

The Determination of Ion-Atom Interaction Potentials

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Abstract

It is shown that given the present state of both theory and experiment the magnitude and form of the well in the interaction potential for an ion-atom system cannot be determined by comparing measured and predicted transport coefficients. The theory of Kumar and Robson (1973) is used to demonstrate that significantly different interaction potentials can be used to predict essentially the same transport coefficient data. Alternative techniques for determining the potential well are discussed, with particular emphasis on the possibility of analysing differential cross-section measurements taken under conditions where the rainbow oscillations are masked by the resolution of a typical apparatus.

Introduction

One of the main objectives of low energy ion swarm research has been to obtain accurate information about the magnitude of ion-atom forces by comparing experimental and theoretical transport coefficients. The problem has been approached theoretically in two ways. The usual approach has been to solve the Boltzmann equation by the method developed by Enskog (1911*a*, 1911*b*) and Chapman (1912), who independently developed the theory of diffusion in a gas in the absence of an electric field. Their formulation has been used to estimate the interaction potential for an ion-atom combination by comparing the measured and predicted dependence of the zero-field transport coefficient on temperature (Mason and Schamp 1958). Kihara (1953) was the first to extend Enskog and Chapman's work to include situations where the motion of the ions is perturbed by the influence of a small electric field. Mason and Schamp (1958) developed Kihara's procedure to obtain an expansion for the mobility in $(E/N)^2$ (E is the electric field strength and N the gas number density), the coefficients in this expansion being related to the interaction potential. More recently Kumar and Robson (1973) have extended the Enskog-Chapman method to a larger E/N range by avoiding this series expansion, and have predicted not only the mobility but all the transport properties of ions in gases (Robson and Kumar 1973; Robson 1973). The second theoretical approach has been that of Skullerud (1973*a*, 1973*b*), who used computer-simulation techniques to investigate the general motion of ions in atomic gases and in particular to study the forces between K^+ ions and argon atoms.

The purpose of this work is to show that it is not possible to determine uniquely the form and magnitude of the well in the interaction potential by analysing the most accurate transport coefficient data presently available. Kumar and Robson's (1973) theory is used to demonstrate that, in the E/N range in which their theory is accurate,

the experimental transport coefficient data can be predicted with several significantly different interaction potentials. The reason for this lack of uniqueness is discussed, together with a possible method of overcoming the problem.

A common feature of all available theoretical transport coefficient calculations is that they are only valid for atomic ions in atomic gases. The conclusions from the present work, in particular those regarding the uniqueness of differential cross sections, are also restricted to ion-atom combinations of this type. It is assumed for convenience that the interaction potential for an ion-atom combination has the general form (Robson and Kumar 1973)

$$V(r) = \varepsilon \{A(r_m/r)^{2p} - B(r_m/r)^6 - C(r_m/r)^4\}, \quad (1)$$

where ε and r_m denote the depth and position of the potential minimum and

$$A = 2(\gamma + 1)/(p - 2), \quad B = 2\gamma, \quad C = \{p - 2\gamma(p - 3)\}/(p - 2).$$

The parameter γ determines the relative strengths of the attractive terms. The coefficient of the dipole polarization term can be written in terms of the polarizability α , an experimentally known quantity, as

$$\varepsilon r_m^4 2\{p - 2\gamma(p - 3)\}/(p - 2) = e^2 \alpha. \quad (2)$$

It can be seen from equation (2) that, for a given value of p , it is necessary in any realistic fitting procedure to vary at least two potential parameters at any one time, and thus it is not possible to determine how the variation of a particular potential parameter affects the transport coefficients. Robson and Kumar (1973) adopted a different fitting procedure. Once p had been chosen, only one parameter was varied at a time and the polarizability restriction was only used to determine the final parameter. Both techniques give rise to the same interaction potentials but the conclusions reached by Robson and Kumar regarding the effect of varying the potential parameters are misleading. The disadvantages inherent in the use of equation (1) are eliminated if the form of the potential adopted by Skullerud (1973*a*, 1973*b*) is used. With this alternative potential both the form parameter (equivalent to γ in equation (1)) and the power of the repulsive term can be independently varied.

In addition to the polarizability restriction Mason and Schamp (1958) suggested that a further constraint on the parameters could be imposed by estimating γ from a consideration of the r^{-6} potential, on the assumption that both the ion and the atom could be treated as point masses. It is clear that, if this restriction is imposed, the form of the potential is slightly more accurate at large distances. However, the restriction unnecessarily limits the flexibility in the fitting procedure and for this reason it was not used by either Skullerud (1973*a*, 1973*b*) or by Robson and Kumar (1973).

