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Effet thermoélectrique dans les dispersions colloïdale

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> Arghya Majee Université de Bordeaux September, 2012

Thermoelectric effect in colloidal dispersions

Abstract

In this work we study the motion induced in a colloidal dispersion by the thermoelectric or Seebeck effect. As its basic principle, the ions of the electrolyte solution start moving in a temperature gradient. In general, the velocity of one ion differs from another. As a result, one observes a charge separation and a macroscopic electric field. This thermoelectric field, in turn, acts upon the charged colloidal particle present in the solution. Thus thermophoresis of the particle comprises of an electrophoretic motion in the thermoelectric or Seebeck field. As an important result, we derive how the corresponding velocity of a colloidal particle depends upon the colloidal volume fraction or on molecular weight for polymers. In a second part, we study the thermoelectric effect due to a hot colloidal particle where a radial temperature gradient is produced by the particle itself. In this temperature gradient the same Seebeck effect takes place in the electrolyte solution. We find that the hot particle carries a significant amount of charge around it. Whereas the amount of surface charges present at the boundaries of the sample container in the onedimensional case is rather insignificant. Possible applications of this thermocharging phenomenon are also discussed.

Keywords: thermoelectrophoresis, thermoelectric effect, Seebeck effect, thermal diffusion, charged colloids, thermocharge

Effet thermoélectrique dans des dispersions colloïdales

Résumé

Cette thèse porte sur le mouvement de particules colloidales induit par l'effet thermoélectrique (ou effet Seebeck). Dans un électrolyte soumis à un gradient de température, les ions ont tendance à migrer à des vitesse qui différent d'une espèce à l'autre. On observe alors une accumulation de charge aux bords de l'échantillon. Ce déséquilibre induit un champ électrique qui agit sur les colloïdes chargés présents dans la solution. Cette contribution électrophorétique dans le champ de Seebeck s'additionne à la contribution directe de thermodiffusion. Comme résultat principal, nous obtenons la vitesse phorétique en fonction de la fraction volumique des particules et, dans le cas de polyélectrolytes, du poids moléculaire. Dans la seconde partie, nous étudions l'effet thermoélectrique pour une particule chauffée par absorption d'un faisceau laser. Le gradient de température est alors radial et l'effet Seebeck induit une charge nette dans le voisinage de la particule. Enfin, nous discutons les applications possibles de ce phénomène de thermocharge.

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Chapter 1 Introduction

Movement of particles suspended in a fluid is important in biotechnology and microfluidics. Particles can be set in a motion by creating non-equilibrium situations using different means [1]: one of the oldest and well known method is to drive a particle by applying an external electric field (electrophoresis) [2]. Dielectric particles can be moved by applying a non-uniform electric field (dielectrophoresis). Recent studies regarding other possibilities deal with mechanisms like diffusiophoresis and thermophoresis. In case of diffusiophoresis, non-equilibrium condition is created by applying a concentration gradient of molecules dissolved in the fluid [3] whereas thermophoresis is the motion of particles in a temperature gradient. The purpose of this thesis is to investigate the thermophoresis of colloids in an electrolyte solution. Applied temperature gradient acts like an external force on the particles and drives them to the cold or to the hot region. Associated drift velocity is proportional to the thermal gradient present in the system and the proportionality constant is known as the thermophoretic mobility.

Although thermophoresis has been known for more than a century, its underlying physical mechanism was developed much later. Regarding thermophoresis of high polymers, Giddings found that the mobility is independent of molecular weight [4]. Later this was explained by Brochard and de Gennes by showing that thermophoresis is insensitive to hydrodynamic interactions within the polymer chain [5]. For short polymers and binary molecular mixtures, thermal diffusion depends upon several parameters like molecular mass [6] or volume fraction of the components in the mixture. The underlying thermodynamic forces arise mainly from dispersion forces and thermal fluctuations of the small molecules. Mass effects are most relevant for light molecules [7]. This is illustrated by the isotope effects observed in experiments on molecular liquids [8, 9] and by numerical simulations [10, 11, 12].

