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Validity of the effective temperature scale for a dilute Li^+ swarm in a Xe gas

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The effective-temperature concept arising from the two-temperature (2T) kinetic theory for the nonreactive migration of a dilute ion swarm in a neutral gas under the action of a uniform electrostatic field has been tested over a wide temperature range by Monte Carlo simulation (MCS). Such a test over the prescribed temperature span has not been made experimentally because of the inherent difficulty in designing an apparatus which permits the temperature of the ion drift chamber to be varied so widely. The MCS test is here applied to Li^+ in Xe, which offers the most favorable conditions for the 2T theory to be a valid approximation of the more sophisticated three-temperature theory. Results established that for such cases it is possible to express the mobility K_0 and transverse diffusion D_T, but not the longitudinal diffusion D_L, in terms of a univariate effective-temperature scale instead of the separate parameters of gas temperature and the ratio of electric field to gas concentration. More remarkably, the ratio D_T/K was found to bear a simple linear relation with T_{eff} over a very wide range.

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INTRODUCTION

In general the transport of a dilute ion swarm, driven by a superposed electrostatic field, in a neutral gas under binary elastic collision conditions is governed by the gas temperature T and the ratio of the applied electric field to gas concentration E/N. However, arising fundamentally from the two-temperature (2T) kinetic theory [1], it is possible to combine additively the separate effects of T and E/N into a single governing parameter known as the effective ion temperature T_{eff}. This T_{eff} concept represents an important merit of the 2T theory in comparison with the more advanced three-temperature (3T) theory of which it is a subset. First, it permits the definition of an effective-temperature scale for the various transport parameters. Second, since the average energy of the ions is directly proportional to the ion temperature it follows that the energy-dependent collision cross section $\sigma(\varepsilon)$ between the ions and the gas molecules may be regarded as a univariate function of T_{eff} alone, and not a bivariate function of T and E/N separately.

An immediate benefit of the T_{eff} scale is that it provides an extremely versatile way to simulate experimentally high-temperature ion–neutral-particle swarm conditions such as those occurring in a flame, in a plasma, or in the upper atmosphere. This is because the difficulty to vary the temperature of the swarm in the laboratory may be easily circumvented by an experimentally simple but equivalent variation of E/N.

However, for the T_{eff} scale to be useful, it is essential to verify its authenticity with substantiative tests by experimental methods or otherwise. Unfortunately, it has hitherto been difficult to design an experimental apparatus that permits the gas temperature to be varied over a sufficiently large range. As a consequence, the T_{eff} scale has so far only been successfully tested over a relatively short range of T only. In view of the inadequate but desirable support for the T_{eff} scale, an alternative test by Monte Carlo simulation is realistic, feasible and timely, and is thus the subject of this paper.

ATTRACTIVENESS AND APPLICABILITY OF THE TWO-TEMPERATURE THEORY

The 3T kinetic theory [1] has been able to reproduce transport coefficients in good agreement with those obtained by Monte Carlo simulation methods using the same input interaction potential [2–6]. These two independent approaches have also been able to reproduce experimental data provided a reliable interaction potential between the ion and the neutral particle is assumed. However, although this success has in principle placed the 3T theory on a firm footing, in practice it entails vast amounts of computation and depends considerably on the rapid convergence of the iterative numerical steps for its ultimate success. The theory further requires the segregation of two physically inseparable components T_L and T_T of ion temperature associated, respectively, with the random ion motion along and perpendicular to the field direction. Experimentally, since these two temperature components cannot be measured directly, it is not possible to verify the 3T theory by direct measurements. Theoretically, both T_L and T_T are complicated functions of m/M, the ion–neutral-atom mass ratio, involving various collision integrals and it is not possible to reduce the dependence of the transport parameters to a single variable analogous to T_{eff}.

