

## Irreversible Thermodynamic Analysis of Electrophoretic Light Scattering Experiments

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### Synopsis

A fluctuation theory for electrolyte solutions is developed based on the coupling between the equations of nonequilibrium thermodynamics and the Poisson equation. The resulting fluctuation theory is applied to the analysis of electrophoretic light scattering. It is shown that in a binary electrolyte solution (two ionic species), the Doppler shift is not determined by the electrical mobility of either ion, but depends instead on the rate of change of transference number with salt concentration. In addition the ionic relaxation time is shown to be proportional to the conductivity of the solution.

### INTRODUCTION

Several theoretical analyses of electrophoretic light scattering have been given since its introduction by Ware and Flygare<sup>1</sup> in 1971. Stephen<sup>2</sup> presented a theoretical treatment based on the assumption that the current of each species of ion is independent of that of the other ions except insofar as long range *electrical* forces cause them to interact. Although this is often a good approximation, it is well known that in a system containing several different species of ions the current of any ionic species is also influenced by the gradients of the *electrochemical potentials* of all of the ionic species present. In this paper we present a treatment which takes into account this extra source of ion interaction. A detailed analysis of the two-ion case is presented. It is found that there is a small electrophoretic shift, whereas in the previous theory no shift should occur.

### THE FUNDAMENTAL EQUATIONS

According to Irreversible thermodynamics,<sup>3</sup> the flux of an ion  $i$  in an electrochemical system is given by the equation

$$\vec{J}_i = -L_{ij} \text{grad } (\tilde{\mu}_j) \quad (1)$$

where  $L_{ij}$  is a phenomenological coefficient,  $\tilde{\mu}_j$  is the electrochemical potential of the  $j$ th component,  $\vec{J}_i$  is the number current of the ion species  $i$ , and the Einstein summation convention, where repeated indexes are summed, is used (as it is throughout this article).

The electrochemical potential may be written as

$$\tilde{\mu}_j = \mu_j + \phi z_j \quad (2)$$

where  $\phi$  is the electrical potential and  $z_j$  is the charge of the  $j$ th ion.

Equation (1) is often used to analyze steady-state electrochemical experiments. For example, in an electrolyte solution consisting of only two ionic species and a solvent, it can be shown<sup>3</sup> that the transference numbers  $t_1$  and  $t_2$  of the two ionic species, the conductivity  $\kappa$  of the solution, and the diffusion coefficient  $D$  of the salt can be related to the coefficients  $L_{ij}$  as follows

$$t_i = \frac{\sum_k z_i L_{ik} z_k}{\sum_{ik} z_i L_{ik} z_k} \quad i = 1, 2 \quad (3a)$$

$$\kappa = \sum_{ik} z_i L_{ik} z_k F^2 \quad (3b)$$

$$D = \frac{z_1 z_2}{\nu_1 \nu_2} \left[ \frac{L_{11} L_{22} - L_{12} L_{21}}{z_1^2 L_{11} + z_1 z_2 (L_{12} + L_{21}) + z_2^2 L_{22}} \right] \left( \frac{\partial \mu_s}{\partial c_s} \right) \quad (3c)$$

where  $F$  is Faraday's constant,  $\nu_1$  and  $\nu_2$  are the stoichiometric coefficients of the ionic species,  $c_s$  is the salt concentration, and  $\mu_s$  is the chemical potential of the salt.

$$\mu_s = \nu_1 \mu_1 + \nu_2 \mu_2$$

It is important to note that because of the reciprocal relations ( $L_{12} = L_{21}$ ), Eqs. (3a)–(3c) can be used to determine all of the kinetic coefficients in terms of the three independently measurable quantities  $t_1$  (or  $t_2$ ),  $\kappa$ , and  $D$ . Actually, Eqs. (3a)–(3c) are not entirely correct because certain corrections are required to express the flux, Eq. (1), in the laboratory fixed axis system. These corrections are small and are therefore omitted here. The detailed calculation incorporating these corrections can be found elsewhere.<sup>4</sup>