Results

The analysis of Kumar and Robson (1973) together with the potential (1) was used to calculate the E/N dependence of the reduced mobility κ , the longitudinal and lateral diffusion coefficients D_L and D_T , and the mean energy for two ion-neutral systems. The reduced mobility data were then compared with the experimental results of Milloy (1973) and the potential parameters adjusted until the predicted variation of κ with E/N lay within the experimental error limits. This procedure was carried out using three different values of p .

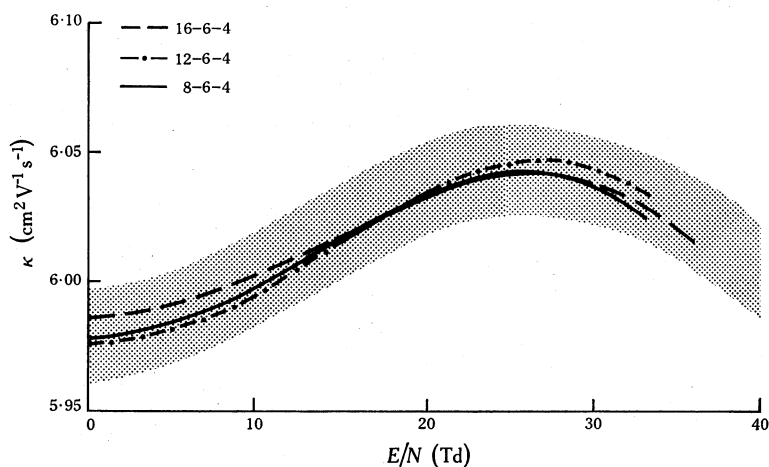


Fig. 1. Experimental error bounds for the reduced mobility κ of Cs^+ ions in neon, together with the best fits using 16-6-4, 12-6-4 and 8-6-4 interaction potentials.

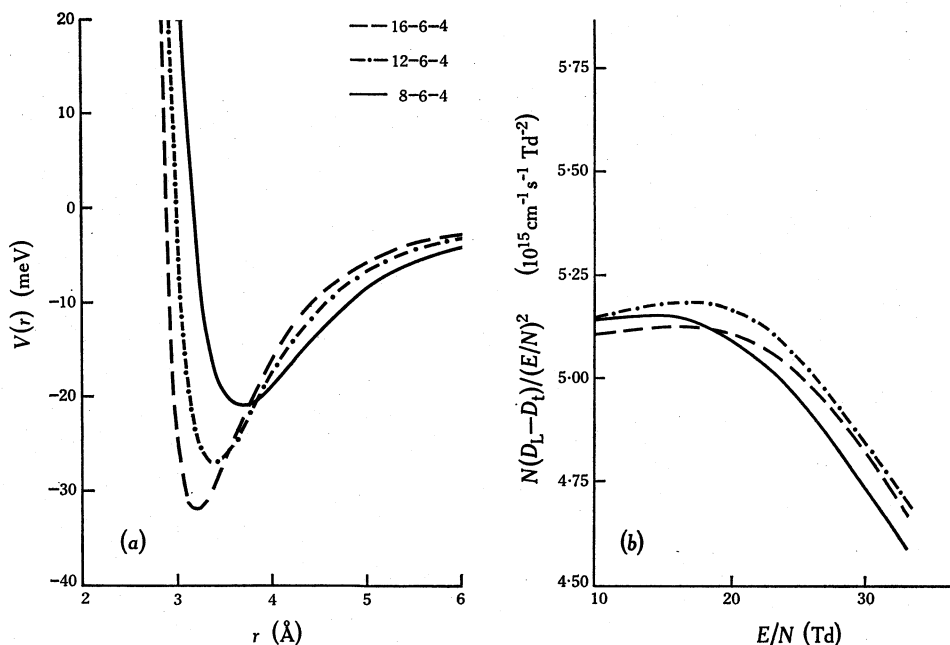


Fig. 2. Showing for Cs^+ ions in neon (a) the interaction potentials which give the best fits to the experimental reduced mobility data, and (b) the variation of the longitudinal diffusion coefficient D_L with E/N as predicted by the three interaction potentials in (a).

The mobility data for the two systems, Cs^+ ions in neon and K^+ ions in helium, were measured by the Bradbury-Nielsen method. This technique has been discussed in detail by many authors (e.g. Huxley and Crompton 1974) and will not be considered further here. The two drift tubes used were those designated as system A and system C by Elford (1971).