In contrast, the more amenable 2T theory requires a much simpler algorithm and is often a more practicable and attractive approximation in those cases when m/M is small. For such cases, the collision is nearly isotropic except in the extreme case of the ion drift energy greatly exceeding its thermal component, and the 2T theory represents a simplification of the 3T theory without any significant loss in accuracy. Considerably less computation is needed, and the experimentally unmeasurable longitudinal and transverse components of ion temperature are unified as the effective temperature of the ion. In consequence, the 2T theory permits the primary transport coefficients to be expressed solely in terms of the effective temperature parameter. Additionally, the insight gained from the T_{eff} concept is the comprehensible understanding of physically combining the separate effects of gaseous thermal motion and ion energy randomization imposed by the buffer gas on the ions.

Mathematically

$$T_{\text{eff}}(T,E/N)=T+\frac{1}{3k_B}Mv_d^2(1+\beta)\ , \tag{1}$$

where T and M are, respectively, the temperature and molecular mass of the gas and k_B is Boltzmann's constant. v_d is the ionic drift velocity given by $v_d=N_0K_0(E/N)$, where N_0 is Loschmidt's number, and K_0 the reduced mobility of the ions. β is a small correction given by

$$\beta=\frac{mM(5-2A^*)}{5(m^2+M^2)+4mMA^*}\,\frac{d\ln(K_0)}{d\ln(E/N)} \tag{2}$$

and vanishes for $m/M\rightarrow 0$. A^* is a dimensionless ratio of collision integrals which varies only slowly with T_{eff} and may be assumed to always lie within the narrow range 1.0–1.2 for a physically realistic repulsive potential.

The case of Li* drifting in Xe gas has perhaps the most favorable condition to apply the 2T theory. The chosen ion–neutral-atom pair has the smallest possible ion–neutral-atom mass ratio for any alkali-ion–rare-gas system thus validating the 2T approximation. The alkali-ion–rare-gas system involves only spinless ${}^1S_0$ ground states with no fine structure and their collision in the energy range relevant here is totally elastic and adiabatic. The interaction potential $V(r)$ is spherically symmetric and a reasonably accurate parametrized form of $V(r)$ is readily available.

For the idealized case of $m/M \ll 1$, and given an accurate interaction potential on which the scattering angle of collision depends, the 2T theory should yield accurate mobility values. This may be effectively tested by checking the constancy of mobility for widely varying combinations of T and E/N that yield the same T_{eff}. However, the same T_{eff} would be expected to yield less consistent diffusion coefficients, particularly when the scattering potential is strongly anisotropic. This is because the diffusion coefficients are more intimately dependent on the isotropy of scattering. Given a fixed T_{eff} formed by a high-T and low-E/N value, the difference between the longitudinal and transverse diffusion coefficients D_L and D_T should be small. However, when the ions are strongly driven by a high E/N, the resulting anisotropic ionic motion would result in a pronounced difference in D_L and D_T. Since the diffusion coefficients for the same T_{eff} formed by the two extreme combinations of T and E/N must deviate it is not possible for Eq. (1) to be valid over unlimited ranges. An objective of the present investigation is to examine this deviation.

EXPERIMENTAL TRANSPORT DATA

Experimental data on transport coefficients are needed to validate the input interaction potential to be adopted in the Monte Carlo simulation (MCS). Both mobility and longitudinal diffusion data are available from Byers, Thackston, Ellis (BTE), and co-workers [7–9] and from Takebe *et al.* (TSIS) [10]. The TSIS mobility data were taken at 304 K while the BTE data were given at 300 K. Nevertheless, the two sets of reduced mobility data agree well except in the very-low- and high-E/N regions. At low E/N, the TSIS mobility tends towards 2.77±0.03 $\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$ while BTE reported a value of 2.68±0.08 $\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$. At high E/N, the TSIS mobility values are considerably higher than the corresponding BTE data.

