Intermolecular Potential Energy Functions for He–Ne, He–Ar, He–Kr, and He–Xe from the Corresponding States Viscosity

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Intermolecular potential-energy functions are given for helium–heavier-noble gas interactions directly from the inversion of experimental reduced viscosity collision integrals obtained from the corresponding-states correlation. The results are in excellent agreement with the potentials proposed by L. J. Danielson and M. Keil.

Direct inversion methods for the potential-energy interactions of noble gases from data on viscosity have been developed by E. B. Smith and others,[1—4] and recently tested by Boushehri[5,6] and Maghari[5,7,8] in connection with the extended law of the corresponding-state. This paper is a continuation of recent work on the He–He, Ne–Ne, and Ne–heavier-noble gas systems.[7,8] The characterization of this family of systems is now complete with the presentation of He–heavier-noble gas systems. We reexamine here the inversion method in order to obtain the potential-energy functions of He–Ne, He–Ar, He–Kr, and He–Xe interactions from the experimental reduced viscosity collision integrals obtained from the corresponding-states correlation. The computed potentials are in excellent agreement with the potentials proposed by Danielson and Keil.[9,10]

Methodology

The kinetic-theory formula for the viscosity (η) of a dilute gas is[11]

$$\eta = \frac{5}{16}\frac{(\pi m k_B T)^{1/2}}{\Omega^{(2,2)}} f_\eta, \tag{1}$$

where k_B is Boltzmann's constant, m is the molecular mass, and f_η represents a higher order kinetic-theory correction that deviates only slightly from unity. The normalization of the collision integral, $\Omega^{(2,2)}$ has been chosen so that it is equal to πd^2 for a rigid sphere of diameter d.

In this paper we consider the extended principle of corresponding-states in terms of the unlike pair potentials. The collision integral $\Omega^{(2,2)*}$, which correlated in the extended principle of corresponding-states is defined as[12]

$$\Omega^{(2.2)*} = 1.1943(C_6^*/T^*)^{(1/3)}\left[1 + a_1(T^*)^{1/3} + a_2(T^*)^{2/3} + a_3(T^*) + a_4(T^*)^{4/3} + a_5(T^*)^{5/3} + a_6(T^*)^2\right], \quad 0 \le T^* \le 1.2, \tag{2a}$$

where

$$a_1 = 0.18$$
$$a_2 = 0$$
$$a_3 = -1.20407 - 0.195866(C_6^*)^{-1/3}$$
$$a_4 = -9.86374 + 20.2221(C_6^*)^{-1/3}$$
$$a_5 = -16.6295 - 31.3613(C_6^*)^{-1/3}$$
$$a_6 = -6.73805 + 12.6611(C_6^*)^{-1/3}$$

$$\Omega^{(2,2)*} = \exp\left[0.46641 - 0.56991(\ln T^*) + 0.1959(\ln T^*)^2 - 0.0379(\ln T^*)^3 + 0.00259(\ln T^*)^4\right], \quad 1.2 \le T^* \le 10 \tag{2b}$$

$$\Omega^{(2,2)*} = \rho^{*2}\alpha^2\left[1.04 + a_1(\ln T^*)^{-1} + a_2(\ln T^*)^{-2} + a_3(\ln T^*)^{-3} + a_4(\ln T^*)^{-4}\right], \quad T^* \ge 10, \tag{2c}$$

where

$$a_1 = 0$$
$$a_2 = -33.0838 + (\alpha_{10}\rho^*)^{-2}\left[20.0862 + \left(\frac{72.1059}{\alpha_{10}}\right) + \left(\frac{8.27648}{\alpha_{10}}\right)^2\right]$$
$$a_3 = 101.571 - (\alpha_{10}\rho^*)^{-2}\left[56.4472 + \left(\frac{286.393}{\alpha_{10}}\right) + \left(\frac{17.7610}{\alpha_{10}}\right)^2\right]$$
$$a_4 = -87.7036 + (\alpha_{10}\rho^*)^{-2}\left[46.3130 + \left(\frac{277.146}{\alpha_{10}}\right) + \left(\frac{19.0573}{\alpha_{10}}\right)^2\right]$$
$$a_{10} = \ln\frac{V_0^*}{10},$$

where $\Omega^{(2,2)*} = \overline{\Omega}^{(2,2)}/\pi\sigma^2$, in which σ is a distance scaling parameter, and the other parameters are given in Table 1.[12] The reduced temperature, (T^*) is defined by the relation $T^* = k_B T/\varepsilon$, where ε is the depth of the potential well.

