133–248	±0.3	0.11
Kalfoglu and Miller [26]	303–773	±0.3	0.19
Holborn and Otto [27]	173–673	±1	0.60
Whalley et al. [28]	273–873	±1.5	0.76
Fender and Halsey [29]	85–101	±1	0.44
Najafi et al. [30]	140–1100	±1	0.64
Hahn et al. [31]	200–273	±1	0.19
Rentschler and Schramm [32]	326–713	±4	0.57
Schramm et al. [33]	202–497	±4	0.63
Schramm and Hebgen [34]	77–90	±6	4.31
Viscosity (μ poise)			
Vogel [16]	293–623	±0.1 to 0.3%	0.23 (0.07)
Clarke and Smith [35, 36]	140–360^c	±1%	0.66 (0.42)
Dawe and Smith [37]	300–1400^c	±1%	3.75 (0.66)
Kestin et al. [38]	300.65	±0.3%	−0.14 (0.06)
Hanley [21]	80–1900^c	±1%	3.23 (0.66)
Watson [22]	250–1800^c	±1%	3.61 (0.55)
Guevara et al. [39]^b	1100–2100	±1%	4.51 (0.61)
Thermal conductivity (mW · m^{-1} · K^{-1})			
Springer and Wingeier [41]	1000–2500	±1.5%	0.373 (0.61)
Chen and Saxena [42]	400–2000^c	±1.5%	0.49 (0.91)
Kestin et al. [38]	300.65	±0.3%	+0.032 (0.18)
Cavers et al. [3]	3800–5500	±3%	2.62 (2.19)
Cavers et al. [3]	2952–5096	±3%	2.61 (2.44)
Collins and Menard [4]	1500–5000	±5%	1.63 (2.30)
Hirschberg [52]	5000–6600	±4%	4.80 (3.46)
Diffusion (cm^2 · s^{-1})			
Vugts et al. [43]	235–418	±0.65%	0.0005 (0.19)
Microscopic properties			
Spectroscopy vibration–rotation spacings (cm^{-1})			
Colbourn and Douglas [13]	—	0.10	0.032
Differential cross sections			
Parson et al. [44]	—	—	0.31
Total cross sections			
van den Biesen et al. [45]			
(1) Glory shape parameter	—	—	0.00443
(2) Glory position parameter (K · nm)		±0.07	−0.002

[a] Values in parentheses refer to rms percentage errors. (Reference is experimental value.)

[b] Values reexpressed in terms of viscosity ratios measured and a reference value based on the present potential at 283 K.

[c] Partial temperature range.

where

$$x = r/r_{\mathrm{m}}$$

It must be realized that various properties probe the potential in different regions. By increasing the range of measurement, one increases the range of the potential function sensed by the property. Consequently, one must perform a fit of the potential to a judiciously selected set of properties. In this way the interaction will be accurately characterized. In Table I, we list various properties and the approximate region of the potential sensed by each property.

A potential of the HFD-B form was constructed for argon [1], with a realistic long range using the new theoretical C_6 value of Kumar and Meath [10], a C_8 value within the bounds given by Tang et al. [11], and a C_{10} consistent with the other two values [12].

The potential was fitted to the vibration–rotation band system of the ultraviolet absorption spectrum observed by Colbourn and Douglas [13], the second virial data of Michels et al. [14, 15], the precise viscosity data of Vogel [16], and SCF calculations [9, 17] (as closely as possible). The parameters are reproduced in Table II.

It is better to use viscosity rather than thermal conductivity [both depend on the same collision integral $\Omega^{(2,2)}$ of kinetic theory] in the fitting procedure because the former can be measured with a higher degree of accuracy. For example, the viscosity of Vogel [16] has an error ranging from 0.1% at 300 K to 0.3% at 623 K. Hence, the fit to the viscosity of Vogel [16] and to the SCF calculations ensure an accurate repulsive wall, while the spectroscopy, virial data, and dispersion data accurately fix the well. All in all, the whole potential is well defined and is able to predict accurately all bulk and microscopic properties over a wide temperature range. Data that the potential is able to predict within experimental error are listed in Table III for the temperature ranges indicated.

