

ME 451C
Winter Quarter, 2004-05
Week # 6

Harvey Lam
lam@princeton.edu

February 8, 2005

Abstract

What happens when different species experience different body forces? A most interesting case is an ionized gas or an electrolyte in the presence of electrical forces. Here we limit ourselves to electric field \mathbf{E} , ignoring the complications of the magnetic field. Once we have settled on a diffusion law involving \mathbf{E} , we can find the composition of the flowing mixture. We shall talk about some interesting applications.

1 Number-averaged velocities

Consider a single component Fluid which is weakly ionized. We mark the neutral particles by subscript o , the positive (singly-charged) ions by subscript i , and the negative (singly-charged) particles (could be electrons) by subscript e , and no subscript at all denotes the whole mixture. We assume all three components have the same temperature T .

So, to fully describe the motion of the three species, we would need to find the velocities $\mathbf{V}_{(.)}$ for each of the components:

$$\mathbf{V}_o = \mathbf{V} + \mathbf{v}_o^*, \quad (1)$$

$$\mathbf{V}_i = \mathbf{V} + \mathbf{v}_i^*, \quad (2)$$

$$\mathbf{V}_e = \mathbf{V} + \mathbf{v}_e^*, \quad (3)$$

where \mathbf{V} is the mixture velocity, and $\mathbf{v}_{(\cdot)}^*$ are the diffusion velocities. In the conventional formulation, \mathbf{V} is the averaged velocity of the mixture. Usually, mass averaging is the way to go. But, we shall see that for this class of problems, number-averaging is the way to go. We shall use number averaging.

Denote the number densities of interest here by n_o, n_i, n_e , with $n = n_o + n_i + n_e$. The composition of the mixture is specified by the number fractions $X_{(\cdot)}$ as follows:

$$X_o = \frac{n_o}{n}, \quad (4)$$

$$X_i = \frac{n_i}{n}, \quad (5)$$

$$X_e = \frac{n_e}{n}. \quad (6)$$

And \mathbf{V} is defined by:

$$\mathbf{V} = X_o \mathbf{V}_o + X_i \mathbf{V}_i + X_e \mathbf{V}_e. \quad (7)$$

We shall denote the mass of each molecule of the three species by m_o, m_i, m_e , respectively.

2 Governing equations

We shall make simplifying assumptions to focus our attention to the diffusion aspect of the problem.

2.1 Continuity equations

If there is no ionization/recombination processes going on, mass conservation and number conservation are the same thing. But if there is ionization/recombination going on—to be represented by \mathcal{W} —then when a neutral is (singly) ionized, a positive ion and a negative ion (electron) are created:

$$\frac{\partial n_o}{\partial t} + \nabla \cdot (n_o \mathbf{V}) + \nabla \cdot (n_o \mathbf{v}_o^*) = -\mathcal{W}, \quad (8)$$

$$\frac{\partial n_i}{\partial t} + \nabla \cdot (n_i \mathbf{V}) + \nabla \cdot (n_i \mathbf{v}_i^*) = \mathcal{W}, \quad (9)$$

$$\frac{\partial n_e}{\partial t} + \nabla \cdot (n_e \mathbf{V}) + \nabla \cdot (n_e \mathbf{v}_e^*) = \mathcal{W}. \quad (10)$$

Summing the three equations, we have (using Eq.(7)):

$$\frac{\partial n}{\partial t} + \nabla \cdot (n\mathbf{V}) = \mathcal{W}. \quad (11)$$

It is understood that \mathcal{W} is some algebraic functions of n_o, n_i, n_e and T .

2.2 Diffusion Laws

For the sake of simplicity, we assume there is no externally applied magnetic field, and whatever magnetic field induced by flowing electric currents can be neglected. We shall adopt the following (phenomenological) diffusion laws:¹

$$n_i \mathbf{v}_i^* = -D_i \nabla n_i + \nu_i n_i \mathbf{E}, \quad (12)$$

$$n_e \mathbf{v}_e^* = -D_e \nabla n_e - \nu_e n_e \mathbf{E}. \quad (13)$$

where \mathbf{E} is the electric field, and D_i, D_e are positive and negative ion's diffusivities, and ν_i, ν_e are their *mobilities*, respectively (usually, ν is denoted by μ , which we reserve for the magnetic permeability of the mixture later). By “weakly ionized,” we restrict our attention to the case $n_i \ll n_o, n_e \ll n_o$ and $n_o \approx n$. We don't have the right to add a diffusion law for the neutrals, since the sum of the diffusion fluxes of all three species adds up to zero.

The following relations between diffusion coefficient and the mobility coefficient is called the Einstein relation (we are in good company):

$$\frac{\nu_i}{D_i} = \frac{e}{kT}, \quad (14)$$

$$\frac{\nu_e}{D_e} = \frac{e}{kT}, \quad (15)$$

where e is the magnitude of the charge of a single electron, and k is the Boltzmann constant. In general, $D_i \propto \lambda_i \sqrt{kT/m_i}$ and $D_e \propto \lambda_e \sqrt{kT/m_e}$ where λ_i and λ_e are mean-free-paths of the positive and negative ions, respectively.² So if the negative ions are actually electrons ($m_i \gg m_e$), $D_e/D_i \gg 1$ and $\nu_e/\nu_i \gg 1$, which merely says what should be physically obvious: electrons diffuse much faster than the fat, chubby positive ions.