Table 1. The Low and High-Temperature Scaling Parameters

	He–Ne	He–Ar	He–Kr	He–Xe
C_6^*	2.940	2.681	2.498	2.346
ρ^*	0.0788	0.0791	0.0772	0.0764
$V_0^* \times 10^{-5}$	10.60	9.740	10.89	13.37

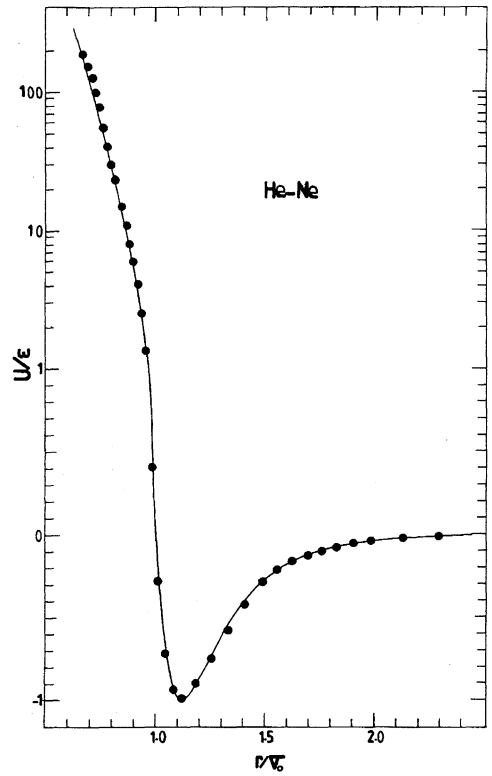

Fig. 1. Reduced pair potential obtained by INVERT of the corresponding–states viscosity for He–Ne (●). Shown for comparison is the Keil and Danielson potential.[10] Note that the scale changes from linear to logarithm at $U/\varepsilon = 0.1$.

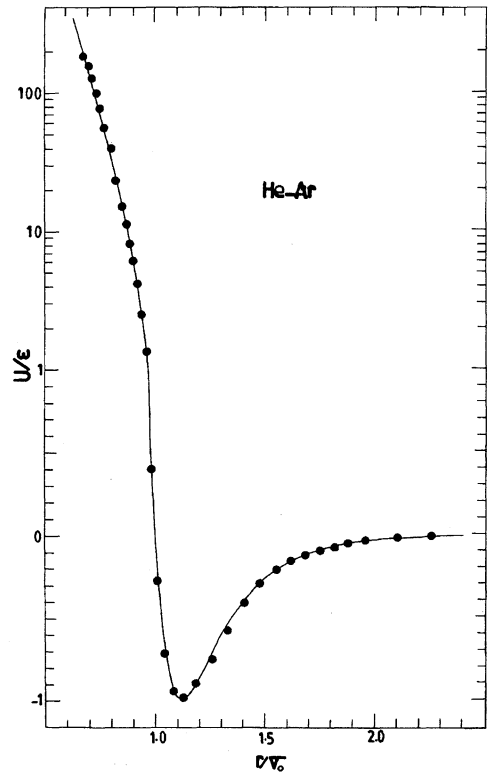

Fig. 2. Reduced pair potential obtained by INVERT of the corresponding–states viscosity for He–Ar (●). Shown for comparison is the Keil and Danielson potential.[9] Note that the scale changes from linear to logarithm at $U/\varepsilon = 0.1$.

