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Theoretical calculation of the transport properties of monatomic lithium vapor

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Transport properties of dilute monatomic gases depend on two body atom–atom interaction potentials. When two ground state (^2S) lithium atoms interact, they can follow either of two potential energy curves corresponding to the Li_2 molecule in the $X\,^1\Sigma_g^+$ or $^3\Sigma_u^+$ state. Transport collision integrals for these states have been calculated by accurately representing quantum mechanical potential energy curves with the Hulburt–Hirschfelder potential. The excellent agreement of calculated viscosities with experimental results provides further evidence that this potential can be used to estimate accurately transport properties under conditions where experimental data are sparse or unavailable.

I. INTRODUCTION

The properties of alkali metals in the gas phase are of both theoretical interest and practical importance. Small clusters of these atoms have been considered as models for investigating catalytic activity[1,2] and there are applications associated with optical and electrical phenomena,[3] heat pipes,[4] dimer lasers,[5,6] fusion reactors,[3,7,8] and isotope separation.[3,8–10]

The purpose of this paper is to report calculations of the transport properties (viscosity, thermal conductivity, and self-diffusion) and the second virial coefficient of monatomic lithium vapor. The procedure used depends on knowledge of the interaction potential between two lithium atoms (i.e., Li_2) for the molecular states which dissociate to the ground state (^2S) atoms, followed by the calculation of the second virial coefficient and of the dilute gas collision integrals for the appropriate Chapman–Enskog expressions for the transport properties.[11] We have previously developed methods for calculating transport properties for any reasonably well behaved atom–atom potential, including those with interesting features such as multiple extrema.[12–15] The focus of much of this work has been on predicting the properties of gases at high temperatures, where laboratory measurements are not feasible. Here, the Hulburt–Hirschfelder potential, for which the parameters can be determined from the spectroscopic constants of the gas dimers, has proven especially valuable.

While our approach was originally developed for use with potentials determined entirely by spectroscopic constants, potentials determined in other ways can also be used.[15] In the present work, we demonstrate how this method can be extended to potentials determined from quantum mechanical calculations by fitting the Hulburt–Hirschfelder potential to *ab initio* results. In particular, we demonstrate how a Nelder–Mead simplex procedure can be used to obtain a fit to the weakly bound $^3\Sigma_u^+$ state of the lithium dimer, for which the required spectroscopic constants are not available.

II. INTERACTION POTENTIALS

The interaction of two ground state (^2S) lithium atoms results in either the singlet ground $X\,^1\Sigma_g^+$ or the triplet $^3\Sigma_u^+$ molecular state of the Li_2 dimer. Contributions from both states must be included in transport property and second virial coefficient calculations. In the case of the singlet state an experimental Rydberg–Klein–Rees[16–18] (RKR) potential energy curve has been determined.[19,20] The Hulburt–Hirschfelder (HH) potential[21,22] is probably the best general purpose[23–27] atom–atom potential for fitting RKR potentials. Indeed, it may represent the true potential better[14] than the representation provided by the RKR potential in some cases. The HH potential depends only on the spectroscopic constants for the well depth ϵ, the fundamental vibrational frequency ω_e, the anharmonicity constant $\omega_e X_e$, the rotational constant B_e, the rotation–vibration coupling constant α_e, and the equilibrium interatomic distance in the dimer r_e. In reduced form, the HH potential is given by[13]

$$V^*(r^*) = e^{-2a(r^*/d-1)} - 2e^{-a(r^*/d-1)} + \beta\left(\frac{r^*}{d}-1\right)^3\left[1+\gamma\left(\frac{r^*}{d}-1\right)\right]e^{-2a(r^*/d-1)}, \tag{1}$$

where

$$V^* = \frac{V}{\epsilon}, \quad r^* = \frac{r}{\sigma}, \quad d = \frac{r_e}{\sigma},$$

and V is the potential energy, r is the interatomic separation, and σ is the smallest interatomic separation at which the potential is zero (the effective hard sphere diameter). Also, with ϵ' the well depth in cm^{-1},

$$a = \frac{\omega_e}{\sqrt{2B_e\epsilon'}}, \quad \beta = ca^3, \quad \gamma = ba,$$

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TABLE I. Ratio of the RKR to the HH potential energy for the ground $X\,^1\Sigma_g^+$ state of Li_2 as a function of interatomic separation.