¹Note that the diffusion matrix is diagonal here.

²Since electrons are so much lighter than ions, collisional energy exchange is very slow. So it is frequently the case that electron and ion temperatures are different. When they are different, the Einstein relations will have the appropriate temperatures on the right hand side.

2.3 Maxwell equations

We now got the electric field \mathbf{E} involved. The Maxwell's equations are:

$$\nabla \cdot \mathbf{E} = \frac{e}{\epsilon}(n_i - n_e), \quad (16)$$

$$\nabla \cdot \mathbf{B} = 0, \quad (17)$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}, \quad (18)$$

$$\nabla \times \mathbf{B} = \mu \mathbf{j} + \frac{1}{c^2} \frac{\partial \mathbf{E}}{\partial t}, \quad (19)$$

where ϵ and μ are *permittivity* and *permeability* of the mixture, $c^2 = 1/(\mu\epsilon)$ is the speed of light in the mixture, and \mathbf{j} is the electric current density which is defined by:

$$\mathbf{j} \equiv e(n_i \mathbf{V}_i - n_e \mathbf{V}_e) = e(n_i \mathbf{v}_i^* - n_e \mathbf{v}_e^*) + e(n_i - n_e) \mathbf{V}. \quad (20)$$

Using Eq.(12) and Eq.(13), we have:

$$\mathbf{j} = e(-D_i \nabla n_i + \nu_i n_i \mathbf{E}) - e(-D_e \nabla n_e - \nu_e n_e \mathbf{E}) + e(n_i - n_e) \mathbf{V}. \quad (21)$$

It is quite a mess.

Under the assumption that \mathbf{B} is negligible in the above equations³, Eq.(18) says \mathbf{E} can be approximated by a gradient:

$$\mathbf{E} \approx -\nabla \phi \quad (22)$$

where $\phi(\mathbf{x}; t)$ has the dimension of voltage. So instead of a vector unknown \mathbf{E} , we need only to deal with a single scalar unknown ϕ . Substituting Eq.(22) into Eq.(16), we obtain the governing equation for ϕ :

$$\nabla^2 \phi = -\frac{e}{\epsilon}(n_i - n_e). \quad (23)$$

We are now ready to go.

3 The Debye length λ_D

Eq.(23) is the new boy in town. What do we do with him?

If we nondimensionalize ϕ by ϕ_R , n_i and n_e by n_R , and the spatial coordinates by L_R where subscript R is used to denote a reference

³Somehow we have to convince Eq.(19) that he has been duely respected.

value, then the following dimensionless parameter Π shows up when we nondimensionalize Eq.(23):

$$\Pi = \frac{\lambda_D^2}{L_R^2} \quad (24)$$

where h_D has the dimension of length and is defined by

$$\lambda_D \equiv \sqrt{\frac{\epsilon\phi_R}{en_R}}. \quad (25)$$

When ϕ_R is chosen to be kT/e , the resulting λ_D is called the *Debye length*. A useful dimensional formula is:

$$\lambda_D(cm) = 6.9 \times \sqrt{\frac{T(^{\circ}Kelvin)}{n_R(cm^{-3})}}. \quad (26)$$

Whenever electrical conduction current is of practical interest, the reference number density n_R is usually large enough to make λ_D is a very small length scale.

In fact, a commonly accepted definition of an electrically conducting *plasma* is that its Debye length is very small (in comparison to the reference length L_R of interest).

4 The quasi-neutral approximation

If we just nondimensionalize the dependent variables of Eq.(23), we obtain:

$$\nabla^2 \left(\frac{\phi}{\phi_R} \right) = \frac{1}{\lambda_D^2} \left(\frac{n_e}{n_R} - \frac{n_i}{n_R} \right). \quad (27)$$

Hence, in the limit of very small λ_D , Eq.(23) says the mixture is electrically approximately neutral:

$$n_i \approx n_e. \quad (28)$$

This is called the quasi-neutral approximation.

You may have noticed that we brought in Maxwell's Poisson's equation to take care of the (irrotational) electric field (\mathbf{E}). And what did it do? It told us we no longer need to find both n_i and n_e . You just need to find the solution of n_e , and the same solution is good for the n_i !

5 Ohm's Law

Using the quasi-neutral approximation in Eq.(21), we obtain:

$$\mathbf{j} = e(-(D_i - D_e)\nabla n_e + (\nu_i + \nu_e)n_e\mathbf{E}) + O(\lambda_D/L_R)^2. \quad (29)$$

where n_i no longer appears. The last term represents the error introduced by the quasi-neutral approximation.