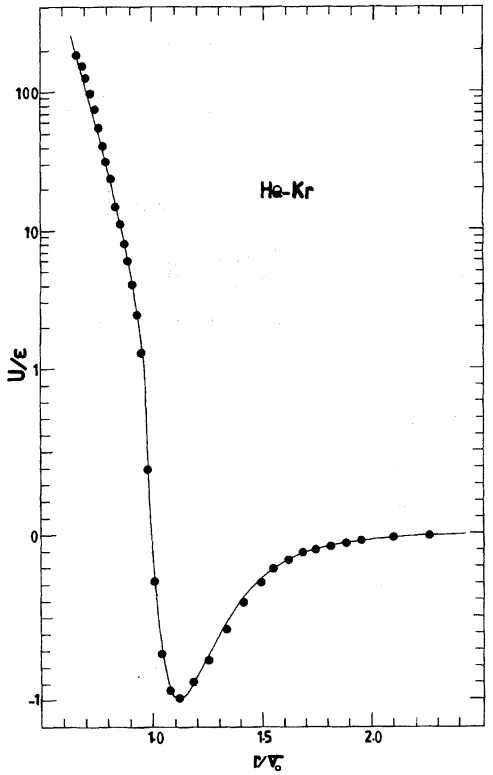

Fig. 3. Reduced pair potential obtained by INVERT of the corresponding–states viscosity for He–Kr (●). Shown for comparison is the Keil and Danielson potential.[9] Note that the scale changes from linear to logarithm at $U/\varepsilon = 0.1$.

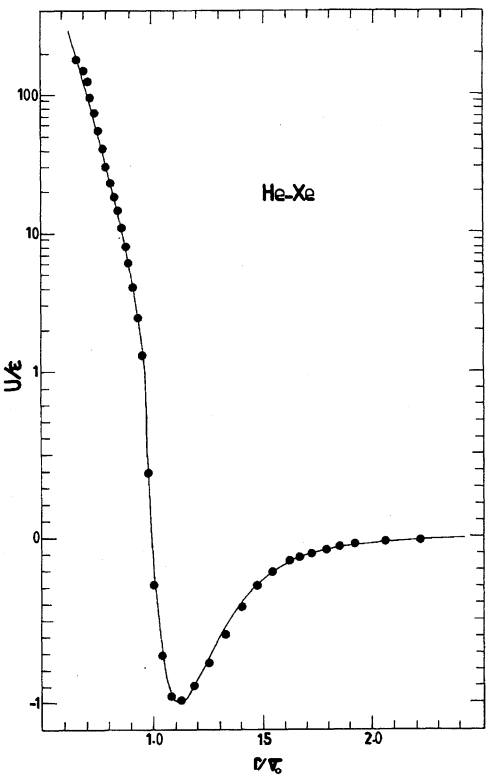

Fig. 4. Reduced pair potential obtained by INVERT of the corresponding–states viscosity for He–Xe (●). Shown for comparison is the Keil and Danielson potential.[9] Note that the scale changes from linear to logarithm at $U/\varepsilon = 0.1$.

A direct-inversion procedure for the viscosity is based on the idea that at a given T^* the value of $\Omega^{(2,2)^*}$ is determined by the potential within a small range of separation distances around a value r, so that

$$\Omega^{(2,2)^*} = (r/\sigma)^2 \quad (3)$$

and

$$U_n(r) = U_n\left[\Omega^{(2,2)^*}(T^*)\right], \quad (4)$$

where the subscript n refers to the iteration number. The initial value of the potential function U_0 ($\Omega^{(2,2)^*}$) is chosen according to the Lennard–Jones (12, 6) potential model. The values of $\Omega^{(2,2)^*}_{(T^*)}$ are given by Viehland et al.[13] The corresponding value of r may be obtained using the collision integral, which is calculated from Eqs. 2a, 2b, and 2c. Therefore, finding $U(r)$ from $\Omega^{(2,2)^*}$ is straightforward when ε is equal to unity. Eqs. 2a, 2b, and 2c can be inverted by the above method to yield $U(r)/\varepsilon$ as a function of r/σ. This process may be repeated until convergence is reached.