In the present work we are mainly interested about the thermophoresis of charged colloids and polyelectrolytes, where solute-solvent interaction arises from electric double layer. For charged surfaces, the essential theory was given by Derjaguin who discussed the origin of thermoosmotic flow due to temperature gradient [13, 14]. Later on, Ruckenstein calculated the velocity of the charged particle in an electrolyte solution [15]. Still untill recently, no general description was available regarding why and in which direction the particle will move. Ruckenstein's calculations show that the particle will always move

towards the cold region whereas various experiments clearly show that the particle can move in either direction. This was explained by introducing the thermoelectric or Seebeck effect of the electrolyte solution [16, 17]. Electrophoresis of particle in Seebeck field of the electrolyte solution gives additional contribution to particle velocity which was missing in Ruckenstein's calculation. Recent experimental studies have established the importance of this electrolyte Seebeck effect and made it clear that very often the direction of motion of the particle is determined by the electrophoresis in Seebeck field [16, 18].

In last decade, however, several detailed studies of colloidal thermophoresis have shown surprising dependencies of the particle's motion on salinity, colloidal volume fraction or molecular weight for polymers or on temperature [19, 20]. As an important part of this thesis, we will discuss the volume fraction dependence of colloidal motion and the molecular weight dependence of polymer transport.

One another aspect will be to discuss the case of spatially varying temperature gradient. Heating a single nanoparticle or micron size domain of an electrolyte solution is by now a standard technique to create spatially varying temperature gradient and perform thermophoretic experiments. Heating a half-metal coated particle (Janus particle) provides a temperature gradient along the particle's surface which leads to selfthermophoresis of the particle [21]. We will discuss about the important role played by thermoelectric or Seebeck effect in these cases of spatially varying temperature gradients.

The thesis is organized in the following way: First, we discuss about the theoretical description of thermophoresis available at present and the potholes of the theory (chapter 2). Then in chapter 3 we will discuss about one new collective effect, namely, colletive thermoelectrophoresis which describes the dependencies of the transport velocity on colloidal volume fraction or molecular weight for polymers. Chapter 4 deals with the heating of a colloidal particle in an electrolyte. Finally, in chapter 5, we discuss about the effects of heating of a particular liquid spot in an electrolyte solution. Details of most of the calculations have been presented in several appendices at the end of the thesis.

Chapter 2 Thermally driven motion of colloids

2.1 Introduction

Movement of colloidal particles in a temperature gradient is known as particle *ther-mophoresis*, which is analogous to the thermodiffusion or Ludwig-Soret effect in the binary liquid mixtures [22]. Although this effect was discovered more than a century ago, still now its theoretical foundation is a matter of debate. Thermophoresis is just a special class of motion which stems out due to the particle-solvent interfacial interaction and in general known as *phoretic motion*. The basic difference between phoretic movement with sedimentation or Brownian diffusion lies in the fact that the Brownian diffusion or sedimentation are motions of the particle driven by external force (e.g. gravitational force for sedimentation) whereas in the earlier case there is no such external force present. This can be easily understood if we discuss the case of electrophoresis which is another class of phoretic motion where instead of thermal gradient the non-equilbrium nature is provided by an external electric field.

In a colloidal dispersion, there is a thin layer of counter-ions surrounding the colloid particle which is known as *electric double layer* [1, 2, 23]. Its thickness is of the order of Debye length (λ) and is usually very small compared to the particle radius. Now although the particle and its double layer are separately charged but to the external field they appear together as a neutral body and that's why electric field does not exert any force. What happens is the rearrangement of counter ions inside the double layer and thus an interfacial motion resulting in a motion of the colloidal macroion. Likewise, thermophoresis is also due to the inhomogeneity caused by the thermal gradient in the interfacial layer. So instead of interacting directly, the external field interacts with the particle indirectly through the interfacial layer. Due to this, the phoretic movement of a particle depends largely on the way it interacts with surrounding fluid or more clearly on the surface properties of the particle as well as on various solvent properties, and that's what makes it so interesting for applications in microfluidic devices.

