

ION MOBILITY AND DIFFUSION IN GAS DETECTORS

Aritra Bal¹

¹Department of Physics,
Indian Institute of Technology Kharagpur

RD51 Collaboration Meeting, 14-18 June 2021



TABLE OF CONTENTS

- 1 TOPICS IN REVIEW
- 2 BASICS
- 3 MOMENTUM-TRANSFER THEORY
- 4 THE BOLTZMANN EQUATION
- 5 TEMPERATURE THEORIES



TOPICS IN REVIEW

- 1 Basics of ion transport and the kinetic theory.
- 2 Momentum-transfer theory for approximate calculations - mobility, diffusion coefficients and the Generalised Einstein Relations.
- 3 The Boltzmann Equation and method of Moments.
- 4 Basis Functions and the Temperature Theories.



TABLE OF CONTENTS

- 1 TOPICS IN REVIEW
- 2 BASICS
- 3 MOMENTUM-TRANSFER THEORY
- 4 THE BOLTZMANN EQUATION
- 5 TEMPERATURE THEORIES



RECAP OF BASICS: I

The ion flux, in first order of the concentration gradient, is-

$$\vec{J} = nk\vec{E} - D\vec{\nabla}n \quad (1)$$

At equilibrium, the ion flux $J = 0$, and the ion distribution function in 3D space is a Boltzmann exponential of the form $n = n_0 \exp(eE \cdot r/kT)$.

Substituting this into (1) at $J = 0$ gives us the well known Nernst-Townsend Relation.

$$\frac{D}{K} = \frac{e}{kT} \quad (2)$$

Unless specified, we assume two things - $n \ll N$ and **all collisions are binary, between ion and neutral gas alone**. At **low** enough fields, we theorise that the ion flux depends only on collisions, and this collision frequency increases directly with N . Therefore, we may assume that J , and by extension, D and K decrease proportionately with N .



RECAP OF BASICS: II

⇒ At a (constant) higher field, this is no longer true - the field will play a role in increasing the ion velocity above the thermal limit. We then assume - field dependence of all parameters is through E/N alone.

⇒ Another conclusion follows from symmetry - the parameters must be even in E/N . With these in hand, we set up the following power series expansions.

$$K(E) = K(0)[1 + \alpha_2(E/N)^2 + \alpha_4(E/N)^4 + \dots] \quad (3)$$

$$ND(E) = ND(0)[1 + d_2(E/N)^2 + d_4(E/N)^4 + \dots] \quad (4)$$

While useful enough for our case, the expansions do not converge well at very high fields.



RECAP OF BASICS: III

Higher order modifications to (1), which include the field dependence in the coefficients give us -

$$\vec{J} = nk\vec{E} - D^{(2)} \cdot \vec{\nabla}n + Q^{(3)} \cdot \nabla^2 n + \dots \quad (5)$$

From rotational symmetry, it can be shown [Mason and Whealton, *Ann. Phys. N.Y.* 1974] that $D^{(2)}$ has only two independent components - the well known D_T and D_L ; and $Q^{(3)}$ has 3. For the sake of convenience, we shall always take E along the Z axis, which allows us to take a diagonal $D^{(2)} = (D_T, D_T, D_L)$. For our purpose, the first order expansion is often enough.



TABLE OF CONTENTS

- 1 TOPICS IN REVIEW
- 2 BASICS
- 3 MOMENTUM-TRANSFER THEORY
- 4 THE BOLTZMANN EQUATION
- 5 TEMPERATURE THEORIES



MOBILITY ESTIMATIONS: I

⇒ Good enough to get the general form of the transport parameters, numerical coefficients however tend to be inaccurate.