$r(10^{-10}\,m)$	RKR/HH[a]	$r(10^{-10}\,m)$	RKR[b]/HH
2.004	1.06	2.849	1.00
2.022	1.04	2.992	1.00
2.041	1.04	3.099	1.00
2.061	1.02	3.191	1.00
2.082	1.02	3.275	1.00
2.105	1.00	3.354	1.00
2.129	1.00	3.429	1.00
2.156	1.00	3.503	1.00
2.185	1.00	3.574	0.99
2.218	1.00	3.644	0.99
2.254	1.00	3.712	0.98
2.296	1.00	3.780	0.98
2.348	1.00	3.847	0.98
2.414	1.00	3.915	0.96
2.517	1.00	3.981	0.96

[a] The HH results were obtained by using the spectroscopic constants given in Ref. 28.
[b] The RKR results are from Ref. 19.

$$c = 1 + a_1\sqrt{\frac{\epsilon'}{a_0}}, \quad b = 2 - \frac{7/12 - \epsilon' a_2/a_0}{c},$$

$$a_0 = \frac{\omega_e^2}{4B_e}, \quad a_1 = -1 - \frac{\alpha_e\omega_e}{6B_e^2}, \quad a_2 = \frac{5}{4}a_1^2 - \frac{2\omega_e\chi_e}{3B_e}.$$

The spectroscopic constants required to use the HH potential are known[28] for the ground $X\,^1\Sigma_g^+$ state of Li_2. These are

$$\omega_e = 35\,143\ m^{-1}, \qquad \omega_e\chi_e = 261.0\ m^{-1},$$
$$B_e = 67.264\ m^{-1}, \qquad \alpha_e = 0.704\ m^{-1},$$
$$\epsilon = 8614\times 10^2\ m^{-1}, \quad r_e = 2.6729\times 10^{-10}\ m.$$

A comparison of the HH and RKR potentials for this state is given in Tables I and II for Refs. 19 and 20, respectively. Agreement between these potentials is seen to be excellent over the range of interatomic separations being considered.

However, alkali metal atoms are subject to significant polarization. Here, the polarizability particularly affects the long-range tail of the potential and any spectroscopically determined potential (such as the RKR and HH potentials) would be expected to be most accurate in the region of the minimum in the potential well and to provide a less sensitive representation of the long-range attractive tail.

TABLE II. Ratio of the RKR to the HH potential energy for the ground $X\,^1\Sigma_g^+$ state of Li_2 as a function of interatomic separation.

$r(10^{-10}\,m)$	RKR/HH[a]	$r(10^{-10}\,m)$	RKR[b]/HH
2.011 93	1.02	2.848 98	1.00
2.028 45	1.02	2.992 13	1.00
2.046 09	1.02	3.098 89	1.00
2.064 99	1.02	3.191 20	1.00
2.085 29	1.02	3.275 46	1.00
2.107 20	1.00	3.354 57	1.00
2.130 99	1.00	3.430 21	1.00
2.157 00	1.00	3.503 42	1.00
2.185 70	1.00	3.574 95	0.99
2.217 75	1.00	3.645 33	0.99
2.254 14	1.00	3.715 01	1.00
2.296 46	1.00	3.784 34	0.98
2.347 61	1.00	3.853 65	0.98
2.413 89	1.00	3.923 21	0.98
2.517 23	1.00	3.993 31	0.98

[a] The HH results were obtained by using the spectroscopic constants given in Ref. 28.
[b] The RKR results are from Ref. 20.

TABLE III. Ratio of the Konowalow–Olson (KO) potential (Ref. 29) to the HH potential for the ground $X\,^1\Sigma_g^+$ state of Li_2 as a function of interatomic separation.

$r(10^{-10}\,m)$	KO/HH	$r(10^{-10}\,m)$	KO/HH
1.46	0.73	4.50	0.88
1.59	0.79	4.76	0.88
1.85	1.07	5.03	0.80
2.12	0.93	5.292	0.75
2.38	0.96	5.821	0.65
2.65	0.98	6.350	0.56
2.91	0.98	7.938	0.39
3.18	1.01	8.996	0.36
3.44	0.99	10.58	0.41
3.70	0.97	12.70	0.77
3.97	0.96	15.88	2.54
4.23	0.93		