Cs⁺ Ions in Neon

The form of the curve of best fit to the experimental data for the reduced mobility of Cs⁺ in neon at 294 K is considered to be in error by less than ±0.3%. The area defined by this curve and the error limits, which include errors due to pressure-dependent effects (Elford and Milloy 1974), is shown in Fig. 1 by the shaded section. The best fit to the experimental data using the analysis of Robson and Kumar (1973) with $p = 4$ (i.e. an 8-6-4 potential) is shown by the continuous line. It can be seen

Table 1. Potential parameters used to fit mobility data

Potential parameter	(a) Cs ⁺ in Ne at 294 K			(b) K ⁺ in He at 293 K		
	$p = 4$	6	8	$p = 4$	6	8
ϵ (meV)	21	27	32	20	25	28
r_m (Å)	3.67	3.37	3.20	2.93	2.71	2.60
γ	1.230	0.438	0.272	1.101	0.277	0.110

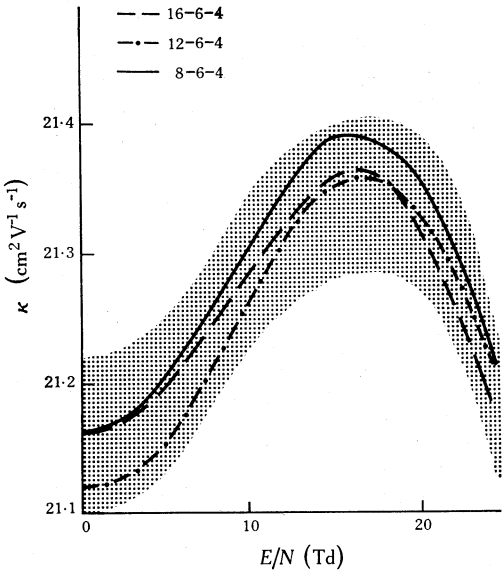


Fig. 3. Experimental error bounds for the reduced mobility κ of K⁺ ions in helium, together with the best fits using 16-6-4, 12-6-4 and 8-6-4 interaction potentials.

that this curve lies everywhere within the experimental error and thus is an adequate fit. The experimental data can also be adequately fitted with a 12-6-4 potential (dash-dot curve) and a 16-6-4 potential (dashed curve). The three potentials used in the fitting procedure are shown in Fig. 2*a* and the potential parameters are listed in Table 1*a*. It can be seen that the well depths vary by as much as 50% and the positions of the minima by 15%.

The three potentials shown in Fig. 2*a* not only give rise to essentially the same mobility data for $E/N \leq 33$ Td but also to very similar diffusion coefficient data. In the case of the longitudinal diffusion coefficient this can be seen in Fig. 2*b*, where $(ND_L - ND_0)/(E/N)^2$ has been plotted to eliminate the primary dependence of ND_L on E/N (D_0 is the zero-field diffusion coefficient). Experimental measurements of ND_L would have to be made with a total error of less than about ±0.5% to determine

which of the three potentials was the most accurate. Data of such accuracy are not available for any ion-gas combination.

By comparing the data shown in Figs 1 and 2b it can be seen that D_L is more sensitive than κ to changes in the interaction potential. Thus, if both D_L and κ were determined with the same accuracy, a more accurate estimate of the interaction potential could be obtained by fitting to the variation of D_L with E/N rather than to the variation of κ .

K⁺ Ions in Helium

Fig. 3 shows the area defined by the curve of best fit and the error limits of the mobility data in this case, together with adequate fits using 8-6-4, 12-6-4 and 16-6-4 potentials. It can be seen from the list of the potential parameters in Table 1b that potentials with well depths varying by as much as 40% can be used to fit the experimental data.

Discussion

The lack of uniqueness in the derived form of the potential well can be understood by considering the distribution of distances of closest approach in the ion-atom collisions. Classically the distribution of these distances increases monotonically with distance at large values but, since large distances of closest approach correspond to small angle scattering and small momentum transfer, these collisions are unimportant in determining the transport properties. It is therefore necessary only to consider that part of the distribution which is important for momentum transfer. In the following discussion this distribution will be referred to as the effective distribution of distances of closest approach. As the mean energy of the ions in a swarm is varied by varying E/N or T this distribution changes. At high mean energies the distribution is centred at a small internuclear separation, since the repulsive forces play a dominant part in determining the ion motion, but as the energy is decreased the mean separation increases.