In last few decades, development of experimental techniques like thermogravitational columns [24, 25], thermal field-flow fractionation, modern optical methods has helped a lot to investigate and shed new light on thermodiffusion [26, 27]. Potential application of thermodiffusion is diverse: it includes biological and medicinal applications like drug

determination [28], DNA trapping [29], stability of biomolecules in bloods and serum, adsorption of small molecules to lipid membranes and many more. With its growing interest from experimental point of view, it is therefore essential to investigate theoretically also. Although far from a detailed microscopic description, analytical as well as rich computational methods discovered in recent years have indeed provided valuable inputs. In this chapter, we intend to discuss the theoretical description available currently for thermophoretic motion along with some experimental results which indicate strong possibilities for further investigations.

2.2 Thermophoresis of charged colloids

In presence of a temperature gradient (∇T) , dispersed colloids move, on top of the Brownian motion, with a drift velocity

$$\mathbf{u} = -D_T \boldsymbol{\nabla} T, \tag{2.1}$$

where D_T is called the mobility. It is defined in such a way that $D_T > 0$ corresponds to the motion of solutes toward cold (known as thermophobic solute) whereas the opposite happens for $D_T < 0$ (thermophilic solute). The drift velocity **u** depends on surface properties of the dispersed colloidal particle; its interaction with the solvent and on various solvent parameters (permittivity, viscosity, salinity) [5, 15]. Typical values for D_T are of the order of a few $\mu m^2 K^{-1} s^{-1}$.

As pointed out earlier, thermophoresis is due to the response of the counter-ions present in the diffuse layer surrounding the particle to the applied thermal gradient. Derjaguin first discussed the origin of a thermo-osmotic flow inside the double layer in a temperature gradient [13, 14]. In the absence of any external field, electric double layer contains a unifrom distribution of the counter-ions to maintain the overall charge neutrality in the interfacial region. Due to the presence of excess ions in the interfacial region compared to the bulk, there is an excess pressure within the double layer region. Each ion remains at a local thermodynamic equilibrium following the Poisson-Boltzman relation which depends on the local temperature of that point. But when non-uniform temperature is present, the symmetry of the double layer is broken. Temperature varies along the particle surface and so do the number densities of the ions present. This leads to a variation in the excess pressure within the double layer: pressure is higher at the cold region and vice versa. As a result, fluid flows from the region of higher pressure to lower pressure or from cold side to hot side. To match the fluid velocity beyond the double layer with the hydrodynamic far field, particle moves in the opposite direction compared to the fluid motion (Fig.2.1a) with the mobility

$$D_T = \frac{\varepsilon \zeta^2}{3\eta T},\tag{2.2}$$

where ε and η are the solvent permittivity and viscosity respectively and ζ is the surface potential of the solute particle. Usually the surface potential is negative and takes the value from -10mV to -100mV for common colloids. The expression for mobility given in Eq. (2.2) was first calculated by Ruckenstein [15]. Important things to note about



Figure 2.1: (a) Osmotic flow within the double layer in presence of a thermal gradient. Number of ions present in the cold side is higher than that in the hot side; thus the hydrostatic pressure is high in the cold side and this causes a flow of ions (green arrow) to the hot region. As a result, the particle moves in a direction opposite to the temperature gradient. (b) In the limit $a \gg \lambda$, particle surface can be assumed to be flat. The velocity of the ions within the diffuse layer increase as we go out from the particle surface and at approximately one Debye length distance it reaches its maximum value.