In this work, the triple integrals are evaluated by using the Gatland version of a computer program developed by O'Hara and Smith.[14,15] The present results converged after two iterations. The value of σ turns out to be equal to the value σ_o, such that $U(\sigma_o) = 0$; the precise values of σ/σ_o for He–Ne, He–Ar, He–Kr, and He–Xe are 1.0014, 1.0015, 1.0016, and 1.0018, respectively. The results obtained here cover the range from the potential-energy minimum inwards to a repulsion of about 120-times the well depth. In this work, the potential well depth (ε) could be obtained as the relative value with respect to a convenient reference system. We chose the HFD potential model as the reference system. The precise values of $\varepsilon/\varepsilon_{ref}$ for He–Ne, He–Ar, He–Kr, and He–Xe are 0.9890, 0.9849, 0.9822, and 0.9826, respectively.

Table 2. The Scaling Parameters σ_o and ε for the He–Heavier Noble Gas System

	σ_o (Å)	ε (meV)
He–Ne	2.6952	1.807
He–Ar	3.1023	2.552
He–Kr	3.2937	2.619
He–Xe	3.5586	2.589

Results and Discussion

An accurate reduced potential was obtained for He–heavier-noble gas systems by performing an INVERT on the

Table 3. Dimensionless Collision Integrals and the Related Rations for He–Ne

$\mathrm{Log}_{10} T^*$	$\Omega^{(2,2)^*}$	A^*	B^*	C^*	E^*	F^*
−1.0	3.6922	1.0533	1.1308	0.8798	0.9104	0.9494
−0.9	3.4140	1.0541	1.1509	0.8912	0.9186	0.9562
−0.8	3.1761	1.0556	1.1716	0.8955	0.9242	0.9556
−0.7	2.9684	1.0609	1.1986	0.8940	0.9285	0.9499
−0.6	2.7812	1.0721	1.2321	0.8867	0.9290	0.9414
−0.5	2.5990	1.0879	1.2638	0.8746	0.9225	0.9325
−0.4	2.4065	1.1039	1.2825	0.8603	0.9095	0.9247
−0.3	2.1984	1.1158	1.2822	0.8476	0.8940	0.9188
−0.2	1.9817	1.1210	1.2642	0.8396	0.8813	0.9153
−0.1	1.7705	1.1198	1.2347	0.8384	0.8751	0.9150
0.0	1.5784	1.1144	1.2013	0.8441	0.8767	0.9183
0.1	1.4138	1.1077	1.1702	0.8551	0.8849	0.9252
0.2	1.2787	1.1021	1.1449	0.8693	0.9974	0.9351
0.3	1.1709	1.0987	1.1262	0.8845	0.9113	0.9468
0.4	1.0858	1.0979	1.1136	0.8987	0.9244	0.9590
0.5	1.0181	1.0994	1.1062	0.9110	0.9356	0.9705
0.6	0.9636	1.1026	1.1024	0.9208	0.9443	0.9807
0.7	0.9183	1.1068	1.1009	0.9282	0.9506	0.9894
0.8	0.8793	1.1161	1.1005	0.9335	0.9547	0.9968
0.9	0.8444	1.1161	1.1006	0.9372	0.9571	1.0029
1.0	0.8123	1.1203	1.1010	0.9397	0.9585	1.0076
1.1	0.7823	1.1242	1.1021	0.9412	0.9596	1.0110
1.2	0.7541	1.1282	1.1047	0.9420	0.9606	1.0132
1.3	0.7275	1.1330	1.1093	0.9418	0.9615	1.0145
1.4	0.7023	1.1390	1.1155	0.9406	0.9617	1.1057
1.5	0.6777	1.1459	1.1213	0.9385	0.9604	1.0176
1.6	0.6525	1.1520	1.1233	0.9364	0.9567	1.0120
1.7	0.6254	1.1543	1.1179	0.9352	0.9509	1.0258
1.8	0.5960	1.1501	1.1040	0.9363	0.9446	1.0305
1.9	0.5652	1.1382	1.0833	0.9405	0.9404	1.0334
2.0	0.5348	1.1196	1.0596	0.9477	0.9403	1.0335
2.1	0.5071	1.0972	1.0367	0.9570	0.9449	1.0312
2.2	0.4837	1.0744	1.0177	0.9673	0.9531	1.0274
2.3	0.4655	1.0538	1.0039	0.9771	0.9633	1.0229
2.4	0.4522	1.0362	0.9952	0.9856	0.9736	1.0189