Ab initio quantum mechanical calculations of the Li–Li interaction potential can be used to provide information about the long-range part of the potential. The best available calculations for the ground state of Li_2 are those of Konowalow and Olson[29] (KO). They claim that their potential energy curve is in error by no more than 1%–3%. A comparsion of the HH potential with their results is shown in Table III. The HH parameters are those listed above except that Konowalow and Olson's recommended experimental value

$$\epsilon = 8500\times 10^2\ m^{-1}$$

has been used. Agreement is, as might be expected, fairly good near r_e, but it is not as good along the repulsive wall or at separations larger than $r = 2r_e$. In the range $2r_e < r < 5r_e$, the results of Konowalow and Olson are, somewhat surprisingly, approaching zero faster than the HH results. However, at large r, the quantum mechanical potential energy curves does approach zero more slowly than the HH potential, as expected. The RKR results of Kusch and Hessel[20] are in good agreement with the potential energy curve of Konowalow and Olson (Fig. 2 of Ref. 29). However, the agreement of the HH and KO potentials is just as good over the same range of interatomic separations. The HH potential gives slightly better agreement than the RKR potential at small values of r and slightly poorer agreement at larger values of r.

The results in Table III suggest that it might be desirable to obtain improved agreement with the quantum mechanical KO potential for the singlet state by fitting the functional form of the HH potential to it. For this task, a standard nonlinear Nelder–Mead simplex optimization procedure[30] has been adapted to fit simultaneously the four HH parameters a, β, γ, and ϵ for various values of the fifth, σ, using a microcomputer with math coprocessor. Results of the fitting procedure are shown in Fig. 1, with excellent agreement seen for both the repulsive wall and the longer range tail of the

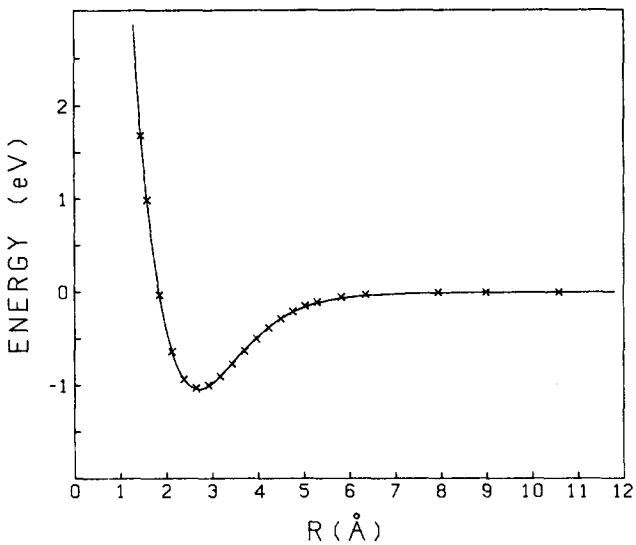

FIG. 1. A comparison of the simplex fit of the HH potential to the KO potential (Ref. 29) for the ground $X\,^1\Sigma_g^+$ state of Li_2. The solid line is the result of the simplex fit and the points (×) are the KO results.

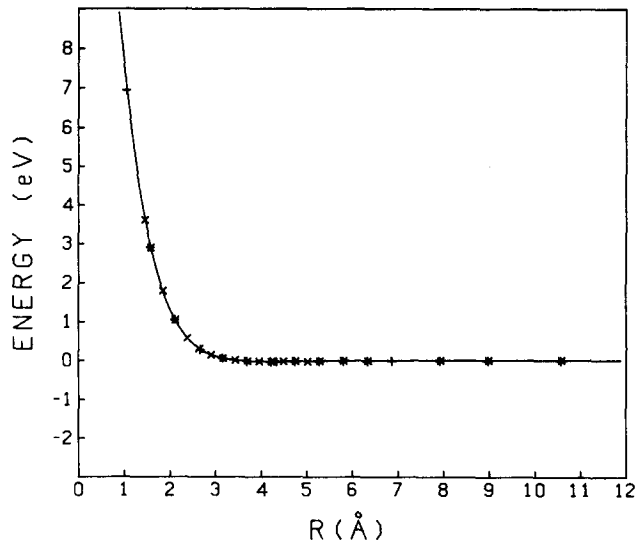

FIG. 2. A comparison of the simplex fit of the HH potential to the potential of Kutzelnigg *et al.* (Ref. 31) and Olson and Konowalow (Ref. 32) for the $^3\Sigma_u^+$ state of Li_2. The solid line is the result of the simplex fit, the points (+) are the results of Kutzelnigg *et al.*, and the points (×) are the results of Konowalow and Olson.

potential. The newly optimized parameters are compared with the original spectroscopically determined parameters for the HH potential in Table IV. It is readily seen that the physically important constants ϵ and r_e are nearly the same for both potentials.