Eq. (2.2) are: (i) mobility is independent of the size of the colloid particle and its concentration in the solution and (ii) D_T is always positive irrespective of the value of the surface potential. A positive value of the mobility means that the particle will always move towards the cold region. However experiments show that both of these have contradictions! We will come to this later. For the moment, we will try to have a different look about the things presented above. When we say that the counter-ions are in local thermodynamic equilibrium at each point within the double layer and employ Poisson-Boltzman distribution function, it is implied that the thickness of the double layer is very small compared to the radius of the dispersed particle. In this limit the particle surface becomes effectively flat for the ions present in the double layer and everything that happens within the diffuse layer becomes insensitive to the size of the particle (Fig.2.1b). Contrary to this, the diffusion coefficient for the Brownian motion of a particle depends upon its size and is given by:

$$D = \frac{k_B T}{6\pi\eta a},\tag{2.3}$$

where a is the radius.

A different picture arises for polymers. Polymers are large molecules (macromolecules) composed of repeating structural units connected through chemical bonds. On an average, each macromolecule has a volume ~ R^3 , where R is called the gyration radius of the molecule and depends upon the number of beads N present in each chain: $R \sim aN^{\nu}$; where a is the radius of each bead. The exponent $\nu = \frac{1}{2}$ for ideal polymers and takes the value $\nu \approx \frac{3}{5}$ for real cases [30].



Figure 2.2: Molecular weight dependence of mobility D_T for polystyrene in different solvents. Reprinted with permission from [32].

While performing Brownian motion each monomer creates a velocity field $v(r) \sim 1/r$ in the surrounding fluid where r is the distance from the center of the monomer. Due to this velocity field, other beads in the polymer also get affected. To calculate the velocity of a given bead we need to sum over the flow due to all other beads in the chain. Evaluation of the response to the Langevin force and corresponding mean-square displacement enables to find the diffusion co-efficient [30]

$$D = \frac{k_B T}{6\pi\eta R_h} \tag{2.4}$$

with the hydrodynamic radius $R_h \approx 0.7R$ [31]. Compared to the diffusion co-efficient of a single-bead of radius a, hydrodynamic interaction thus reduces the value by a factor a/R_h and slows down the particle velocity. The most striking feature of Eq. (2.4) is that: D depends upon the number of beads or monomers present in the polymer chain and thus on the molecular weight M_w .

Contrary to this, in case of motion driven by interfacial or surface forces (eg. thermophoresis), mobility or the velocity of a single polymer chain in weak electrolyte solution is independent of the molecular weight M_w . For example, the data by Giddings and coworkers [4] for polystyrene in different solvents shows clearly that the mobility remains constant within a range of molecular weight from 20000 to 160000; see Figure (2.2). As an explanation for this behavior, we should consider the fact that hydrodynamic interaction between the beads within a chain has no effect on the thermophoretic movement of the polymer chain [5, 34]. If we consider a single chain having N beads at positions \mathbf{r}_n ; at any moment each bead at position \mathbf{r}_n experiences the velocity field $\mathbf{v}(\mathbf{r})$ due to other beads at positions \mathbf{r}_m $(m \neq n)$ where $\mathbf{v}(\mathbf{r}) \sim 1/r^3$. Moreover, according to Eq. (2.1), in presence of non-uniform temperature, each bead of a single chain has a velocity \mathbf{u} . So, we can write the velocity of \mathbf{n}^{th} monomer (\mathbf{U}_n) as:

$$\mathbf{U}_n = \mathbf{u} + \sum_{m \neq n} \mathbf{v}(\mathbf{r}_n - \mathbf{r}_m).$$

Due to very weak hydrodynamic interaction, the motion of a bead hardly gets affected



Figure 2.3: Velocity field in a frame attached to the polymer chains: (a) External force driven motion (e.g. sedimentation or diffusion), hydrodynamic interaction between beads takes place and as a result the chain occupies a volume $\sim \frac{4}{3}\pi R^3$. (b) In case of phoretic motion only surface forces are present; there is no hydrodynamic interaction between the beads and fluid passes through the chain almost without any perturbation. Reprinted with permission from [34]. Copyright (2007) by the American Physical Society.