Table 4. Dimensionless Collision Integrals and the Related Ratios for He–Ar

$\mathrm{Log}_{10} T^*$	$\Omega^{(2,2)^*}$	A^*	B^*	C^*	E^*	F^*
−1.0	3.5943	1.0593	1.1208	0.8854	0.9132	0.9573
−0.9	3.3333	1.0590	1.1410	0.8973	0.9222	0.9643
−0.8	3.1119	1.0596	1.1626	0.9019	0.9282	0.9637
−0.7	2.9191	1.0643	1.1912	0.9002	0.9325	0.9576
−0.6	2.7446	1.0748	1.2269	0.8925	0.9326	0.9482
−0.5	2.5728	1.0898	1.2607	0.8797	0.9257	0.9381
−0.4	2.3888	1.1054	1.2812	0.8646	0.9123	0.9291
−0.3	2.1874	1.1169	1.2822	0.8510	0.8964	0.9221
−0.2	1.9755	1.1220	1.2649	0.8422	0.8832	0.9178
−0.1	1.7676	1.1207	1.2357	0.8403	0.8764	0.9168
0.0	1.5773	1.1152	1.2024	0.8453	0.8775	0.9196
0.1	1.4136	1.1084	1.1711	0.8559	0.8854	0.9261
0.2	1.2789	1.1025	1.1455	0.8698	0.8976	0.9356
0.3	1.1711	1.0990	1.1267	0.8847	0.9113	0.9471
0.4	1.0859	1.0981	1.1140	0.8988	0.9244	0.9591
0.5	1.0183	1.0996	1.1065	0.9110	0.9353	0.9704
0.6	0.9683	1.1028	1.1028	0.9207	0.9444	0.9805
0.7	0.9185	1.1072	1.1015	0.9280	0.9506	0.9893
0.8	0.8795	1.1121	1.1013	0.9332	0.9547	0.9967
0.9	0.8446	1.1169	1.1016	0.9368	0.9571	1.0029
1.0	0.8125	1.1213	1.1021	0.9392	0.9584	1.0076
1.1	0.7824	1.1254	1.1035	0.9407	0.9594	1.0111
1.2	0.7540	1.1296	1.1062	0.9413	0.9603	1.0133
1.3	0.7272	1.1346	1.1109	0.9410	0.9611	1.0146
1.4	0.7017	1.1408	1.1173	0.9397	0.9612	1.0158
1.5	0.6768	1.1479	1.1232	0.9376	0.9598	1.0177
1.6	0.6512	1.1540	1.1252	0.9354	0.9560	1.0212
1.7	0.6237	1.1563	1.1197	0.9341	0.6500	1.0260
1.8	0.5939	1.1520	1.1055	0.9353	0.9437	1.0307
1.9	0.5626	1.1399	1.0845	0.9395	0.9395	1.0335
2.0	0.5319	1.1210	1.0604	0.9468	0.9394	1.0337
2.1	0.5040	1.0984	1.0372	0.9563	0.9441	1.0313
2.2	0.4805	1.0753	1.0179	0.9668	0.9525	1.0275
2.3	0.4721	1.0544	1.0039	0.9767	0.9628	1.0230
2.4	0.4487	1.0373	0.9952	0.9853	0.9732	1.0188