The data for longitudinal diffusion coefficient D_L from both BTE and TSIS were obtained from the arrival time spectrum of the ions at the end of a drift tube. Both sets of data were reported in the form ND_L, and these were converted to D_L/K values using the mobility data obtained by the respective authors. The BTE data were reported in two separate papers [8,9]. The units for the ND_L data in the earlier paper should be $\text{cm}^{-1}\,\text{s}^{-1}$ while those in the second paper should be multiplied by a factor of 10. The corrected BTE values from their second paper given in tabulated form with a quoted error of ±15% was adopted. The TSIS data were also available in numerical form and were obtained at 303.5 K with an estimate error of up to 10%. However, the TSIS data have since been found to contain some systematic errors due to suspected clustering reactions at E/N below 30 Td.

There has apparently been no recorded experimental data on the transverse diffusion of Li^+ in Xe.

For all the above experimental data the effective temperature values were calculated using Eq. (1) but with β set to zero.

MONTE CARLO SIMULATION

Using MCS on an NEC SX1A supercomputer running at 665 Mflop, calculations of the primary transport coefficients were made for a dilute swarm of Li^+ ions drifting in Xe gas at different T_{eff} obtained from different combinations of preset gas temperatures T and electric-field parameters E/N. T was varied from 4 to 2500 K while E/N was varied from 5 up to 500 Td, which is well above the range of available experimental data. The simulation algorithm used was similar to that previously reported [6] with due account being given to both the velocity distribution of the gas particles, assumed Maxwellian, as well as the energy dependence of the collision cross section. As elaborated previously [2], it was necessary to set an arbitrary cutoff deflection angle $\chi_{\min}$ such that all collisions resulting in $\chi > \chi_{\min}$ were considered positive collisions while those with $\chi \le \chi_{\min}$ were regarded as marginal collisions whose integrated effect was accounted for by the addition of a correction term to the positive collision cross section. This is an inherent problem with all procedures which simulate *real* collisions because of the singularity of the differential scattering cross section at $\chi=0°$. The correction term was adjusted so that the sum of the contributions from all collisions with $\chi \le \chi_{\min}$ to the momentum transfer cross section (which is finite) is the same as what they would contribute had all such collisions been scattered at a fixed angle equal to $\chi_{\min}$. The size of the correction term thus varies considerably with different impact parameters b and relative collision energies ε. However, preliminary tests revealed that the resulting transport coefficients obtained were not significantly changed for variations of $\chi_{\min}$ from 0.10 to 0.20 rad, and hence a uniform value of $\chi_{\min}=0.15$ rad was chosen for all subsequent calculations.

All collisions were assumed elastic and the improbable clustering of Li^+ with Xe was not taken into account. Several input interaction potentials were tested, and the potential due to Koutselos, Mason, and Viehland (KMV) [11] was eventually adopted since it was computationally simple and able to reproduce fairly well the experimental transport coefficients data. The simulation was carried over 2.5 million collisions which was statistically large enough to yield a typical standard error of at worst 0.5% for mobility and 2.5% for diffusion coefficients.

RESULTS AND DISCUSSION

Results of the MCS calculations for K_0, D_T/K, and D_L/K at $T=4$, 77, 309, 1000, and 2500 K are shown in Table I. For each combination of T and $[E/N]$ the effective temperature T_{eff} was calculated from the T and K_0 values using Eq. (1) again with $\beta=0$. Figure 1 shows both the experimental and representative MCS mobility values on the T_{eff} scale. The fairly good agreement among all the MCS derived data on the T_{eff} plot obtained at widely different T's provides reaffirmation of the applicability of the 2T theory. The satisfactory agreement between the room-temperature experimental and calculated mobilities provides further evidence that the KMV potential (in the relevant energy range) assumed in the calculation is reasonably accurate. At T_{eff} beyond the mobility peak, the MCS calculations support the BTE data against the TSIS data, which are too high. At low T_{eff} the calculated data tend towards a steady value of 2.77 $cm^2\,V^{-1}\,s^{-1}$ in close agreement with TSIS's data obtained at 304 K, but not with the BTE data. For T_{eff} beyond about 30 000 K, no experimental data are available for comparison, but the various MCS calculations are self-consistent.