To accurately determine the form of the well, two conditions must be fulfilled. First, the effective distribution of distances of closest approach must not be much larger than the width of the well. The second condition is that the change in the mean ion energy must be large enough to ensure that the distribution of distances of closest approach is moved across the potential well; that is, there is a minimum range of E/N or T over which theory and experiment need to be compared. It is not known to what extent either of these two conditions were fulfilled in the present work. Although the mean energy of Cs^+ ions in neon increases by a factor of 7 when E/N is increased from 0 to 33 Td, it has been pointed out by H. R. Skullerud (personal communication) that the change in energy in the centre of mass frame is much less, and is in fact about a factor of 2 for this case. It follows that part of the reason for the lack of uniqueness in the derived potential may be due to a large overlap in the distribution functions even at the ends of the available E/N range. It is therefore possible that a more accurate form for the potential well could have been derived if theory and experiment could have been compared over a larger E/N range. Apart from perhaps resolving the form of the well more accurately, comparison of theory and experiment over a larger E/N range would make it possible to determine the potential over a larger range of internuclear spacings. Unfortunately the use of

Monte Carlo techniques is the only way in which transport coefficient data at high E/N can be predicted at present.

One of the ways in which the form and magnitude of the potential well could be determined more accurately from swarm data would be to use more accurate experimental data. However, there are severe experimental difficulties associated with increasing the accuracy of transport coefficient data. Apart from the effects discussed by Elford and Milloy (1974), the measurement of the gas number density with error limits significantly less than 0.1% is a major unsolved problem.

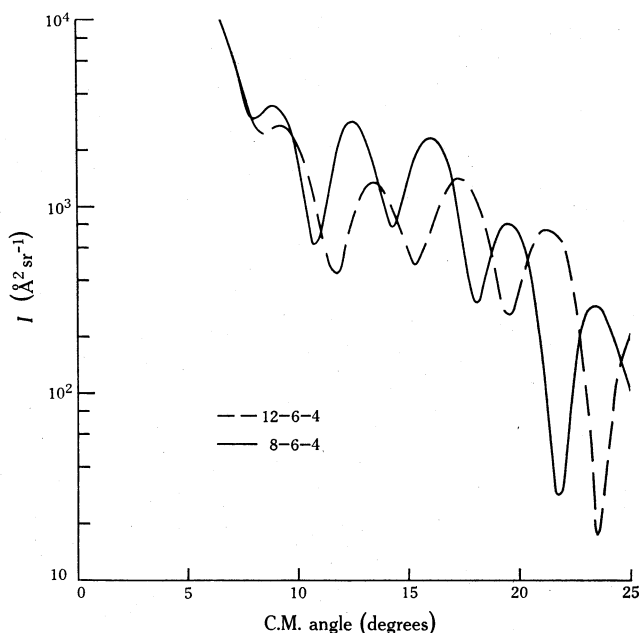


Fig. 4. Calculated differential scattering cross sections I for Cs^+ ions in neon at a laboratory energy of 40 meV ($\epsilon_{\text{lab}} = 1.5 kT$) for the 12-6-4 and 8-6-4 potentials plotted in Fig. 2a.

It is clear from the above considerations that it is not possible at present to obtain an accurate form for the potential well by analysing transport coefficient data. A similar conclusion has been found in studies on neutral systems. The bulk properties of a neutral gas can be predicted with many different interaction potentials, and it is only possible to obtain an accurate potential when experimental data from the solid and liquid phases are used (Barker *et al.* 1971). Accurate potentials for neutral systems have also been obtained from differential scattering cross-section measurements and from vibrational level spacings of the van der Waals dimers. Of these two alternative techniques the only one which has been applied to the ion-atom interaction is the analysis of the rainbow oscillations in the differential scattering cross section. The power of this technique is illustrated in Fig. 4 which shows the differential cross sections at a laboratory energy of 40 meV for the 8-6-4 and 12-6-4 potentials used in the earlier calculations and plotted in Fig. 2a. The cross sections were calculated using the Numerov technique (Watts 1974). It can be seen that the cross sections are out of phase and differ by as much as a factor of 10, yet the potentials