⇒ We work in the centre of mass frame of the ion (m, v) and gas molecule (M, V), and define the momentum-transfer cross section as -

$$Q_D(\bar{\epsilon}) = 2\pi \int_0^\pi (1 - \cos \theta) \sigma(\theta, \bar{\epsilon}) \sin \theta d\theta \quad (6)$$

Here, $\bar{\epsilon} = 1/2 \mu \overline{v_r^2}$ is the mean relative energy (and velocity) of collision. The ion-gas molecule collision frequency is defined as $\nu(\bar{\epsilon}) = N \overline{v_r} Q_D$. Then, the momentum transfer per unit time (i.e the force) is $\mu v_d \nu(\bar{\epsilon})$ and this must be balanced by the electric field eE at steady state.

Meanwhile, we assume-

- While calculating momentum-transfer, random fraction of the velocity will average to zero and only the drift fraction (from the field) will contribute.



MOBILITY ESTIMATIONS: II

- Ion scattering is isotropic in the CM frame - valid only for hard-sphere scattering. Won't work for the clusters we are more interested in.
- Cross terms vanish on averaging, i.e. $\overline{v_r^2} = \overline{(v - V)^2} = \overline{v^2} + \overline{V^2}$

With these, it's easy to show -

$$\frac{1}{2}m\overline{v^2} = \frac{1}{2}M\overline{V^2} + \frac{1}{2}m\overline{v_d^2} + \frac{1}{2}M\overline{v_d^2} \quad (7)$$

This formula is rather general. At this point, we can safely assume the first term to be thermal and equal to $3/2 kT$. Its convenient to define an effective temperature as -

$$\frac{3}{2}kT_{eff} = \bar{\epsilon} = \frac{3}{2}kT + \frac{1}{2}Mv_d^2 \quad (8)$$

which leads us to -

$$K = \frac{v_d}{E} = \frac{e}{N} \left(\frac{1}{3\mu kT_{eff}} \right)^{1/2} \frac{1}{Q_D(T_{eff})}$$



MOBILITY ESTIMATIONS: III

A first order Chapman-Enskog approximation gives an error of $\approx 20\%$, but the general form is correct.

$$K = \frac{v_d}{E} = \frac{3e}{16N} \left(\frac{1}{2\pi\mu kT_{eff}} \right)^{1/2} \frac{1}{Q_D(T_{eff})} \quad (10)$$

We have taken a fixed momentum-transfer cross section, assuming hard sphere scattering, which should actually be averaged over a distribution -

$$\Omega(T) = \frac{1}{2}(kT)^{-3} \int_0^\infty Q_D(\epsilon) \exp(-\epsilon/kT) \epsilon^2 d\epsilon \quad (11)$$

Having done this, a simple Taylor expansion of Q_D about T_{eff} , followed by some substitutions yields -

$$K(E) = K(0) \left[1 - \frac{m+M}{m} \left(\frac{1}{2} + \frac{d \ln Q_D}{d \ln T} \right) \left(\frac{e}{3kTQ_D} \right)^2 \left(\frac{E}{N} \right)^2 + \dots \right] \quad (12)$$

This is the α_2 encountered in (3).



WHAT ARE HIGH/LOW FIELDS?

Our criterion for low field behaviour is that the thermal energy is more than the field-dependent one.

$$\frac{1}{2} M v_d^2 \ll \frac{3}{2} kT \quad (13)$$

For rigid spheres, at $T = 300K$ and using (9), one gets -

$$\frac{E}{N} (Td) \ll 0.78 \left(\frac{m}{m+M} \right)^{1/2} Q_D (\text{\AA}) \quad (14)$$

The converse gives us the "cold-gas" expansion ([Skullerud and Forsth, J. Phys. B12, 1979](#))

It must be stated that the high field limit $3kT/Mv_d^2 \ll 1$ can be attained by either allowing $T \rightarrow 0$ or $E/N \rightarrow \infty$. The two are however not equivalent. The second approach leads to "ion runaway" due to acceleration, and no steady state is ever reached!