by the other beads. As a result, with respect to the thermal gradient, the orientation of the beads are completely random and this leads to a zero orientational average of the velocity field: $\langle \mathbf{v}(\mathbf{r}_n - \mathbf{r}_m) \rangle = 0$. Thus each monomer as well as the whole polymer moves with a velocity \mathbf{u} , which is independent of the length or molecular weight of the chain. Consequently, the thermophoretic mobility of high polymers in dilute solutions is also independent of N or M_w . Now for dilute electrolyte solutions, Debye length (λ) can be hundreds of nanometers which is large compared to the size of one bead of a polymer chain ($a \ll \lambda$). In this small particle limit, mobility can be calculated using Debye-Hückel approximation [35] and is given by (truncating at leading order terms in $\frac{a}{\lambda}$)

$$D_T = -\frac{\zeta^2}{3\eta} \frac{d\varepsilon}{dT},\tag{2.5}$$

where $\frac{d\varepsilon}{dT}$ is the derivative of permittivity with respect to temperature. The ratio $\left(\frac{T}{\varepsilon}\right)\frac{d\varepsilon}{dT}$ is very close to unity. For water, at room temperature it takes the value 1.4. In view of

this, polymer mobility given by Eq. (2.5) very much resembles that for particles given by Eq. (2.2). D_T here is due to the dielectrophoretic force. In general, there are three contributions to the mobility: dielectrophoretic contribution, the electrolyte Soret effect and a charge term. However in the limit $a \ll \lambda$; the dielectrophoretic term $(\sim \zeta^2/a^2)$ dominates over the other two terms $(\sim \zeta^2/\lambda^2)$.

2.3 Thermoelectric Effect

As mentioned in the discussion of Eq. (2.2); irrespective of the sign of surface potential ζ , thermophoretic mobility D_T can only have positive values. That means, all the solute particles will move toward the cold region. But this is not true in reality. Various experiments show that D_T can take positive as well as negative values. It can change sign with the varying salt conentration [36], pH value [16] or even with the temperature [37, 38]. For example, we discuss here the data measured by Putnam and Cahill for polystyrene beads of 13nm radius in a CAPS buffered solution [16]. The high pH value (~ 10.5) of this buffered solution indicates its basic nature and corresponds to a hydroxyl ion concentration of $\sim 12 \text{ mM/l}$. When we add excess salt (NaCl or LiCl) to this solution, polystyrene beads become thermophilic $(D_T < 0)$ to thermophobic $(D_T > 0)$; see Figure (2.4). Another experiment by Vigolo *et al.* reports a similar behavior [18]. They have used a mixed electrolyte solution $\operatorname{NaCl}_{1-x}\operatorname{OH}_x$ and have measured the Soret coefficient $(S_T = D_T/D)$ of a negatively charged particle as a function of the parameter x. As they vary x from 0 to 1; the solution changes gradually from NaCl to a basic (NaOH) one and the Soret coefficient changes sign at some value of x depending upon the ionic strength of the solution; see Figure (2.5).

This change of sign of the mobility was first explained by Putnam and Cahill [16]. As suggested by them, this is due to the Seebeck or thermoelectric effect of the electrolyte solution. Although the Seebeck or thermoelectric effect is very well known phenomenon in case of metals, it is comparatively less known for fluids. When we apply a temperature gradient to a uniform electrolyte solution, the ions start moving (due to their temperature dependent solvation energy) and create a current. Depending on their ionic heat of transport or dimensionless Soret coefficient the current for different ions could be different. As a result, the ions move along or opposite to the direction of the temperature gradient. This motion of the ions break the uniformity of the solution and charge separation occurs. After some time, positive and negative charges appear at two different boundaries creating an electric field known as thermoelectric or Seebeck field. This field, in turn, acts on the ions and drives them. This process continues until the diffusion current is cancelled by the thermal and electric field driven current. In this steady-state, a macroscopic electric field is present in the system. Thus to sum up, the Soret effect of the ions of the electrolyte solution results in a salinity gradient and eventually a macroscopic thermoelectric field. The direction and magnitude of this electric field depends upon the Soret coefficient of the ions present in the solution.