In an electrophoretic light scattering experiment the electrical potential may be written as

$$\phi = \phi_e + \phi_I \quad (4)$$

where  $\phi_e$  is due to the externally applied field and  $\phi_I$  is due to the charge density within the experimental solution itself. Substituting Eqs. (2) and (4) into Eq. (1) and using the divergence theorem gives

$$\frac{\partial c_i}{\partial t} = \text{div} [L_{ij} \text{grad} (\mu_j + (\phi_I + \phi_e) z_j)]$$

where  $c_i$  is the concentration of the  $i$ th ion. Trivial manipulation gives

$$\frac{\partial c_i}{\partial t} = \text{div} \left[ L_{ij} \left\{ \left( \frac{\partial \mu_j}{\partial c_l} \right) \text{grad} c_l + \bar{E}_I z_j + \bar{E}_e z_j \right\} \right] \quad (5)$$

where  $\bar{E}_e$  is the externally imposed electric field and  $\bar{E}_I$  is the part of

the electric field due to the distribution of charge within the experimental solution. This internal electric field,  $\vec{E}_1$ , depends on the charge density  $\rho$  through the Poisson equation

$$\text{div} (\vec{E}_e + \vec{E}_1) = \text{div} \vec{E}_1 = \frac{4\pi}{\epsilon} \rho \quad (6)$$

where  $\epsilon$  is the dielectric constant and the second equality follows from the assumption that the externally applied field is homogeneous ( $\text{div} \vec{E}_e = 0$ ). Since the charge density,  $\rho$ , is determined by the ionic concentrations  $c_i$ , through the equation

$$\rho = F \sum_i z_i c_i \quad (7)$$

where  $F$  is Faraday's constant. Equations (5), (6), and (7) form a closed set of equations for the local concentrations  $\{c_i(\vec{r}, t)\}$ .

In an equilibrium solution, the local concentration  $c_i(\vec{r}, t)$ , fluctuates around the equilibrium concentration  $c_i^0$ , and can thus be expressed as

$$c_i(\vec{r}, t) = c_i^0 + \delta c_i(\vec{r}, t) \quad (8)$$

where the concentration fluctuation  $\delta c_i$  is usually very small compared to  $c_i^0$ . Dynamic light scattering is completely determined by the correlation functions

$$F_{ij}(\mathbf{q}, t) \equiv \langle \delta c_i^*(\mathbf{q}, 0) \delta c_j(\mathbf{q}, t) \rangle \quad (9)$$

where  $\delta c_i(\mathbf{q}, t)$  is the spatial Fourier transform of  $\delta c_i(\vec{r}, t)$ , and  $\mathbf{q}$  is the Bragg vector or scattering vector. The heterodyne spectrum of the scattered light is determined by the time Fourier transforms of  $F_{ij}(\mathbf{q}, t)$ ; that is

$$S(\mathbf{q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{i\omega t} \text{Re} \left[ \sum_{ij} \alpha_i \alpha_j F_{ij}(\mathbf{q}, t) \right] \quad (10)$$

where  $\alpha_i = (\partial\epsilon/\partial c_i)$  is the designated concentration derivative of the dielectric constant. We proceed by combining Eqs. (5), (6), and (7). The resulting equation is then linearized in the concentration fluctuations. This linearized equation is then spatially Fourier transformed yielding the fundamental set of linearized equations

$$\frac{\partial \delta c_i(\mathbf{q}, t)}{\partial t} = - \sum_l [q^2 D_{il} + \lambda_{il} - i\omega_{il}(\mathbf{q})] \delta c_l(\mathbf{q}, t) \quad (11a)$$

where

$$D_{il} \equiv \sum_k L_{ik} \left( \frac{\partial \mu_k}{\partial c_l} \right) \quad (11b)$$

$$\lambda_{il} = \frac{4\pi}{\epsilon} F^2 \sum_k L_{ik} z_k z_l \quad (11c)$$

$$\omega_{il}(\mathbf{q}) = \left[ \frac{\partial}{\partial c_l} \sum_k L_{ik} z_k F \right] (\mathbf{q} \cdot \mathbf{E}_e) \quad (11d)$$