extended principle of corresponding states viscosity with no additional information. The obtained results are in excellent agreement with the potentials proposed by Danielson and Keil.[9,10] Figures 1, 2, 3, and 4 show the results for He–Ne, He–Ar, He–Kr, and He–Xe, respectively. The values of the scaling parameters (σ_0 and ε) obtained in this work are given in Table 2. These accurate potentials can be used to obtain collision integrals and their ratios, which are needed to calculate other transport properties more accurately. The ratios of the collision integrals are found according to the following formulas:

$$A^* = \Omega^{(2,2)^*} / \Omega^{(1,1)^*}, \tag{5a}$$

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

$$C^* = \Omega^{(1,2)^*} / \Omega^{(1,1)^*}, \tag{5c}$$

$$E^* = \Omega^{(2,3)^*} / \Omega^{(2,2)^*}, \tag{5d}$$

$$F^* = \Omega^{(3,3)^*} / \Omega^{(1,1)^*}, \tag{5e}$$

The viscosity collision integrals, ($\Omega^{(2,2)^*}$) and their ratios for He–Ne, He–Ar, He–Kr, and He–Xe are given in Tables 3, 4, 5, and 6, respectively.

Table 5. Dimensionless Collision Integrals and the Related Ratios for He–Kr

$\mathrm{Log}_{10} T^*$	$\Omega^{(2,2)^*}$	A^*	B^*	C^*	E^*	F^*
−1.0	3.5218	1.0649	1.1138	0.8882	0.9147	0.9627
−0.9	3.2701	1.0635	1.1330	0.9009	0.9235	0.9706
−0.8	3.0564	1.0625	1.1544	0.9060	0.9294	0.9706
−0.7	2.8706	1.0652	1.1835	0.9048	0.9340	0.9646
−0.6	2.7036	1.0741	1.2205	0.8972	0.9348	0.9547
−0.5	2.5402	1.0882	1.2564	0.8842	0.9285	0.9436
−0.4	2.3650	1.1034	1.2792	0.8686	0.9153	0.9334
−0.3	2.1715	1.1152	1.2820	0.8542	0.8992	0.9252
−0.2	1.9659	1.1207	1.2657	0.8447	0.8855	0.9200
−0.1	1.7622	1.1199	1.2368	0.8420	0.8782	0.9184
0.0	1.5746	1.1148	1.2033	0.8465	0.8786	0.9206
0.1	1.4123	1.1081	1.1718	0.8566	0.8860	0.9267
0.2	1.2784	1.1024	1.1460	0.8702	0.8979	0.9360
0.3	1.1710	1.0989	1.1269	0.8849	0.9115	0.9473
0.4	1.0860	1.0981	1.1143	0.8989	0.9245	0.9591
0.5	1.0185	1.0996	1.1069	0.9110	0.9358	0.9703
0.6	0.9641	1.1031	1.1035	0.9206	0.9446	0.9804
0.7	0.9190	1.1078	1.1025	0.9278	0.9508	0.9892
0.8	0.8801	1.1130	1.1026	0.9329	0.9548	0.9966
0.9	0.8451	1.1182	1.1030	0.9363	0.9570	1.0028
1.0	0.8129	1.1229	1.1038	0.9386	0.9582	1.0077
1.1	0.7825	1.1272	1.1052	0.9399	0.9590	1.0112
1.2	0.7538	1.1316	1.1080	0.9404	0.9597	1.0135
1.3	0.7266	1.1366	1.1126	0.9401	0.9604	1.0149
1.4	0.7006	1.1427	1.1188	0.9388	0.9604	1.0160
1.5	0.6752	1.1496	1.1246	0.9367	0.9589	1.0180
1.6	0.6492	1.1556	1.1263	0.9345	0.9551	1.0214
1.7	0.6213	1.1557	1.1206	0.9334	0.9492	1.0262
1.8	0.5911	1.1531	1.1061	0.9346	0.9430	1.0308
1.9	0.5597	1.1408	1.0849	0.9389	0.9389	1.0336
2.0	0.5289	1.1217	1.0605	0.9464	0.9389	1.0337
2.1	0.5009	1.0988	1.0372	0.9666	0.9437	1.0314
2.2	0.4774	1.0756	1.0178	0.9666	0.9522	1.0275
2.3	0.4590	1.0546	1.0039	0.9766	0.9625	1.0231
2.4	0.4457	1.0374	0.9950	0.9853	0.9731	1.0189