We can now divide \mathbf{E} into three parts, \mathbf{E}_{ambi} , $\mathbf{E}_{\#}$ and \mathbf{E}_{ohmic} , where \mathbf{E}_{ambi} is defined by:

$$\mathbf{E}_{ambi} \equiv -\frac{D_e - D_i}{\nu_i + \nu_e} \frac{\nabla n_e}{n_e}, \quad (30)$$

and $\mathbf{E}_{\#} = O(\lambda_D/L_R)^2$ when the quasi-neutral approximation is valid. Note that \mathbf{E}_{ambi} is *not* associated with any current \mathbf{j} . Eq.(29) now becomes:

$$\mathbf{j} = \sigma\mathbf{E}_{ohmic} \quad (31)$$

where

$$\sigma = e(\nu_i + \nu_e)n_e. \quad (32)$$

where σ —as given by Eq.(32)—is called the *electrical conductivity* of the quasi-neutral plasma, and Eq.(31) is generally referred to as the Ohm's Law of this electrically conducting material. Note that σ depends linearly on n_e (which is one of the unknowns).

It is straightforward to derive from the continuity equations of the positive and negative ions that:

$$\nabla \cdot \mathbf{j} = 0. \quad (33)$$

Using Eq.(32) for \mathbf{j} and Eq.(22) for \mathbf{E} , we have:

$$\nabla \cdot (\sigma\nabla\phi) = 0. \quad (34)$$

6 The ambi-polar diffusion flux

Let us introduce \mathbf{f} , the *ambi-polar flux*, by the following definition:

$$\mathbf{f} = \left(\frac{\nu_e}{\nu_e + \nu_i}\right)n_i\mathbf{v}_i^* + \left(\frac{\nu_i}{\nu_e + \nu_i}\right)(n_e\mathbf{v}_e^*). \quad (35)$$

Using the diffusion laws Eq.(12) and Eq.(13) and the quasi-neutral approximation, we have:

$$\mathbf{f} \approx -D_{ambi}\nabla n_e \quad (36)$$

where

$$D_{ambi} = \frac{\nu_e D_i + \nu_i D_e}{\nu_e + \nu_i}. \quad (37)$$

This ambi-polar flux \mathbf{f} is defined in such a way that it has no explicit dependence on \mathbf{E} .

7 The quasi-neutral n_e distribution

Multiplying Eq.(9) by $\nu_e/(\nu_e + \nu_i)$ and Eq.(10) by $\nu_i/(\nu_e + \nu_i)$ and adding the results, we obtain:

$$\frac{\partial n_e}{\partial t} + \nabla \cdot (n_e \mathbf{V}) + \nabla \cdot \mathbf{f} = \mathcal{W}. \quad (38)$$

7.1 The constant transport properties case

Using Eq.(36) for \mathbf{f} , we obtain (assuming all transport properties to be constants):

$$\frac{\partial n_e}{\partial t} + \nabla \cdot (n_e \mathbf{V}) = D_{ambi} \nabla^2 n_e + \mathcal{W}. \quad (39)$$

We now have a convection-diffusion-reaction PDE for the distribution of n_e . Note that the distribution of n_e of the quasi-neutral mixture has no explicit dependence on \mathbf{E} .

8 Boundary conditions

For Eq.(33) and Eq.(34), we need to entertain the possibility that electrical currents may flow from a solid conducting wall (an electrode) to the electrically conducting mixture. Or, we may to specify the value of the electrical potential ϕ at the solid boundaries.

For Eq.(39), we must have an appropriate model on what happens to the charged particles when they strike the solid boundaries. Are the wall “ideal” absorbers of charge particles? If charged particles, such as electrons, are coming off a solid surface, what law of physics should apply?

More importantly, we cannot expect the quasi-neutral approximation to remain valid all the way to a solid surface—*e.g.* our physical boundary conditions at the wall may not be quasi-neutral. Obviously, for such problems at distances of the order of the local Debye length

from a solid surface, we can expect the quasi-neutral approximation to fail. The very thin layer adjacent to solid surfaces in contact with an electrically conducting mixture is called an electrostatic *sheath* in the literature. In the sheath, Eq.(23) must be brought back in, and $\mathbf{E}_\#$ is no longer small—in fact, the potential drop in the very thin sheath can be comparable (or even bigger) than the potential drop across the big quasi-neutral region.

9 Miscellaneous applications

We shall talk in class about the current voltage characteristics of an electrode which surface is a good absorber of charged particles, showing the phenomena of current saturations. We shall talk about the basic operating mode of thermionic energy converters. Finally, we shall provide a simple demonstration of the concept of “critical mass” (a well known concept in nuclear reactors or bombs) using Eq.(39)

10 Mid-Term

The “homework” for this week will be the mid-term.

All registered, enrolled students are expected to hand in this mid-term on 2/15/05.

My plan is to post the mid-term on the course webpage in the late evening of 2/8, Tuesday, and send everybody an email at the same time. I have a pretty good idea on what is in store for the mid-term, but I will not finalize it until after the tuesday class.