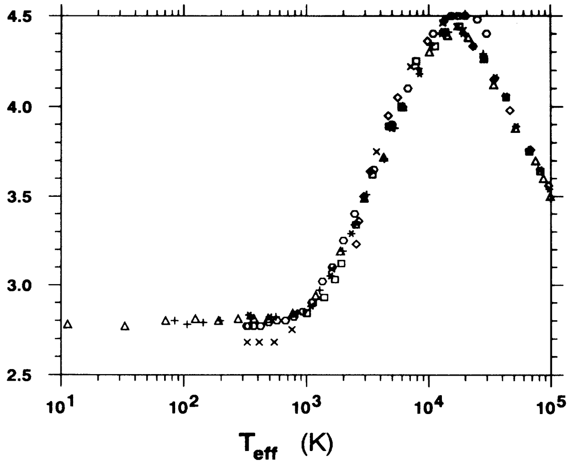

FIG. 1. Linear-log plots of reduced mobility against T_{eff} obtained with different combinations of T and E/N. Triangles, pluses, asterisks, squares, and diamonds represent MCS calculated data with $T=4$, 77, 309, 1000, and 2500 K, respectively. Crosses and hexagons are experimental data of Thackston *et al.* [8] and Takebe *et al.*[10]. Note that not all data from Table I are included so as not to congest the plots.

It is worth noting that even for the lowest T_{eff} of 11.3 K covered in the calculations, K_0 has still not tended to the theoretical polarization limit of $K_{\text{pol}}=2.68$ $cm^2\,V^{-1}\,s^{-1}$. This is because the contribution of the inverse sixth and eighth power terms to the potential at this collision energy is still significant. The average collision energy at $T_{\text{eff}}=11.3$ K is 5.4×10^{-5} hartree corresponding to an internuclear distance of about 22 a.u. At this separation the combined hyperpolarizability terms still contribute about 1.5% to the total attractive potential. Because the decay of the attractive potential is rather slow, K_0 increases very slowly as T_{eff} increases from its lowest value. The large range of T_{eff} in which K_0 is fairly flat may be attributed to the fact that the Li^+-Xe interaction has the largest potential well among the alkali-ion–rare-gas systems which is widely but shallowly spread out.

In the middle region where the mobility coefficient rises rapidly with T_{eff} the calculated data with different combinations of T and E/N are more scattered and have higher error margins. Nevertheless, the agreement among the calculated data is still within ±2%, although it seems possible to discern that data at higher gas temperatures yield slightly higher K_0 than the corresponding lower temperature data with the same T_{eff}.

To examine the effect of the second-order correction term β, a calculation of its values was made for the set of readings with $T=309$ K [Table I(c)] and with A^* set to the average typical value of 1.1. $d(\ln K_0)/d\ln(E/N)$ was obtained directly from the mobility curve. The value of β was found to peak at 0.19 at $T_{\text{eff}}\approx3500$ K, and the value of T_{eff} corrected with the calculated β differs from the uncorrected T_{eff} by a maximum of 1.7%. The smallness of the β correction allows it to be neglected with the introduction of only a small error, and represents a further simplification and endorsement of the validity of the T_{eff} concept. The largest discrepancy between the β-corrected and uncorrected data in the mid T_{eff} region is reflected by the largest (discernible) difference between the low- and high-T data (for the same T_{eff}) in this region.

Figures 2 and 3 show, respectively, the various plots of D_T/K and D_L/K against T_{eff} for widely different combinations of T and $[E/N]$. The logarithmic scale for both abscissa and ordinate is deliberately chosen to expand the low-E/N region where the effect of the temperature variation is most pronounced. Also included in both figures are comparative data obtained by using the improved generalized Einstein relation (GER) formulas [1] with $T=309$ K:

TABLE I. MCS calculated values of K_0, D_T/K, and D_L/K for Li^+ in Xe using the KMV potential at gas temperature of (a) 4 K, (b) 77 K, (c) 309 K, (d) 1000 K, and (e) 2500 K.