Table 6. Dimensionless Collision Integrals and the Related Ratios for He–Xe

$\mathrm{Log}_{10} T^*$	$\Omega^{(2,2)^*}$	A^*	B^*	C^*	E^*	F^*
−1.0	3.4599	1.0705	1.1104	0.8908	0.9167	0.9662
−0.9	3.2189	1.0692	1.1293	0.9035	0.9257	0.9737
−0.8	3.0151	1.0686	1.1494	0.9088	0.9319	0.9739
−0.7	2.8387	1.0718	1.1775	0.9078	0.9367	0.9682
−0.6	2.6801	1.0809	1.2144	0.9006	0.9374	0.9588
−0.5	2.5238	1.0949	1.2513	0.8878	0.9308	0.9480
−0.4	2.3542	1.1096	1.2755	0.8722	0.9172	0.9378
−0.3	2.1650	1.1205	1.2797	0.8576	0.9008	0.9295
−0.2	1.9625	1.1251	1.2647	0.8476	0.8868	0.9238
−0.1	1.7610	1.1233	1.2368	0.8444	0.8791	0.9214
0.0	1.5746	1.1174	1.2039	0.8482	0.8793	0.9230
0.1	1.4129	1.1101	1.1727	0.8578	0.8864	0.9284
0.2	1.2792	1.1039	1.1468	0.8709	0.8981	0.9371
0.3	1.1717	1.1000	1.1275	0.8853	0.9115	0.9480
0.4	1.0866	1.0987	1.1145	0.8991	0.9244	0.9596
0.5	1.0189	1.0999	1.1067	0.9111	0.9355	0.9708
0.6	0.9643	1.1030	1.1028	0.9208	0.9443	0.9808
0.7	0.9189	1.1072	1.1013	0.9281	0.9506	0.9895
0.8	0.8798	1.1119	1.1009	0.9334	0.9546	0.9968
0.9	0.8448	1.1165	1.1010	0.9370	0.9570	1.0029
1.0	0.8126	1.1207	1.1013	0.9395	0.9584	1.0076
1.1	0.7825	1.1245	1.1023	0.9411	0.9594	1.0111
1.2	0.7541	1.1284	1.1047	0.9418	0.9604	1.0133
1.3	0.7274	1.1331	1.1090	0.9417	0.9613	1.0147
1.4	0.7021	1.1389	1.1149	0.9406	0.9615	1.0159
1.5	0.6774	1.1455	1.1204	0.9387	0.9603	1.0178
1.6	0.6522	1.1513	1.1222	0.9367	0.9567	1.0212
1.7	0.6251	1.1534	1.1166	0.9357	0.9510	1.0259
1.8	0.5959	1.1491	1.1027	0.9369	0.9450	1.0305
1.9	0.5652	1.1372	1.0822	0.9411	0.9409	1.0333
2.0	0.5351	1.1187	1.0587	0.9483	0.9409	1.0335
2.1	0.5077	1.0964	1.0361	0.9576	0.9454	1.0311
2.2	0.4845	1.0737	1.0173	0.9677	0.9536	1.0273
2.3	0.4664	1.0533	1.0037	0.9775	0.9637	1.0229
2.4	0.4532	1.0365	0.9952	0.9858	0.9739	1.0187

The accuracy of these values is better than 0.1%. The quantum effects in the low-temperature region were considered in obtaining $\Omega^{(2,2)^*}$, since quantum-mechanical correction for the collision integrals was considered by Najafi et al.[12]

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