DIFFUSION AND THE EINSTEIN RELATIONS: I

Rob has already spoken about these in detail earlier. To just recap, the momentum-balance equation must include a pressure gradient.

$$ne\vec{E} - \nabla \cdot p_i = n\mu\nu(\epsilon)\bar{v} \quad (15)$$

The pressure tensor is defined from the usual kinetic theory calculation. It is convenient to introduce the two ion temperatures in the form of a tensor $p_i = nkT_i$, where we have -

$$kT_T = m\overline{v_x^2} = m\overline{v_y^2} \quad \text{and} \quad kT_L = m(\overline{v_z^2} - \overline{v_z^2}) \quad (16)$$

The diffusion tensor is then defined by the excess ion flux that arises other than due to the field.

$$n(\bar{v} - v_d) = -D.\nabla n \quad (17)$$



DIFFUSION AND THE EINSTEIN RELATIONS: II

The Generalised Einstein Relations (GER) are derived by considering the spatially homogenous case $\bar{\nu} = \nu_d$, where no gradients exist, and expanding ν about ν_d . The results are shown below.

$$\frac{D_T}{K} = \frac{kT_T}{e} \quad (18)$$

$$\frac{D_L}{K} = \frac{KT_L}{e} \left(1 + \frac{d \ln K}{d \ln E} \right) \quad (19)$$

At low fields, one recovers the Nernst-Townsend relation; and at high fields, calculations in [H. R Skullerud, *J. Phys.* **B9**, 1976](#), taken at different exponents of an ion-neutral gas interaction potential (C/r^n) show almost perfect agreement for heavy ions in light gas (as is the case for our clusters).

It is possible to find a relation for the ion temperatures of the form of (8), but the results from momentum-transfer theory show large deviations from more rigorous



DIFFUSION AND THE EINSTEIN RELATIONS: III

calculations. The accurate results can be found in [Wannier, Bell Syst. Tech. J., 1953](#) with later corrections to the value of T_L computed in [Skullerud, 1976](#).

$$kT_{T,L} = kT + \zeta_{T,L} M v_d^2 \left(1 - \beta_{T,L} \frac{1 - 4/n}{2 - 4/n} \right) \quad (20)$$

where we have -

$$\zeta_T = \frac{(m + M)[Q^{(2)}/Q^{(1)}]}{4m + 3M[Q^{(2)}/Q^{(1)}]}$$

$$\zeta_L = \frac{4m - (2m - M)[Q^{(2)}/Q^{(1)}]}{4m + 3M[Q^{(2)}/Q^{(1)}]}$$

$$Q^{(i)} = 2\pi \int_0^\pi (1 - \cos^i \theta) \sigma(\theta, \bar{\epsilon}) \sin \theta d\theta$$

Here, $\beta_T = 0$, and β_L is taken from tabulated values in [Skullerud, 1976](#). An empirical relation also exists -

$$\beta_L \approx \frac{m}{m + M} + \frac{mM}{(m + M)^2}$$



WHAT ABOUT MIXTURES?

Also covered by Rob earlier, we have Blanc's Law -

$$\frac{1}{K} = \sum_j \frac{x_j}{K_j} \quad (21)$$

In principle, very useful, but doesn't help since most ions undergo reactions and mobility data K_j in pure component j (at **same** number density) doesn't exist for most cases.

Blanc's Law is the low-field limit (i.e collision frequency assumed thermal) of the more general equation -

$$\frac{1}{K} = \sum_j \frac{x_j}{K_j} \frac{\langle \nu_j \rangle_{mix}}{\langle \nu_j \rangle} \quad (22)$$



TABLE OF CONTENTS

- ① TOPICS IN REVIEW
- ② BASICS
- ③ MOMENTUM-TRANSFER THEORY
- ④ THE BOLTZMANN EQUATION
- ⑤ TEMPERATURE THEORIES



THE BOLTZMANN EQUATION AND METHOD OF MOMENTS: I

In principle, we need only the ion density distribution function $f(v, r, t)$.