3. THERMAL CONDUCTIVITY COEFFICIENTS

The thermal conductivity coefficients are calculated in third-order approximation using Chapman–Cowling expressions given by Hirschfelder et al. [2]. The required collision integrals are determined using the ACQN program of O'Hara and Smith [18–20] to an accuracy of 0.01%. Deviations of the various sets of primary experimental thermal conductivity values calculated on the basis of the HFD-B potential are shown in Figs. 1a and 1b. Similar plots are given in Figs. 2a and 2b for the various correlations of thermal conductivity. The correlations treated are those of

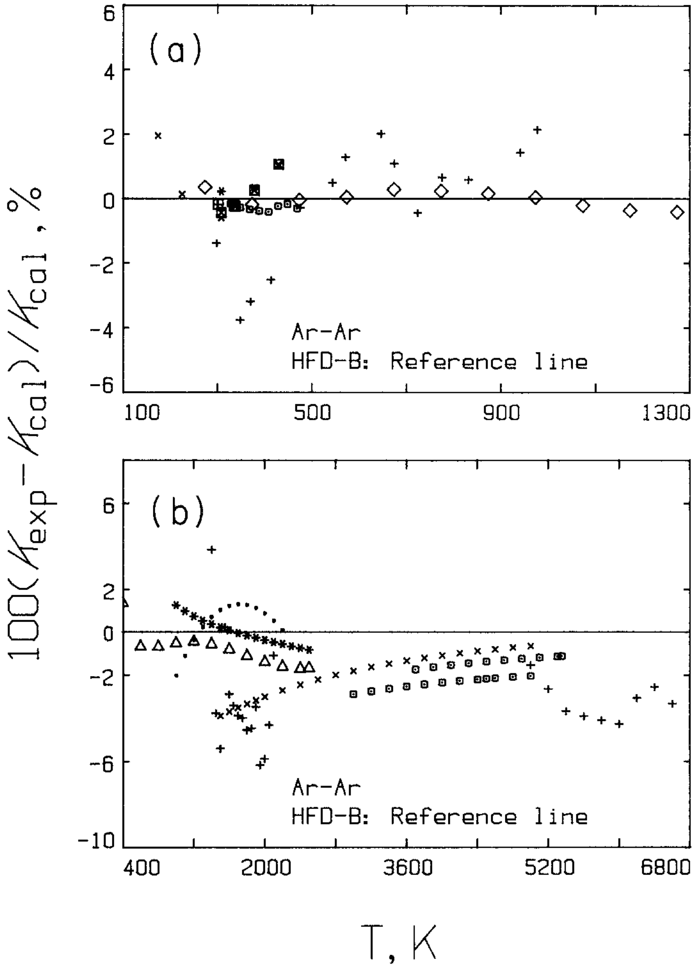

Fig. 1. Deviations of primary thermal conductivity data from predictions of HFD-B potential. (a) For temperature range 100 to 1300 K: (×) Mardolcar et al. [50]; (+) Le Neindre [47]; (⊞) Kestin et al. [38]; (⊠) Haran et al. [49]; (⊡) Haarman [46]; (∗) Assael and Wakeham [48]; (◇) Vargaftik and Zimina [40]. (b) For temperature range 400 to 6800 K: (·) Stefanov [51]; (∗) Springer and Wingeier [41]; (△) Chen and Saxena [42]; (+) Hirschberg [52]; (×) Collins and Menard [4]; (⊡) Cavers et al. [3].