The time correlation functions  $F_{ij}(\mathbf{q}, t)$  can easily be determined from this set of equations. These turn out to be a linear combination of exponential functions  $\{e^{s_a(q)t}\}$  with different weighting factors where the decay rates  $\{s_a(q)\}$  are the roots of the dispersion equation

$$\det [s\delta_{\alpha\beta} + q^2D_{\alpha\beta} + \lambda_{\alpha\beta} - i\omega_{\alpha\beta}(q)] = 0 \quad (12)$$

### LIGHT SCATTERING FROM BINARY ELECTROLYTE SOLUTIONS

In the two-ion case we are dealing with a system which consists of a single salt dissolved in a neutral solvent. To lowest order in  $q$ , Eq. (12) has two roots,

$$s_{\mp} = \begin{cases} -q^2D_s + i\omega_s(q) & \text{(slow)} \\ -\Gamma_f + q^2D_f + i\omega_f(q) & \text{(fast)} \end{cases} \quad (13a)$$

$$(13b)$$

where  $q^2D_f$  and  $\omega_f(q)$  are negligible compared to  $\Gamma_f$ . The crucial parameters are

$$\Gamma_f \equiv (\lambda_{11} + \lambda_{22}) = \frac{4\pi}{\epsilon}\kappa \quad (13c)$$

$$D_s \equiv D \quad (13d)$$

$$\omega_s(q) \equiv \frac{1}{2}(\mathbf{q} \cdot \mathbf{E}_e)\kappa \left[ \frac{1}{\nu_1 z_1 F} \left( \frac{\partial t_1}{\partial c_s} \right) + \frac{1}{\nu_2 z_2 F} \left( \frac{\partial t_2}{\partial c_s} \right) \right] \quad (13e)$$

$s_-$ , the slow root, describes the relaxation of electrically neutral concentration fluctuations, whereas  $s_+$ , the fast root, describes the relaxation of concentration fluctuations which produce a separation of charge. Thus  $\Gamma_f^{-1}$  may be regarded as the "lifetime" of a fluctuation leading to a separation of charge, or equivalently as the relaxation time of a local fluctuation away from electroneutrality. The concentration fluctuation correlation functions are then linear combinations of the two terms

$$e^{-\Gamma_f |t|} \quad (14a)$$

$$e^{-[q^2D \pm i\omega_s(q)]|t|} \quad (14b)$$

and the spectrum is a superposition of a very broad Lorentzian of width  $\Gamma_f$  centered on the frequency  $\omega = 0$ ,

$$\frac{\Gamma_f}{\omega^2 + \Gamma_f^2} \quad (15a)$$

and two narrow Lorentzians each of width  $q^2D$ , centered at frequencies  $\omega = \pm\omega_s(q)$

$$\frac{q^2 D}{[\omega \pm \omega_s(q)]^2 + [q^2 D]^2} \quad (15b)$$

Thus  $\omega_s(q)$  (given by Eq. (13e) is the Doppler shift. It is proportional to the electric field. The slow decay  $s_-$  is determined by diffusion and by a process dependent on the external field. The diffusion is characterized by a diffusion constant which agrees exactly with the result found in the analysis of classical electrolyte diffusion experiments, Eq. (3a). The term proportional to the electric field may be thought of as an electrophoresis-like term but it actually describes the mobility of concentration boundaries rather than true electrophoresis which *cannot* occur in a simple salt solution (at least in the low- $q$  limit). True electrophoresis requires the presence of a third type of ion. It is easy to see that the imaginary part of the second root does not measure the velocity of any particular ion. It is proportional to the mobility of a concentration fluctuation which may be quite different from the velocity of the ions themselves.