E/N (Td)	T_{eff} (K)	K_0 [$\text{cm}^2/\text{V s}$]	D_T/K (mV)	D_L/K (mV)
(a) $T=4$ K				
5	11.3	2.78	0.96	1.03
10	33.2	2.77	2.81	3.04
15	71.0	2.80	5.77	6.34
20	124	2.81	10.2	11.3
25	190	2.80	16.0	17.6
30	275	2.81	22.5	25.6
35	371	2.81	30.2	33.5
40	483	2.81	40.0	45.3
50	767	2.84	66.0	84.6
60	1 189	2.94	108	171
70	1 893	3.19	183	337
80	2 962	3.49	294	584
90	4 257	3.72	430	782
100	6 092	4.00	588	916
110	7 853	4.13	767	1048
120	10 108	4.30	943	1139
140	14 341	4.39	1266	1327
170	21 086	4.38	1853	1736
200	27 866	4.28	2375	2072
230	34 188	4.12	3009	2382
260	42 342	4.06	3561	2848
300	51 584	3.88	4539	3498
340	62 299	3.77	5502	4157
380	74 993	3.70	6514	5124
420	86 626	3.60	7374	5891
460	98 492	3.50	8687	6854
(b) $T=77$ K				
5	84	2.80	7.29	7.38
10	106	2.78	9.13	9.38
15	144	2.79	12.4	12.9
20	196	2.80	16.3	17.3
30	347	2.81	28.3	31.7
40	560	2.82	46.2	50.6
50	843	2.84	73.5	92.9
60	1 284	2.97	118	185
70	1 972	3.19	189	346
75	2 461	3.34	246	434
80	3 073	3.51	313	589
85	3 615	3.59	354	594
90	4 313	3.71	434	732
95	5 176	3.86	513	779
100	6 156	4.00	589	922
110	8 226	4.21	750	1045
120	10 383	4.34	942	1171
140	14 560	4.41	1267	1370
170	21 047	4.37	1763	1656
200	28 048	4.29	2334	2051
230	34 328	4.13	2978	2410
260	42 207	4.05	3567	2828
300	52 535	3.92	4531	3503
350	65 775	3.76	5624	4488
400	80 935	3.65	6841	5377
450	97 242	3.55	8283	6612
500	112 222	3.44	9855	7947
(c) $T=309$ K				
5	317	2.83	27.6	27.0
10	339	2.83	28.6	29.0
15	377	2.82	32.0	33.4
20	430	2.82	36.7	38.2
25	498	2.82	42.3	43.3
30	577	2.80	49.6	50.6
40	799	2.84	69.8	76.8
45	930	2.84	80.7	97.7
50	1 097	2.88	95.8	124
55	1 330	2.98	117	183
60	1 578	3.05	150	225
70	2 324	3.29	235	400
80	3 441	3.59	343	606
90	4 942	3.88	474	794
100	6 434	4.02	619	903
110	8 342	4.18	797	1072
120	10 473	4.31	975	1157
130	12 741	4.40	1131	1233
140	14 661	4.39	1309	1391
160	19 140	4.40	1622	1576
180	23 390	4.33	2029	1756
200	28 020	4.27	2402	2010
230	35 143	4.16	3028	2448
260	42 622	4.06	3616	2949
300	52 081	3.89	4434	3527
350	66 234	3.76	5668	4454
400	81 167	3.65	7031	5495
440	93 638	3.56	7847	6227
450	96 802	3.54	8212	6567
(d) $T=100$ K				
5	1 008	2.84	86.6	82.6
10	1 032	2.92	86.4	84.9
15	1 068	2.83	91.0	89.5
20	1 128	2.90	95.1	102
25	1 196	2.87	105	107
30	1 286	2.89	114	121
35	1 400	2.93	124	139
40	1 554	3.02	137	167
45	1 706	3.03	155	203
50	1 925	3.12	174	235
60	2 526	3.34	233	349
70	3 440	3.62	332	534
80	4 680	3.89	449	678
90	5 924	4.00	572	801
100	7 863	4.25	711	987
120	11 258	4.33	1015	1196
130	13 488	4.41	1181	1300
140	15 549	4.42	1418	1387
150	17 853	4.44	1580	1485
170	21 874	4.36	1914	1688
200	28 581	4.26	2478	2108
230	35 657	4.15	3109	2481
260	43 047	4.05	3694	2858
300	53 159	3.91	4544	3500

TABLE I. (*Continued*).