In the case of the weakly bound triplet state of Li_2, no experimental spectroscopic constants are available and an alternate procedure is therefore required to obtain a suitable potential. Fortunately, quantum mechanical calculations of the potential energy curve for the $^3\Sigma_u^+$ state have been published by Kutzelnigg *et al.*[31] and by Olson and Konowalow[32] (KOK potential). Both sets of calculations are in good agreement, thus providing a consistent basis for our fitting procedure. As in the case of the singlet state, we have applied our simplex optimization technique to fit the HH potential to the *ab initio* results. Here, some additional weighting factors were incorporated into the procedure to improve the quality of the fit in the very shallow well and in the tail regions of the triplet potential. Our results (called simplex fit 1) are shown in Fig. 2, with a much expanded plot of the fit in the shallow well region given in Fig. 3. Again, the results of the fit are very satisfactory with the predicted parameters ϵ and r_e given and compared with other estimates in Table V.

Recently, Konowalow *et al.*[33] have proposed a "most likely" potential energy curve (KRR) for the triplet state of Li_2, using the previous calculations[31,32] and some more recent[34,35] quantum mechanical results. We have also applied our simplex optimization procedure to these results (called simplex fit 2). This is shown in Fig. 4 with an expanded scale plot around the shallow minimum shown in Fig. 5. The equilibrium separation and well depth predicted from this fit are given in Table V. Agreement is seen to be quite good but the results for r_e and, especially ϵ, are somewhat different than the results obtained omit from earlier quantum mechanical calculations.[31,32]

TABLE IV. The HH parameters for the ground $X\,^1\Sigma_g^+$ state of Li_2 obtained from the spectroscopic constants and from a best fit to the Konowalow–Olson (KO) potential (Ref. 29).

	Spectroscopy	KO potential
a	2.3084	2.4474
β	2.1158	4.0345
γ	1.7743	1.1681
$r_e(10^{-10}\,\mathrm{m})$	2.6729	2.7001
$\epsilon(10^{-19}\,\mathrm{J})$	1.711	1.667

III. THERMOPHYSICAL PROPERTIES

According to the kinetic theory of gases,[11] the viscosity of a pure gas η is given by

$$\eta = \frac{5}{16}\left(\frac{mkT}{\pi}\right)^{1/2}\frac{1}{\sigma^2\Omega^{(2,2)*}}, \tag{2}$$

where m is the molecular mass, k is Boltzmann's constant, T is the temperature, and $\sigma^2\Omega^{(2,2)*}$ is the viscosity collision integral. Also, the thermal conductivity of a pure gas λ is given by

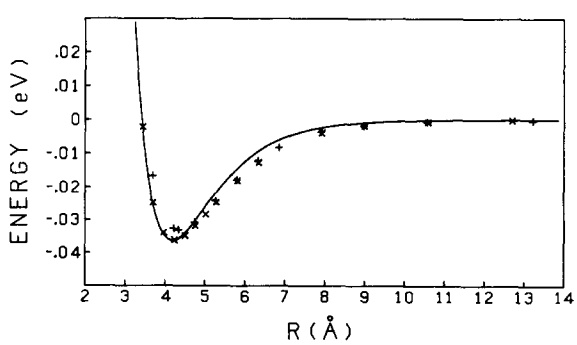

FIG. 3. The same comparison as in Fig. 2 but the energy scale has been expanded to emphasize the fit in the region of the potential minimum.

TABLE V. Equilibrium separation and well depth for the $^3\Sigma_u^+$ state of Li_2.

	$r_e(10^{-10}\,m)$	$\epsilon(10^{-21}\,J)$
Kutzelnigg *et al.*[a]	4.35	5.288
Olson and Konowalow[b]	4.234	5.80
Simplex fit 1	4.184	5.825
Konowalow *et al.*[c]	4.11	6.766
Simplex fit 2	4.100	6.881

[a] Reference 31.
[b] Reference 32.
[c] Reference 33.

$$\lambda = \frac{25}{32}\left(\frac{kT}{\pi m}\right)^{1/2}\frac{c_v}{\sigma^2\Omega^{(2,2)*}}, \tag{3}$$

where c_v is the specific heat per particle, taken to be $3k/2$, and the self-diffusion coefficient D is given by

$$D = \frac{3}{8}\left(\frac{kT}{\pi m}\right)^{1/2}\frac{1}{\rho\sigma^2\Omega^{(1,1)*}}, \tag{4}$$

where ρ is the particle density and $\sigma^2\Omega^{(1,1)*}$ is the diffusion collision integral.