### ESTIMATES OF THE CONCENTRATION BOUNDARY MOBILITY AND OTHER PARAMETERS

In this section we compute the mobility of the concentration boundary on the basis of the Debye-Hückel theory.

According to the Debye-Hückel theory the electrical mobility  $\gamma_i$  of an ion of species  $i$  is

$$\gamma_i = \frac{z_i}{6\pi\eta R_i} \frac{1}{1 + q_0 R_i} \quad (16)$$

The conductance of a solution containing two different ionic species is

$$\kappa = F \sum_{i=1}^2 \gamma_i c_i z_i \quad (17)$$

The transference number of species  $i$  is

$$t_i = \gamma_i c_i z_i / \left( \sum_{i=1}^2 \gamma_i c_i z_i \right) \quad (18)$$

In these formulas,  $\eta$  is the solution viscosity,  $R_i$  is the radius, and  $c_i$  is the molar concentration of ions of species  $i$ .  $q_0$  is the inverse Debye screening length, given by

$$q_0^2 \equiv \frac{4\pi}{\epsilon} \left( \sum_{i=1}^2 z_i^2 \nu_i \right) F^2 c_s \quad (19)$$

where  $\epsilon$  is the dielectric constant of the solution.

Combining Eqs. (13e), (16), (17), and (18) gives for the ratio,  $X_1$ , of

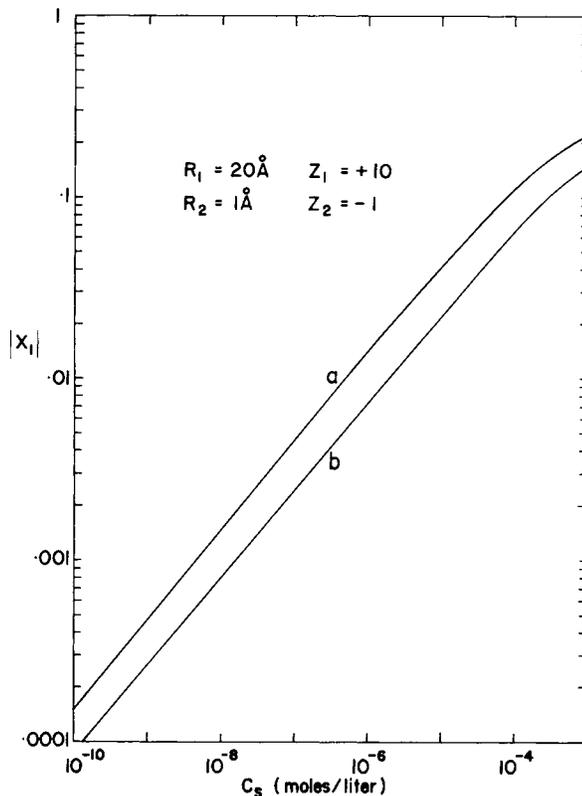


Fig. 1.  $|X_1|$ , the magnitude of the ratio of the Doppler shift in a binary electrolyte solution to that predicted on the basis of the individual ion electric mobility, is plotted versus the salt concentration for the conditions indicated. Curve a corresponds to the ordinary definition (cf. Eq. (19)) of the ionic strength, whereas curve b corresponds to the modified definition (cf. Eq. (22)).

the concentration boundary mobility  $\omega_s(q)/(\mathbf{q} \cdot \mathbf{E}_l)$  to the polyelectrolyte mobility  $\gamma_1$  (the polyelectrolyte is denoted by label 1)

$$X_1 = \frac{1}{2} \left( \frac{q_0 R_1}{1 + q_0 R_1} \right) \left\{ \left( \frac{q_0 R_2}{1 + q_0 R_2} \right) \times \left( \frac{z_1(1 + q_0 R_2)^2 - z_2(1 + q_0 R_1)^2}{z_1(1 + q_0 R_2)(q_0 R_2) - z_2(1 + q_0 R_1)(q_0 R_1)} \right) - 1 \right\} \quad (20)$$

In terms of this ratio, the Doppler shift is

$$\omega_s(q) = (\mathbf{q} \cdot \mathbf{E}_e) X_1 \gamma_1 \quad (21)$$

so that  $X_1$  represents the diminution in the Doppler shift that will be observed. It should be noted that the maximum value of  $X_1$  is 0.5.