Under the application of a generalised force like temperature gradient or electric field or concentration gradient, there is a flow of heat or charges or mass in a complex fluid.



Figure 2.4: Variation of the mobility D_T as a function of the salinity for ploystyrene beads of radius a=13 nm in CAPS buffered and Citric acid buffered NaCl solution (Fig. a) and LiCl solution (Fig. b). pH of the solutions were kept fixed; for Cytric acid buffered solution pH \approx 10.5 and for CAPS buffered solution pH \approx 3.3. Reprinted (adapted) with permission from [16]. Copyright (2005) American Chemical Society.

According to the first principle followed in non-equilibrium thermodynamics, as long as the applied generalised force is weak, the flux-force relation remains linear [22]. For example, Fick's law of mass diffusion, Fourier's law of heat conduction or Ohm's law for electrical conduction, all of them obey this linear relation. But more strikingly, this linear relation also holds true for cross effects like Soret effect where a temperature gradient results in a mass diffusion. Now let us consider a non-uniform electrolyte solution with ions having charge $q_i = z_i e$ and densities n_i (index *i* denotes different species present in the solution). If we apply a temperature gradient ∇T to this system, the ions start moving and a current is established in the system. Under the linearised condition stated above the current for each species of the solution can be written as [17, 32]

$$J_i = -D_i \left(\nabla n_i + 2n_i \alpha_i \frac{\nabla T}{T} - n_i \frac{q_i E}{k_B T} \right), \qquad (2.6)$$



Figure 2.5: Variation of the Soret coefficient of SDS micelles as a function of the electrolyte composition for a complex electrolyte $\operatorname{NaCl}_{1-x}\operatorname{OH}_x$. As we vary x from 0 to 1, the solution becomes NaCl to NaOH one and as reported S_T changes sign at some value of x depending upon the ionic strength of the solution. Reprinted (adapted) with permission from [18]. Copyright (2010) American Chemical Society.

where the first term in the right hand side corresponds to the Fick's law of diffusion with the Einstein coefficient D_i , second term describes the thermal diffusion with the reduced Soret parameters α_i and the last term represents the electrophoresis of the ions in presence of the macroscopic Seebeck field E, which is yet to be determined. The numbers α_i are called the reduced Soret coefficients and describe the drift of the ions in presence of the temperature gradient. The values for the most common ions have been determined by Agar from thermopotential measurements of electrolyte solutions [39]; our notation and Agar's "heat of transport" Q_{\pm}^* are related through $\alpha_{\pm} = Q_{\pm}^*/2k_BT$. Typical values range from $\alpha \approx 0$ for Li⁺ to $\alpha \approx 3$ for OH⁻; those of the most common ions are given in Table 2.1. Following reference [17], for the convenience in future calculations, we define three quantities: salinity (n_0) , the reduced Soret coefficient (α) and a dimensionless coefficient $(\delta \alpha)$ as

$$n_0 = \frac{1}{2} \sum_i n_i,$$

$$\alpha = \sum_i \alpha_i \frac{n_i}{n_0} \quad \text{(weighted average of } \alpha_i\text{)},$$

$$\delta\alpha = \sum_i z_i \alpha_i \frac{n_i}{n_0} \quad \text{(weighted average of } z_i \alpha_i\text{)}.$$

1 -

For a binary electrolyte this simplifies to $\alpha = \alpha_+ + \alpha_-$ and $\delta \alpha = \alpha_+ - \alpha_-$.



Figure 2.6: Seebeck field arising in a binary electrolyte solution in presence of a temperature gradient ∇T . Positive and negative ions appear at the opposite boundaries to form a charge layer which is about a few Debye length thick (not to scale). In the bulk solution charge density is zero and there is a constant electric field E. The above picture describes the situation for a solution having $\delta \alpha > 0$ and the situation depicted in the lower picture happens for a solution having $\delta \alpha < 0$.