Using the transport collision integral program described elsewhere,[12,13,15] viscosity collision integrals for monatomic lithium (collisions corresponding to the Li_2 singlet state) have been calculated for both the HH potential determined by spectroscopy[36] and for the KO potential as fit to the HH function. Ratios of the results are shown in the second column of Table VI, and it is seen that the HH and KO collision integrals differ by about 10% over a wide temperature range with the HH results being larger. Since the HH potential decays exponentially with r at large distances; i.e., faster than a potential with the r^{-6} dependence due to dispersion forces,[11] such a ratio might be expected to allow assessment of contributions from the longer range attractive part of the potential. That is, according to the random phase treatment,[37] a potential which underestimates the attractive tail, but is otherwise accurate, would be expected to underestimate the transport collision integrals at low temperatures. Even though the differences between the HH and KO results do decrease slightly with increasing temperature, consistent with decreased sensitivity to the long-range tail, the observed effect is quite small. This is probably due to two factors. First is the fact that the KO potential goes to zero faster than the HH potential in the intermediate region from $2r_e < r < 5r_e$. Second is that regardless of the quality of the fit to the KO potential over the range of *ab initio* results, the "HH" fitting function itself will scale to exponential decay at large r.

A similar comparison of results for the triplet state of Li_2 obtained using the KOK and KRR potentials as fit to the HH function is shown in the third column of Table VI. Here, the two potentials are seen to give viscosity collision integrals for monatomic lithium that are essentially the same.

The combined viscosity collision integrals for the two states are obtained by averaging the contribution from each

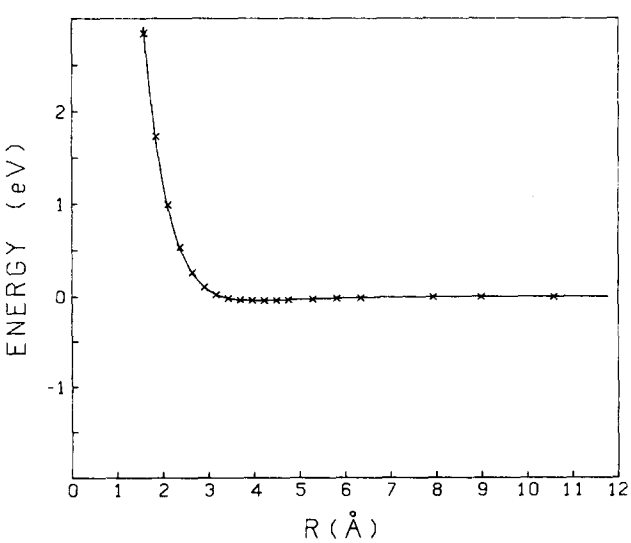

FIG. 4. A comparison of the simplex fit of the HH potential to the KRR potential (Ref. 33) for the $^3\Sigma_u^+$ state of Li_2. The solid line is the result of the simplex fit and the points (×) are the KRR results.

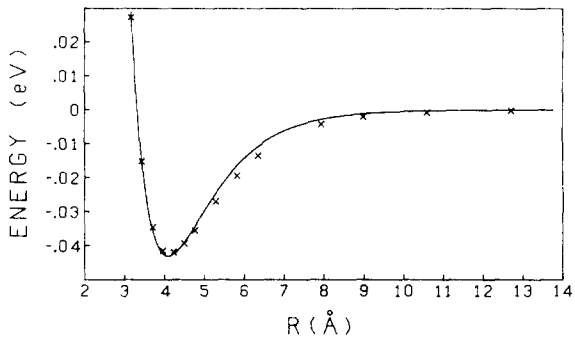

FIG. 5. The same comparison as in Fig. 4, but the energy scale has been expanded to emphasize the fit in the region of the potential minimum.

TABLE VI. Ratio of viscosity collision integrals for different representations of the potentials for the $X\,^1\Sigma_g^+$ and $^3\Sigma_u^+$ states of Li_2.