In Figure 1,  $X_1$  is plotted versus the salt concentration for the case where  $z_1 = 10$ ,  $z_2 = -1$ , and  $R_1 = 20 \text{ \AA}$ . In curve a Eqs. (19) and (20)

were used, whereas for curve b Eq. (20) is used but the Debye shielding length is computed from

$$q_0^2 = \frac{4\pi}{\epsilon} [ |z_1| \nu_1 + z_2^2 \nu_2 ] F^2 c_s \quad (22)$$

For reasons explained by Tanford, this is to be used for polyelectrolyte solutions instead of Eq. (19). In Figure 2  $X_1$  is likewise plotted for  $z_1 = 500$ ,  $z_2 = -1$ , and  $R_1 = 10^4 \text{ \AA}$ ,  $R_2 = 2 \text{ \AA}$ . The differences between curves a and b are the same as above.

Several things should be noted about these curves. (1) The observed Doppler shift should be considerably smaller than would be given by the usual ionic mobility. (2) For 1-micron spheres, experiments performed at a concentration  $c_s < 10^{-12}$  mole/liter give rise to a theoretical Doppler shift which is approximately one-tenth of that calculated from the Stokes-Einstein electrical mobility.

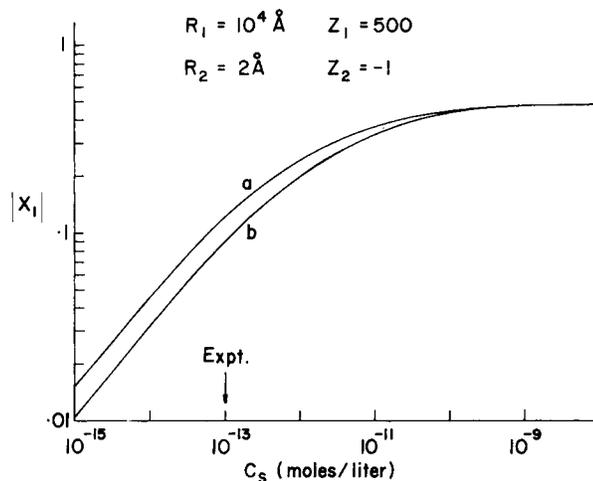


Fig. 2. See description of Figure 1.

Needless to say, these estimates are based on the Debye-Hückel theory and are thereby limited by its limitations. Nevertheless, the lesson is important. One should exercise great caution in interpreting electrophoretic light scattering. Even at very high  $c_s$ , the Doppler shift for a binary electrolyte solution is only one-half that given from the electric mobility.

Most experiments are done in ternary solutions or even more complicated solutions. We expect that for high enough ionic strength, the conventional analysis will be valid. Nevertheless, we have not yet studied the details of this.

### SUMMARY AND CONCLUSIONS

We have applied irreversible thermodynamics to a solution that contains electrolytes and have derived a set of equations that should be applicable to the analysis of electrophoretic light scattering experiments. In order to close this set of equations it was necessary to use Maxwell's equation for the divergence of the electric field. When these equations are applied to a solution which contains only two types of ions to which an external field is applied, it is found that the heterodyne light scattering spectrum is shifted. Unlike the usual case, where more than two types of ion are present and where the shift is proportional to the velocity of one of the types of ions in the solution, the shift in the two ion case is proportional to the rate of change of a transference number with concentration, a result which is considerably different from that of the simple theories. In addition the ionic relaxation rate is found to be proportional to the conductivity of the solution.

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