$$n(r, t) = \int f(v, r, t) dv \quad (23)$$

$$\langle \psi(r, t) \rangle = \frac{1}{n} \int (\psi(v) f(v, r, t) dv) \quad (24)$$

The ion distribution function can also, in principle, be found from the Boltzmann Equation.

$$\begin{aligned} \frac{\partial f}{\partial t} + v \cdot \nabla_r f + a \cdot \nabla_v f = \sum_j \int \int \int [f(v', r, t) F_j(V_j', r, t) - f(v, r, t) F_j(V_j, r, t)] \\ |v - V_j| \times \sigma_j(\theta, |v - V_j|) \sin \theta \, d\theta \, d\phi \, dV_j \end{aligned} \quad (25)$$

We define $v_{rj} = |v - V_j|$ to compress the notation.



THE BOLTZMANN EQUATION AND METHOD OF MOMENTS: II

But this too has limitations -

- ❶ No ion-ion collision/interaction terms of the form $f_i f_j$.
- ❷ Ion number is conserved, hence no reactions.
- ❸ Internal degrees of freedom are ignored.

The last two can be dealt with within this framework, but not the first. We may also take the neutral molecule velocities to be a Maxwell-Boltzmann Distribution of zero mean -

$$F_j = N_j \left(\frac{M_j}{2\pi kT} \right)^{3/2} \exp(-M_j V_j^2 / 2kT)$$

At the outset, we abandon all hope of solving the Boltzmann Equation completely and try just to get a few averages of interest (perhaps $K, D_T, D_L?$). Rather, we



THE BOLTZMANN EQUATION AND METHOD OF MOMENTS: III

set up a moment equation by multiplying the function we wish to average and integrating -

$$\begin{aligned} \frac{\partial}{\partial t} \int \psi f dv + \int \psi \mathbf{v} \cdot \nabla_r f dv + \frac{e}{m} \int \psi \mathbf{E} \cdot \nabla_v f dv \\ = \sum_j \int \int \int \psi (f' F'_j - f F_j) v_{rj} \sigma_j d\Omega_j dV_j dv \end{aligned} \quad (26)$$

At this stage, its convenient to define a *linear collision* operator J_j as -

$$J_j \psi = \frac{1}{N_j} \int \int F_j [\psi(v) - \psi(v')] v_{rj} \sigma_j d\Omega_j dV_j$$



THE BOLTZMANN EQUATION AND METHOD OF MOMENTS: IV

Integrating by parts (with the assurance that $\int f dv = n$ is velocity independent), we end up with -

$$\frac{\partial}{\partial t} n \langle \psi \rangle + \nabla_r \cdot (n \langle v \psi \rangle) - n \frac{e}{m} E \cdot (\langle \nabla_v \psi \rangle) = -n \sum_j N_j \langle J_j \psi \rangle \quad (27)$$

This can be greatly simplified with a few assumptions -

- 1 Ion density gradient is small enough for Fick's Law (first order) to be valid. Other ion properties (ψ) are assumed to be spatially independent ($\nabla_r \psi = 0$), or more accurately, even smaller compared to $\nabla_r n$. This is, in general, not true for electrons.
- 2 We can neglect all time derivatives other than $\partial n / \partial t$ under the assumption that ion number density changes only through their (rather slow) motion. The ψ 's, being functions of v change rapidly and are dissipated away very fast, allowing us to set their time derivatives to zero.