T(K)	$X\,^1\Sigma_g^+$: HH[a]/KO[b]	$^3\Sigma_u^+$: KOK[c]/KRR[d]
1 000	1.11	0.97
1 250	1.11	0.99
1 500	1.11	1.00
1 750	1.11	1.00
2 000	1.10	1.01
2 250	1.10	1.01
2 500	1.11	1.01
2 750	1.10	1.02
3 000	1.10	1.02
3 500	1.09	1.02
4 000	1.09	1.02
4 500	1.08	1.02
5 000	1.08	1.02
6 000	1.07	1.02
7 000	1.07	1.02
8 000	1.07	1.02
9 000	1.07	1.02
10 000	1.07	1.02

[a] The HH results were obtained by using the spectroscopic constants given in Ref. 28.
[b] The KO results were obtained by fitting the results in Ref. 29.
[c] The KOK results were obtained by fitting the results in Refs. 31 and 32.
[d] The KRR results were obtained by fitting the results in Ref. 33.

TABLE VII. The degeneracy averaged diffusion and viscosity collision integrals, in 10^{-20} m^2, for monatomic lithium.

T(K)	$\sigma^2\Omega^{(1,1)*}$	$\sigma^2\Omega^{(2,2)*}$
1 000	18.3730	18.8990
1 250	16.6310	17.1960
1 500	15.2191	16.0119
1 750	14.1492	15.1187
2 000	13.2997	14.4065
2 250	12.6028	13.3223
2 500	11.9582	13.2758
2 750	11.3177	12.7276
3 000	10.7644	12.2473
3 500	9.8544	11.4451
4 000	9.0584	10.6824
4 500	8.3909	10.0217
5 000	7.8246	9.4433
6 000	6.8970	8.4508
7 000	6.1762	7.6610
8 000	5.6078	7.0015
9 000	5.1455	6.4672
10 000	4.7617	6.0202

state according to its degeneracy.[38] Using the KO potential for the singlet state and the KRR potential for the triplet state, we obtained the results shown in Table VII. The transport properties are given in Table VIII. Monatomic lithium vapor becomes important at temperatures above 1000 K (the normal boiling point of lithium[39] is 1590 K). The first ionization potential[39] is 8.64×10^{-19} J and Li^+ becomes important at temperatures above about 10 000 K.

The first theoretical calculation of the transport properties of monatomic lithium was reported by Krupenie *et al.*[19] They essentially used an RKR curve to represent the singlet ground state and a relatively crude semiempirical procedure[40] to represent the triplet state, which was assumed to be purely repulsive. They also included RKR representations of the excited $A\ ^1\Sigma_u^+$, $B\ ^1\pi_u$, and $C\ ^1\pi_u$ states in their calculations. Their results for the transport collision integrals are

TABLE VIII. The theoretically calculated transport properties viscosity (η), thermal conductivity (λ), and self-diffusion (D) of monatomic lithium as a function of temperature.

T(K)	$\eta(10^{-5}$ kg/m s)	$\lambda(10^{-1}$ W/m K)	$D(10^{-4}$ m^2/s)
1 000	1.177	0.5284	1.717
1 250	1.446	0.6494	2.651
1 500	1.701	0.7640	3.808
1 750	1.946	0.8740	5.161
2 000	2.183	0.9807	6.708
2 250	2.413	1.084	8.447
2 500	2.649	1.190	10.43
2 750	2.898	1.302	12.71
3 000	3.145	1.413	15.23
3 500	3.635	1.633	20.96
4 000	4.164	1.870	27.86
4 500	4.707	2.115	35.89
5 000	5.266	2.365	45.07
6 000	6.446	2.895	67.22
7 000	7.680	3.450	94.59
8 000	8.984	4.035	127.3
9 000	10.32	4.634	165.5
10 000	11.68	5.247	209.5

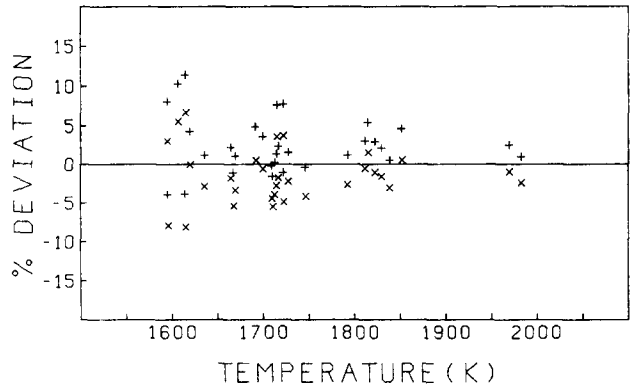

FIG. 6. Percentage deviation of the viscosity of monatomic lithium calculated in this work (×) and by Yargin in Ref. 42 (+) compared to the experimental results in Refs. 53 and 54. The plotted deviation is $[(\eta_{exp}-\eta_{theory})/\eta_{exp}]\times100$.