Table 2.1: Reduced Soret coefficient α_{\pm} of several salt ions at room temperature. The values of the heat of transport Q_{\pm}^* are taken from Ref. [39]. The parameters α_{\pm} are calculated from $\alpha_{\pm} = Q_{\pm}^*/2k_BT$.

Ion	H^+	Li ⁺	K ⁺	Na ⁺	OH ⁻	Cl-
Q_i^* (kJ/Mol)	13.3	0.53	2.59	3.46	17.2	0.53
α_i	2.7	0.1	0.5	0.7	3.4	0.1

Now we will proceed further to calculate the macroscopic thermoelectric field in a stationary or steady state where currents due to each species becomes individually zero and also the charge density in the bulk solution vanishes due to the huge electrostatic energy. This means, in this situation

$$J_i = 0 \text{ or } \sum_i J_i = 0;$$
 (2.7)

and also

$$\sum_{i} q_i n_i = 0. \tag{2.8}$$

We arrive at this steady state when the diffusion current $(\propto \nabla n)$ is cancelled by the thermal $(\propto \nabla T)$ and electric field driven current $(\propto E)$. The condition of charge neutrality is applied in the bulk of the solution; near the boundaries there is an accumulation of charge. But typically the thickness of this charged layer is very small (of the order of Debye length) compared to the dimension of the system. Applying the conditions given by Eqs. (2.7) and (2.8) to Eq. (2.6) we obtain the steady-state electric field as

$$E = \delta \alpha \frac{k_B \nabla T}{e}, \qquad (2.9)$$

with the reduced Soret parameter $\delta \alpha$ defined above. Depending upon the sign of $\delta \alpha$, thermoelectric field can be in either direction. For example, $\delta \alpha = 0.6 \ (> 0)$ for NaCl whereas it takes the value $-2.7 \ (< 0)$ for NaOH. That's why the Seebeck field is toward the hot region for NaCl solution whereas it's in the opposite direction (towards cold region) for NaOH solution. It is important to understand that the thermoelectric field E is not an externally applied field; it is generated inside the system due to the charge separation caused by the thermal gradient. The potential difference between the two boundaries of the sample container is called the thermopotential and is related to the electric field by $E = -\psi \frac{\nabla T}{T}$ [32]. Thus the thermopotential reads as

$$\psi = -\delta \alpha \frac{k_B T}{e},\tag{2.10}$$

with a constant. Now under the action of this bulk eletric field the ions move due to electrophoresis; velocity of this movement can be written using the usual Helmholtz-Smoluchowski electrophoretic mobility $\varepsilon \zeta / \eta$ as

$$u = -\frac{\varepsilon \zeta \psi}{\eta} \frac{\nabla T}{T},\tag{2.11}$$

where ε is the permittivity, ζ is the surface potential or zeta potential and η is the viscosity. Eq. (2.11) along with Eqs.(2.1) and (2.2) give the final expression for the mobility

$$D_T = \frac{\varepsilon \zeta}{\eta T} \left(\frac{\zeta}{3} + \psi \right). \tag{2.12}$$

Clearly this mobility depends upon two different mechanisms: the first term which is proportional to the square of the zeta potential is similar to the Ruckenstein's term discussed earlier and the second term which is proportional to the surface potential as well as the thermopotential represents the electrophoresis in the macroscopic field E or potential difference ψ . For most of the colloids, ζ is usually negative but irrespective of the sign of the surface potential the first term is always positive whereas the thermopotential for mostly used electrolytes can have both signs and it has the same order of magnitude as the surface potential. Thus the second term in Eq.(2.12) can take both the signs and can invert the sign of the mobility. The condition for this sign inversion can be easily found: for a negatively charged colloid ($\zeta < 0$), the mobility changes its sign if $\psi > \frac{1}{3}\zeta$.