E/N (Td)	T_{eff} (K)	K_0 [cm^2/V s)]	D_T/K (mV)	D_L/K (mV)
350	66 383	3.75	5662	4436
400	81 486	3.64	6965	5423
450	97 093	3.53	8277	6597
		(e) $T=2500$ K		
5	2 511	3.39	211	201
10	2 540	3.23	234	221
15	2 595	3.33	222	220
20	2 671	3.36	235	235
25	2 787	3.48	244	246
30	2 919	3.50	248	266
35	3 103	3.60	274	301
40	3 304	3.64	288	315
50	3 827	3.74	351	406
60	4 597	3.92	428	523
70	5 549	4.05	515	653
80	6 810	4.21	628	763
90	8 254	4.32	715	882
100	9 723	4.36	883	981
120	13 408	4.47	1173	1164
140	17 220	4.45	1482	1441
170	23 088	4.33	2049	1715
200	29 823	4.24	2584	2100
220	34 202	4.15	2920	2470
250	41 394	4.05	3609	2890
270	46 441	3.98	4010	3143
300	54 112	3.88	4710	3525
350	68 128	3.76	5801	4733
400	82 460	3.63	7128	5723
440	95 464	3.56	8173	6679
450	98 375	3.53	8467	6674

$$\frac{D_T}{K}=\frac{k_B T_T}{e}\left[1+\Delta_T\frac{K'}{1+K'}\right], \tag{3}$$

$$\frac{D_L}{K}=\frac{k_B T_L}{e}[1+(1+\Delta_L)K'], \tag{4}$$

where for $m \ll M$,

$$\Delta_T=\frac{2K'}{3(2+K')} \tag{5}$$

and

$$\Delta_L=\frac{K'}{2(2+K')}, \tag{6}$$

with

$$K'=\frac{d\ln(K_0)}{d\ln(E/N)}. \tag{7}$$

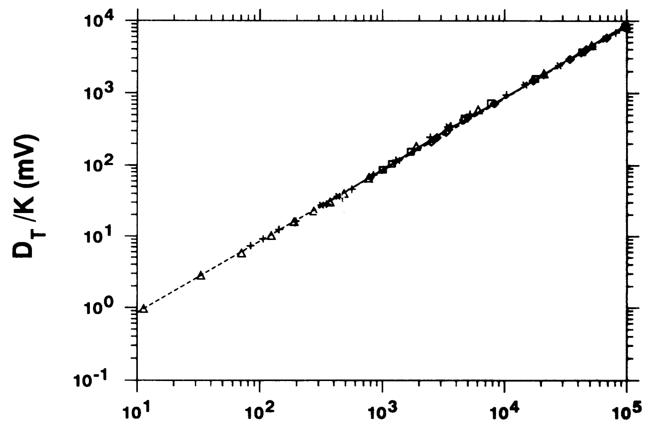

FIG. 2. Log-log plots of D_T/K against T_{eff} obtained with different combinations of T and E/N. Triangles, pluses, asterisks, squares, and diamonds represent MCS calculated data with $T=4$, 77, 309, 1000, and 2500 K. The solid line represents theoretical data obtained from the improved GER relationships with $T=309$ K. It is almost indistinguishable from the unit-slope dashed line. Note that not all data from Table I are included so as not to congest the plots.