about twice as high at 1000 K and three times as high at 10 000 K as the results reported here. Since the RKR curves for the excited states are similar to the singlet ground state RKR curve (see Fig. 1 of Ref. 19), these states should give similar contributions to the transport collision integrals.[41] This indicates that the differences between the results of Krupenie and the results presented in the present paper are primarily due to the use by Krupenie of a representation of the triplet state which does not include a shallow potential minimum. Yargin[42] has shown that the effect of such a potential minimum on the triplet state collision integrals is important.

Davies *et al.*[43] have also calculated the lithium transport properties. Their singlet state representation was essentially the same as that of Krupenie *et al.*[19] but a scaling procedure[43,44] was used for estimating the triplet curve, leading to reduced numerical values for this potential (more in line with the quantum mechanical calculations[31–35]) and reduced values for the triplet collision integrals. The resulting averaged collision integrals of Davies *et al.*[43] are larger than those presented here by about 60% at 1500 K and 70% at 10 000 K, considerably closer to the present results than those of Krupenie *et al.*[19]

Several other calculations of the transport properties of monatomic lithium are also available,[45–48] based on semiempirical representations of the triplet state potential. However, Yargin[42] has calculated the transport properties using quantum mechanical potentials. Here, singlet state collision integrals were obtained by using an exponential attractive potential to fit (only) the attractive part of a potential energy curve based on the work of Velasco *et al.*[49] and by using tabulated collision integrals.[50] These results differ from our singlet viscosity collision integrals based on the KO potential by only 4% at 1000 K and 1% at 2500 K, i.e., they are essentially in agreement.

Yargin[42] also fit the triplet state results of Olson and Konowalow[32] with an exponential repulsive potential, used tabulated collision integrals,[51] and then corrected[42,52] for the attractive well. His viscosity collision integrals differ from our triplet state results based on the KRR potential by 14% at 1000 K and 2% at 2500 K. The discrepancy at lower

TABLE IX. Ratio of the second virial coefficients B obtained in this work (TW) to these obtained by Mies and Julienne (MJ) (Ref. 57).

T(K)	B(TW)/B(MJ)	T(K)	B(TW)/B(MJ)
500	10.88	2100	1.22
600	3.18	2200	1.13
700	4.63	2300	1.04
800	4.57	2400	0.96
900	3.59	2500	0.97
1000	2.47	2600	1.00
1100	1.56	2700	1.01
1200	0.94	2800	1.02
1300	1.09	2900	1.03
1400	1.25	3000	1.03
1500	1.36	3500	0.99
1600	1.42	4000	0.99
1700	1.43	4500	1.00
1800	1.41	5000	0.99
1900	1.36	5500	1.00
2000	1.30	6000	1.00

TABLE X. The theoretically calculated second virial coefficient (B) of monatomic lithium as a function of temperature.

T(K)	B(10^{-3} m^3/mol)
2 250	− 1.848
2 500	− 1.039
2 750	− 0.750 6
3 000	− 0.557 7
3 500	− 0.328 6
4 000	− 0.228 9
4 500	− 0.171 0
5 000	− 0.133 4
6 000	− 0.091 02
7 000	− 0.067 86
8 000	− 0.053 49
9 000	− 0.042 97
10 000	− 0.035 72

temperatures probably arises from Yargin's rather empirical procedure for including the effect of the attractive minimum on the triplet state. His degeneracy averaged viscosity collision integrals differ from those in Table VII by 8% at 1000 K and 2% at 2500 K.

Very recently, Vargaftik *et al.*[53] and Stepanenko *et al.*[54] have reported the first experimental data on the viscosity of lithium vapor. Since lithium vapor dimerizes slightly,[3] a correction to the monatomic calculations must be made in order to compare theory with experiment. Using this correction,[42] a comparison of our calculated results and Yargin's theoretical results with experiment is shown in Fig. 6. Both theoretical calculations are seen to be in good agreement with the available experimental results from 1595 to 1983 K. The net deviations of theory from experiment show the average of Yargin's results to be about 3% high and ours are about 1% low, both within the estimated experimental error. The root mean square percentage error or Yargin's and our calculations is 4.5% and 3.8%, respectively. This experimental data became available to us after we had finished our calculations, and the agreement provides convincing evidence of the utility of our computational method for predicting transport properties.