THE BOLTZMANN EQUATION AND METHOD OF MOMENTS: V

Setting $\psi = 1$ gives us the familiar equation of continuity -

$$\frac{\partial n}{\partial t} + \nabla_r \cdot (n \langle v \rangle) = 0 \quad (28)$$

Using (28) and the assumptions above, we drop the various derivatives and find -

$$\frac{e}{m} E \cdot (\nabla_v \psi) - [\langle v \psi \rangle - \langle v \rangle \langle \psi \rangle] \cdot \nabla_r \ln n = \sum_j N_j \langle J_j \psi \rangle \quad (29)$$

To simplify the math, we choose an orthogonal basis to represent the ψ 's, and form the collision operator matrix. They are taken to be orthogonal with respect to a weight function $g(v)$ which is chosen according to the theory.

$$J_j \psi_p = \sum_q a_{pq}^{(j)} \psi_q \quad (30)$$

$$\int g(v) \psi_p^\dagger \psi_q dv = \delta_{pq} \int \psi_p^\dagger \psi_q dv$$



TABLE OF CONTENTS

- 1 TOPICS IN REVIEW
- 2 BASICS
- 3 MOMENTUM-TRANSFER THEORY
- 4 THE BOLTZMANN EQUATION
- 5 TEMPERATURE THEORIES



Calculations are quite complicated at times, these theories are distinguished by their choice of weight and/or basis functions. We start by constructing a series expansion of the ion distribution f , about some zero order approximation $f^{(0)}$.

$$f = f^{(0)} \sum_q c_q \phi_q^\dagger$$

We construct orthogonal ϕ 's using the normalisation condition -

$$\int f^{(0)} \phi_q^\dagger \phi_p dv = n N_p \delta_{pq}$$

It is then easy to show that (29) simplifies to -

$$\frac{e}{m} E \cdot (\nabla_v \psi) - [\langle v \psi \rangle - \langle v \rangle \langle \psi \rangle] \cdot \nabla_r \ln n = \sum_{j,q} N_j \langle \phi_q \rangle f_{pq}^{(j)} \quad (32)$$



BASIS FUNCTIONS AND TEMPERATURE THEORIES: II

The steps for representing $\langle J_j \phi_p \rangle$ are simple, and they contain the following term -

$$f_{pq}^{(j)} = \frac{1}{nN_q} \int f^{(0)} \phi_q^\dagger (J_j \phi_p) dv$$

In the one-temperature theory, we use the zero order ion distribution function as our weight function, and take it to be a Maxwell-Boltzmann distribution.

$$f^{(0)} = n \left(\frac{m}{2\pi kT} \right)^{3/2} \exp(-mv^2/2kT) \quad (33)$$

Letting $w^2 = mv^2/2kT$ to simplify the notation, the basis functions in spherical coordinates happen to be Burnett Functions.

$$\psi_{lm}^{(r)} = w^l S_{l+1/2}^{(r)}(w^2) Y_l^m(\theta, \phi) \quad (34)$$

$$\cos \theta = v_z/v$$



BASIS FUNCTIONS AND TEMPERATURE THEORIES: III

The $S(w^2)$ is a generalised Laguerre Polynomial, and the Y 's are the well known spherical harmonics.

In the two-temperature theory, we stick with the same basis functions, but introduce an additional parameter T_b - the ion basis temperature.

$$f^{(0)} = n \left(\frac{m}{2\pi kT} \right)^{3/2} \exp(-mv^2/2kT_b) \quad (36)$$

and let $w_b^2 = mv^2/2kT_b$. The choice of T_b is a question in its own - in many cases its convenient to replace it by the mean ion energy as $kT_b = 1/2m \langle v^2 \rangle$



CONCLUSION

- 1 Garfield++ ion mobility calculations do not represent accurate calculations, the data is only for pure ions in their own gas. The goal over the summer is to create an accurate model for this.
- 2 Ion mobility and diffusion calculations are much more complicated than electrons, where we can safely neglect the thermal energies to get analytical expressions for the quantities.
- 3 Momentum transfer theory calculations and kinetic theory get us close to the answer, and often yield the correct form of the expressions, but errors still persist, which must be dealt with using the more accurate temperature theories.
- 4 Chemical reactions need to be dealt with in the Boltzmann equation, for a rigorous model, but the approach outlined here can help us compute the transport properties of the clusters assuming the reactions have already occurred.



THANK YOU!