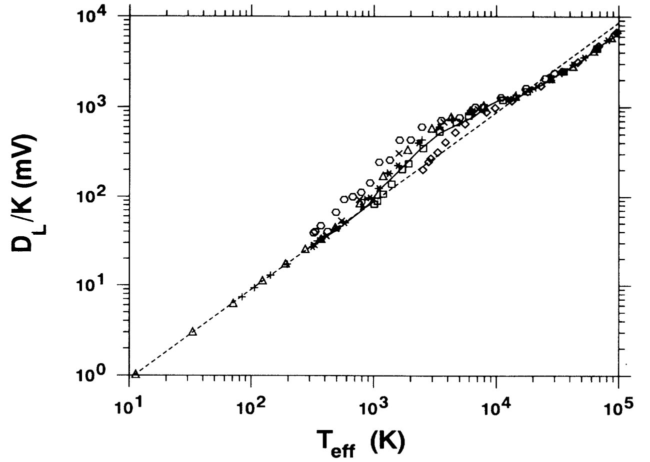

FIG. 3. Log-log plots of D_L/K against T_{eff} obtained with different combinations of T and E/N. Triangles, pluses, asterisks, squares, and diamonds represent MCS calculated data with $T=4$, 77, 309, 1000, and 2500 K, respectively. Crosses and hexagons represent the BTE [9] and TSIS [10] experimental data, respectively. The solid line represents theoretical data obtained from the improved GER relationships with $T=309$ K. The dashed line represents the straight line with unit slope that best fit the data at very low T_{eff}. Note that not all data from Table I are included so as not to congest the plots.

For $m \ll M$, the longitudinal and transverse ion temperatures T_L and T_T are the same as the effective temperature. This considerably simplifies the GER equations and it is possible to calculate D_T/K and D_L/K without invoking the value of any collision integral.

As shown in Fig. 2, all the MCS-derived transverse diffusion data agree well among themselves on the entire $T_{\rm eff}$ scale thus demonstrating once again the applicability of the effective temperature concept for the present ion–neutral-atom pair. The D_T/K data lie nearly in a straight line with unit slope suggesting a simple linear relationship of D_T/K with $T_{\rm eff}$. An important implication of this simple relationship is that the quantity $[D_T/K]$ is perhaps more fundamental than its separate components, i.e., D_T and K, neither of which bears such a simple relationship with $T_{\rm eff}$. This result has therefore reinforced our belief [6,12] that $[D_T/K]$ should be regarded as a single entity rather than as a ratio of two quantities, in analogy with the drift field parameter $[E/N]$, which is known to govern the transport parameters as a single entity.

Figure 3 includes the TSIS and the corrected BTE experimental data (converted to the D_L/K form). Of these, the TSIS data were inconsistently high, possibly because of systematic errors. The corrected BTE data obtained at 300 K generally agree well with the MCS calculated data at 309 K. The further agreement between the MCS and GER calculations at 309 K using totally different methods provides mutual support for both approaches.

However, the MCS calculations for different T's differ appreciably in the intermediate range of $T_{\rm eff}$ where D_L deviates most from D_T thus showing that D_L/K is a less consistent function of $T_{\rm eff}$ than D_T/K. At low $T_{\rm eff}$ the collision energy is small and only the induced dipole polarization force is important. For this inverse fifth power force law (Maxwell model), the average ion energy is given by the well-known Wannier equation which is equivalent to Eq. (1) with $\beta=0$. Hence the $T_{\rm eff}$ concept is valid because $D_L \approx D_T$, and, as is evident in Fig. 3, the plot of $\ln(D_L/K)$ against $\ln(T_{\rm eff})$ at low $T_{\rm eff}$ lies close to the unit-slope line.

In the intermediate region of $T_{\rm eff}$, the collision model deviates from the Maxwellian and the corresponding deviation of the $\ln[D_L/K]-\ln(T_{\rm eff})$ curve from the unit-slope line reveals a nonlinear function of $T_{\rm eff}$. More significantly, this deviation varies for different combinations of T and E/N making up the same $T_{\rm eff}$. For a particular $T_{\rm eff}$, the deviation is progressively reduced as T increases while E/N decreases. This is consistent with the fact that the ionic motion is less anisotropic as the thermal component of its random energy increasingly prevails over the drift component. Because D_L/K cannot be uniquely defined in this region by $T_{\rm eff}$, the use of the effective temperature scale is not quite suitable here even with an ideal ion–neutral-atom mass ratio.