Second virial coefficients for monatomic lithium have been determined by several authors.[55–57] For the reaction

$$2\mathrm{Li(g)} \rightarrow \mathrm{Li_2(g)},$$

the second virial coefficient B of monatomic lithium is given by[58]

$$B = -RTK_p = -K_c, \tag{5}$$

where R is the gas constant, K_p is the equilibrium constant in terms of pressure, and K_c is the equilibrium constant in concentration units. The most accurate second virial coefficients for monatomic lithium are probably those of Mies and Julienne.[57] They used the singlet and triplet potentials of Konowalow and Olson,[29] i.e., the KO potential for the singlet state and the potential of Olson and Konowalow[32] for the triplet state, and evaluated the partition functions quantum mechanically.

A comparison of the results of our calculation of the second virial coefficient, using a previously developed computer code,[59–61] with those of Mies and Julienne[57] is given in Table IX. Our results are given in Table X. The triplet state potential used in our calculation is slightly different than the potential used by Mies and Julienne. However, recalculation of the virial coefficients using the same triplet state potential as Mies and Julienne has virtually no effect on the comparison. Here, our results are seen to agree quite well with those of Mies and Julienne above 2000 K. The differences at lower temperatures can probably be attributed primarily to the fact that our calculation[59,60] of B is classical and quantum mechanical effects can be important for monatomic lithium.[57] Also, virial coefficients are especially sensitive to the long-range tail of the potential while transport properties are more sensitive to the core and well region of the potential[61–63] and the long-range tail is probably least accurately represented by the HH potential.

We have also examined the very recent *ab initio* potential energy curves for the singlet and triplet states of Li_2 reported by Schmidt-Mink *et al.*[64] to ensure that these results do not give a substantially different prediction for the thermophysical properties of lithium vapor. Again, we have applied our simplex fitting procedure (not shown) and calculated the transport collision integrals and second virial coefficients for each state. The degeneracy averaged results from 1000 to 10 000 K are in excellent agreement with the transport collision integrals shown in Table VII (within 2% at the lowest temperature and much better at higher temperatures), and are in very good agreement for the virials in Table IX except at the lowest temperatures. Since the results based on the potentials of Konowalow and co-workers[29,33] are in somewhat better agreement with the virial coefficients of Mies and Julienne,[57] these potentials were used in predicting the transport properties we report here.

Simple correlations given by

$$\eta(10^{-5}\mathrm{kg/m\,s}) = 0.312\,12 + 8.6825\times10^{-4}\,\mathrm{T} + 2.6333\times10^{-8}\,\mathrm{T}^2$$

for the viscosity, and

$$D(10^{-4}\ \mathrm{m^2/s}) = 2.0641\times10^{-2}\ T^{1/3} + 6.6181\times10^{-6}\ T^{5/3} + 8.2596\times10^{-8}\ T^{7/3}$$

for the self-diffusion coefficient give good agreement with the results in Table VIII. The thermal conductivity (in 10^{-1} W/m K) can be obtained from the viscosity correlation by multiplying it by 0.4484.

IV. CONCLUSION

The transport properties of gaseous monatomic lithium, including the viscosity, thermal conductivity, and self-diffusion, have been calculated using the Hulburt–Hirschfelder potential, spectroscopic constants, and a new technique for fitting the HH potential to *ab initio* results. The accuracy of these results can be estimated using the general rule of thumb[19] that an error of a factor of 2 in the potential leads to an error of 20%–40% in the transport collision integrals. The potentials used in these calculations are very accurate. Based on this consideration, from 2000 to 6000 K, the error in the transport properties given in Table VIII should be 5% or less. At lower temperatures one would expect both quantum mechanical effects and any inaccuracies in the long-range tail to become more significant.[37] These considerations would suggest an error estimate of up to about 15% at the lowest temperatures considered here. However, the very good agreement of our transport property calculations with the experimental results for the viscosity of monatomic lithium, from about 1600 to 2000 K, indicates that the errors may be somewhat less in this region.

At temperatures above about 4000 K, excited electronic states begin to contribute to the transport properties.[57,65] Here, however, since the potential energy curves of low lying excited states are similar to the ground state potential energy curve (the r_e values, in particular, being similar[28,29]), the contribution from excited electronic states would not be expected to significantly change the overall transport properties.[41] As a result, for temperatures above 6000 K, the errors in the transport properties reported here are estimated to be 10% or less.

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