give essentially the same transport coefficient data. If it is assumed that a minimum exists in the potential then its magnitude and form can be determined by noting the positions of the rainbow oscillations in the cross section (Mittman *et al.* 1971) and thus it is only necessary to carry out a relative experiment. So far this technique has only been used for proton scattering (Mittman *et al.* 1971). For more massive ions it becomes difficult to produce and focus a low energy beam but, more importantly, the oscillations in the cross section become, for a given energy, more closely spaced and the structure is masked by the finite angular and energy resolution of the experiment. The effect of finite angular and energy resolution is shown in Fig. 5, where the calculated results for Li^+ ions in helium at a laboratory energy of 2.75 eV are plotted for two 12-4 potentials. Curve A corresponds to a potential with $r_m = 1.98 \text{ \AA}$, $\epsilon = 64 \text{ meV}$ and curve B to a potential with $r_m = 2.11 \text{ \AA}$, $\epsilon = 50 \text{ meV}$. In each case it has been assumed that the energy distribution of the incident beam is Gaussian with an FWHM of 275 meV (lab.) and that the collector accepted a Gaussian angular distribution with an FWHM of 3° c.m. ($\sim 1^\circ \text{ lab.}$). The true cross section for the potential used to generate curve A is also shown for comparison (curve C). It is clear that, with the assumed experimental conditions, information about the form and magnitude of the well could only be obtained by carrying out an accurate absolute experiment.

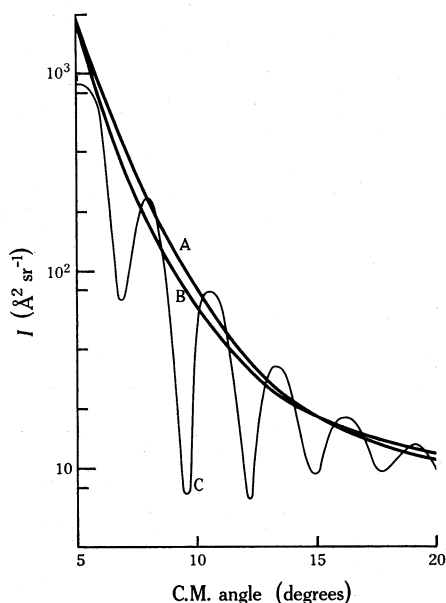


Fig. 5. Calculated differential cross sections I for Li^+ ions in helium at a laboratory energy of 2.75 eV for two 12-4 potentials:

A, $r_m = 1.98 \text{ \AA}$, $\epsilon = 64 \text{ meV}$;

B, $r_m = 2.11 \text{ \AA}$, $\epsilon = 50 \text{ meV}$.

Curve C is the true cross section for the potential used to generate curve A.

Conclusions

It has been shown that it is not always possible to determine accurately the form of the well in the interaction potential for an ion-atom system by comparing measured and predicted transport coefficients. It therefore follows that, for some ion-atom combinations, experimental transport coefficient data cannot be used to determine the accuracy of *ab initio* interaction potential calculations. Even if the calculated potential predicts the experimental data, there may be several alternative

potentials which would also adequately fit the data. It should be noted, of course, that an *ab initio* calculated potential that does not predict the observed transport coefficients can be dismissed.

In principle the form of the potential well can be determined by analysing low energy differential cross section data, but in practice this approach presents severe problems, except in the case of proton scattering, because at the energies at which a beam experiment is possible the oscillations in the cross section are usually masked by the finite resolving power of the apparatus and the observed cross sections are relatively insensitive to changes in the form of the well.

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References

- Barker, J. A., Fisher, R. A., and Watts, R. O. (1971). *Mol. Phys.* **21**, 657.
Chapman, S. (1912). *Phil. Trans. Roy. Soc. London A* **211**, 433.
Elford, M. T. (1971). *Aust. J. Phys.* **24**, 705.
Elford, M. T., and Milloy, H. B. (1974). *Aust. J. Phys.* **27**, 211.
Enskog, D. (1911a). *Phys. Z.* **12**, 56.
Enskog, D. (1911b). *Phys. Z.* **12**, 533.
Huxley, L. G. H., and Crompton, R. W. (1974). 'The Diffusion and Drift of Electrons in Gases' (Wiley: New York).
Kihara, T. (1953). *Rev. Mod. Phys.* **25**, 844.
Kumar, K., and Robson, R. E. (1973). *Aust. J. Phys.* **26**, 187.
Mason, E. A., and Schamp, H. W. (1958). *Ann. Phys. (New York)* **4**, 233.
Milloy, H. B. (1973). Ph.D. Thesis, Australian National University.
Mittman, H. U., Weise, H. P., Ding, A., and Henglein, A. (1971). *Z. Naturforsch. A* **26**, 1112.
Robson, R. E. (1973). *Aust. J. Phys.* **26**, 203.
Robson, R. E., and Kumar, K. (1973). *Aust. J. Phys.* **26**, 187.
Skullerud, H. R. (1973a). *J. Phys. B* **6**, 728.
Skullerud, H. R. (1973b). *J. Phys. B* **6**, 918.
Watts, R. O. (1974). *Aust. J. Phys.* **27**, 227.

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