Further insight on the difference in dependence of D_T/K and D_L/K on $T_{\rm eff}$ may be elicited from an expansion of their expressions given in Eqs. (3) and (4) as polynomial series of K'. Thus

$$\frac{D_T/K}{k_B T_T/e}=1+K'^2/3-K'^3/2+\cdots \tag{8}$$

and

$$\frac{D_L/K}{k_B T_L/e}=1+K'+K'^2/2-K'^3/4+\cdots . \tag{9}$$

The first nonzero term containing K' in Eq. (8) is the K'^2 term while that in Eq. (9) is the K' term. Thus for small K' its effect on D_L/K is of first order while that on D_T/K is only of second order. It is the first order K' term in Eq. (9) that mainly accounts for the deviation of the $\ln[D_L/K]$ versus $\ln(T_{\rm eff})$ curve from the unit-slope line. In the region of rising K_0 for $T_{\rm eff}$ up to about 14 000 K, K' is positive and the curve lies about the unit-slope line. Thereafter K_0 decreases with E/N, and K' becomes negative so that the curve swings slightly below the unit-slope line.

At the extreme of very high $T_{\rm eff}$, the dominant interaction affecting the collision corresponds to the steep repulsive potential wall of the interaction potential which approaches a hard-sphere model as $T_{\rm eff}$ increases. For such interactions the collision becomes more and more isotropic and higher harmonics in a spherical harmonics expansion of the ion energy distribution function employed in the 2T theory can be neglected, so that D_L should once again merge with D_T. Unfortunately, the expected isotropic scattering condition lies beyond the $T_{\rm eff}$ scale in Fig. 3, although some evidence of this approach is apparent. Attempts to test the hypothesis of hard-sphere approximation at very high $T_{\rm eff}$ were not successful because the KMV potential becomes increasingly inaccurate as $T_{\rm eff}$ increases beyond 100 000 K. For instance, it has an unsatisfactory artificial maximum value of only 67.2 hartree at zero internuclear separation. Efforts to circumvent this limitation by adding an effective hard-sphere term to the KMV potential were also unsuccessful partly because of wild fluctuations in the stochastic calculations of the mobility values bearing evidence of the onset of runaway conditions [13], and partly because the calculated mobility values depended very much on the effective radius of the hard-sphere potential assumed.

CONCLUSION

The agreement of the calculated transport parameters at room temperature with available experimental measurements at around the same temperature confirms that the input KMV potential used for the Li^+-Xe interaction is a good approximation in the appropriate energy range. Theoretically, the agreement on the effective-temperature scale among the mobility and transverse diffusion data obtained by MCS calculations with widely varying gas temperatures establishes the validity of the $T_{\rm eff}$ concept for these two transport parameters for this ion–neutral-atom pair. It lends firm support to the applicability of Eq. (1) equating a variation of E/N with that of gas temperature T for the case where m/M is small. The simple relationship of $[D_T/K]$ with $T_{\rm eff}$ further suggests that this ratio itself should be regarded as a fundamental quantity of an ion swarm and not as the ratio of two separate parameters.

The failure to consistently describe D_L/K as solely a function of T_{eff}, especially in the intermediate-energy range, implies that extra caution is necessary when applying the 2T theory to longitudinal diffusion. However, it is hoped that the trend of the deviation revealed in this investigation would help spur the search for a modification to Eq. (1) so as to more accurately correlate the longitudinal diffusion coefficients obtained at different temperatures. Hopefully, the experience and results gained for the Li^{+}-Xe system would throw valuable light on similar investigations on the validity of T_{eff} for less favorable ion–neutral-molecule pairs.

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