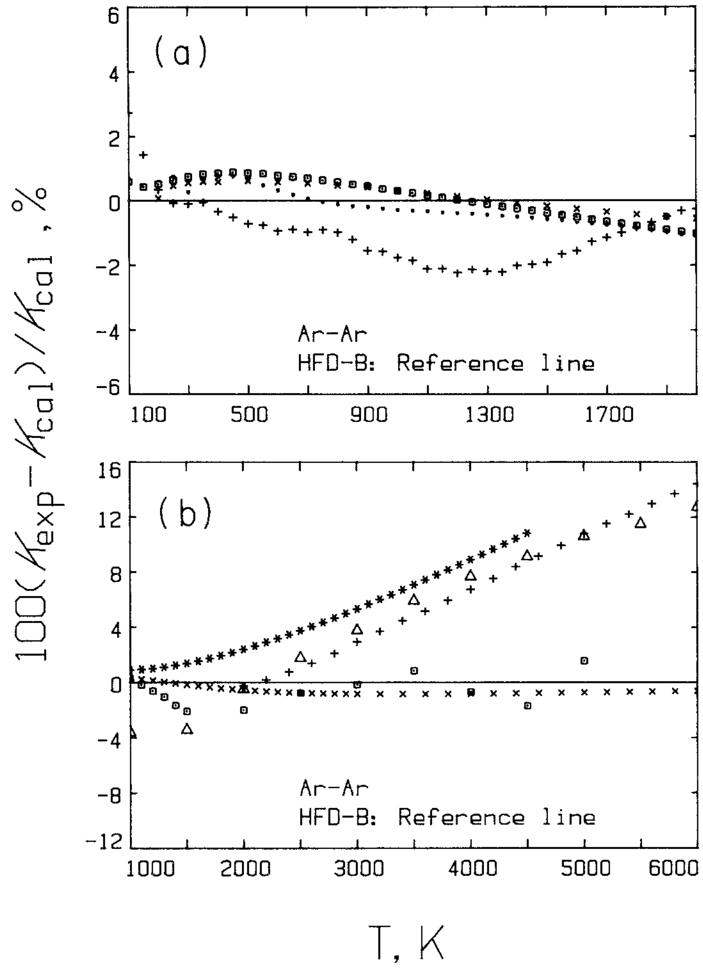

Fig. 2. Deviations of various thermal conductivity correlations from predictions of HFD-B potential. (a) For temperature range 100 to 2000 K: (□) Hanley [21]; (×) Kestin et al. [23]; (•) Watson [22]; (+) TPRC [53]. (b) For temperature range 1000 to 6000 K: (×) Kestin et al. [23]; (∗) Hoshino et al. [5]; (+) TPRC [53]; (□) Vargaftik [24]; (△) Amdur and Mason [25].

Hanley [21], Watson [22], Kestin et al. [23], Hoshino et al. [5], Vargaftik [24], and Amdur and Mason [25].

Details of the rms deviations for various sets of conductivity data are given in Table IV. From Table IV, we see that our values compare favorably with most of the primary data including the high-temperature shock-tube data of Cavers et al. [3], and Collins and Menard [4] (see Fig. 1b) but differ substantially from those presented by Hoshino et al. [5]. In particular, the data of Vargaftik and Zimina [40] and Kestin and co-workers [23, 30, 38] are accurately predicted. In Table V, we display numerical values of recommended thermal conductivity coefficients. For convenience, these are expressed in terms of a correlation function for the purposes of interpolation:

$$\kappa = \exp[A + B \ln T + C(\ln T)^2 + D(\ln T)^3 + E(\ln T)^4] \tag{4}$$

Table IV. Thermal Conductivity: Deviations from Primary and Correlated Data (Units of $\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$)

Data	Temperature range (K)	Accuracy (%)	rms deviation[a]	Max/min deviation[a] (%)
Primary data				
Haarman [46]	328–468	±0.3	0.066 (0.30)	+0.16 to +0.41
Le Neindre [47]	298–977	±2.5	0.498 (1.88)	−2.10 to +3.92
Springer and Wingeier [41]	1000–2500	±1.5	0.373 (0.61)	−1.27 to +0.84
Chen and Saxena [42]	400–2500	±1.5	0.760 (1.14)	−1.29 to +1.71
Kestin et al. [38]	300.65	±0.3	0.032 (0.18)	+0.18
Assael and Wakeham [48]	308.15	±0.2	0.041 (0.23)	−0.23
Haran et al. [49]	308–429	±0.3	0.124 (0.55)	−1.06 to +0.44
Hirschberg [52]	5000–6600	±4	4.800 (3.46)	+1.57 to +4.45
Mardolcar et al. [50]	174–429	±0.3	0.156 (1.02)	−1.91 to +0.60
Stefanov [51]	1000–2200	±3	0.569 (1.03)	−1.22 to +2.14
Vargaftik and Zimina [40]	273–1273	—	0.121 (0.30)	−0.35 to +0.42
Collins and Menard [4]	1500–5000	±5	1.683 (2.30)	+0.66 to +4.05
Cavers et al. [3]	3800–5500	±3	2.62 (2.19)	+1.98 to +2.49
Cavers et al. [3]	2952–5096	±3	2.61 (2.44)	+2.08 to +2.97
Correlation data				
Kestin et al. [23]	50–3273	±0.5	0.297 (0.72)	−0.58 to +2.05
Hanley [21]	100–2000	±1	0.290 (0.61)	−0.87 to +1.04
Watson [22]	250–2000	±1	0.348 (0.61)	−0.71 to +1.17
Hoshino et al. [5]	1000–4500	±3 to ±9	6.221 (5.42)	−9.77 to −0.87
Vargaftik [24]	100–5000	—	0.767 (1.32)	−3.83 to +2.13

[a] Reference is experimental value.

Coefficients for this expression, the range of applicability, and the corresponding standard deviation are given in Table VI. Estimated errors for various temperature regions are given in Table VII.

4. CONCLUSIONS

Not only can the potential accurately predict second virials and viscosity coefficients but it can accurately predict microscopic (spectroscopic, differential, and total scattering cross sections) and condensed

Table V. Thermal conductivity of argon (Units of mW · m^{-1} · K^{-1})

T(K)	κ	T(K)	κ	T(°C)	κ	T(°C)	κ
100	6.35	1800	64.65	0	16.38	1600	66.40
150	9.44	1900	67.03	50	18.87	1700	68.75
200	12.40	2000	69.38	100	21.21	1800	71.07
250	15.16	2200	73.96	150	23.41	1900	73.36
300	17.74	2400	78.42	200	25.49	2000	75.61
350	20.14	2600	82.75	250	27.48	2200	80.01
400	22.41	2800	86.99	300	29.40	2400	84.31
450	24.54	3000	91.14	350	31.23	2600	88.52
500	26.57	3200	95.20	400	33.00	2800	92.63
550	28.52	3400	99.18	450	34.72	3000	96.66
600	30.39	3600	103.10	500	36.39	3200	100.62
650	32.19	3800	106.96	550	38.02	3400	104.52
700	33.93	4000	110.75	600	39.60	3600	108.35
750	35.62	4200	114.49	650	41.15	3800	112.12
800	37.27	4400	118.18	700	42.66	4000	115.85
850	38.87	4600	121.83	750	44.15	4200	119.52
900	40.43	4800	125.43	800	45.62	4400	123.15
950	41.96	5000	128.99	850	47.04	4600	126.74
1000	43.47	5200	132.51	900	48.46	4800	130.28
1100	46.38	5400	135.99	950	49.85	5000	133.79
1200	49.20	5600	139.44	1000	51.21	5200	137.26
1300	51.94	5800	142.85	1100	53.89	5400	140.69
1400	54.60	6000	146.23	1200	56.50	5600	144.09
1500	57.20	6200	149.59	1300	59.06	5800	147.46
1600	59.73	6400	152.91	1400	61.55	6000	150.80
1700	62.21	6600	156.20	1500	64.00	6200	154.12
Extended temperature range[a] (units of K and mW · m^{-1} · K^{-1})							
6500	154.6	7500	170.7	8500	186.3	9500	201.5
7000	162.7	8000	178.6	9000	193.9	10000	208.9

[a] Negligible ionization is assumed.

Table VI. Parameters for Correlation Function [Eq. (4)]

Parameter	Temperature range (K)	
	100–1000	1000–6600
A	5.54830	−9.27601
B	−5.54767	4.70128
C	1.88531	−0.715852
D	−0.233009	0.0557330
E	0.0102716	−0.00159839
SD	0.0027	0.0015

phase properties (binding energy, pair correlation functions, etc.). Hence, the potential behaves as an all-encompassing correlation function. Indeed, it contains a great deal of information in compact form. As a result, the thermal conductivity values predicted by the potential are, in all probability, very accurate. Recommended values for the thermal conductivity for the range 100 to 6600 K are presented in tabular form and by an empirical correlation function for purposes of interpolation. The values presented compare favorably with most of the primary literature data including the high-temperature shock-tube data of Cavers et al. [3] and the earlier work of Collins and Menard [4] but not the recently published values of Hoshino et al. [5]. With the assumption of the onset of negligible ionization, predicted values are given in the extended temperature range from 6500 to 10,000 K in Table V.

Table VII. Estimated Errors for Thermal Conductivity [Eq. (4)]

T (K)	Error (%)
200	±0.2
300	±0.1
600	±0.2
1000	±0.4
2000	±0.6
3000	±1.0
4000	±1.5
6000	±3.0

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