This Seebeck effect in fluids has its quite analogus counterpart in case of solids where the temperature difference between two sides of a metal junction creates a voltage difference across the junction. In case of solids, the thermopower or Seebeck coefficient is defined as $S = -\frac{\Delta \psi}{\Delta T}$; where $\Delta \psi$ is the potential difference between the two ends and ΔT is the temperature difference. Similarly we define the Seebeck coefficient for the electrolyte solution as

$$S = -\frac{\psi}{T} = \delta \alpha \frac{k_B}{e}.$$
(2.13)

Although higher values for Seebeck coefficient are observed in some metal oxides, for common metals its value is much less: a few $\mu V K^{-1}$ whereas the value of Seebeck coefficient for most of the common electrolyte is much larger, of the order of hundreds of $\mu V K^{-1}$ [40]. Values of Seebeck coefficient for some standard electrolytes are listed in Table (2.2).

Table 2.2: Thermopotential and Seebeck coefficient for different electrolytes at room temperature

	$\delta \alpha$	ψ (mV)	S ($\mu V K^{-1}$)
NaCl	0.6	-16	50
NaOH	-2.7	70	-210
HCl	2.6	-68	205
KCl	0.4	-10	30

Seebeck effect of charge carriers in solids is a reversible effect and the reverse effect is known as Peltier effect where heat is either absorbed or generated as current passes through a metal junction. Similarly the reverse effect in case of fluids is known as Dufour effect where a thermal gradient develops when concentration gradient is applied to an originally isothermal fluid mixture.

Now let us go back to the experiments by Putnam and Cahill on variation of the mobility with salinity discussed earlier. Figure (2.7) shows the fit for the data points



Figure 2.7: Thermophoretic mobility as a function of salinity for polystyrene beads of radius 13nm. Data points taken from figures 4(a) and (b) of [16]. There are two sets of data points: in one case the added salt is NaCl (indicated by circles) and for the other LiCl was added (indicated by squares). The pH of the solutions were kept fixed (pH= 10.5) using CAPS buffer. The solid lines indicate the fits using the Eq. (2.12) and assuming a constant charge density $\sigma = -0.12 \text{nm}^{-2}$. Reprinted with permission from [17]. Copyright (2008) by the American Physical Society.

using Eq. (2.12) [17] and the parameter $\delta \alpha$ defined as

$$\delta \alpha = \frac{n_{\text{NaOH}} \delta \alpha_{\text{NaOH}} + n_{\text{salt}} \delta \alpha_{\text{salt}}}{n_{\text{NaOH}} + n_{\text{salt}}}.$$

The points represent the mobility data for polystyrene (PS) beads of 13nm radius in CAPS buffered electrolytes. Two different electrolytes were used: NaCl and LiCl. Now they used NaOH as conjugate base with the CAPS buffer (cyclohexylamino-propanesulfonic acid-NaOH). So at low salinities the solution is NaOH solution. From Table (2.2), we know that for NaOH, the reduced Soret coefficient $\delta \alpha$ is negative ($\delta \alpha = -2.7$). Thus the thermoelectric field will act in a direction opposite to the temperature gradient and drive the negatively charged polystyrene beads to the warm region. As a result, D_T is negative for low salinities. When we increase the added salt concentration, relative strength of NaOH decreases and the salt strength increases gradually diminishing the effect of NaOH. At sufficiently large salinity D_T changes sign and becomes positive. However the thermoelectric effect for NaCl or LiCl is much weaker than that for NaOH ($\delta \alpha_{\text{LiCl}}, \delta \alpha_{\text{NaCl}} \ll \delta \alpha_{\text{NaOH}}$). Thus for higher salt concentrations mobility is effectively determined by the first term or the double layer term in Eq. (2.12).

2.4 Overview of recent experimental findings

So far we have discussed about the dependence of mobility on salinity but have not shed any light on its dependence upon the colloidal concentration. This is because of the fact that most of the thermophoretic experiments are done using dilute solutions where the number of added salt-ions are much larger than the number of colloidal macroions present. In case of such dilute solutions the existing theory predicts the thermophoretic mobility D_T and the diffusion coefficient D to be independent of colloidal volume fraction or molecular weight for polymers. And quite obviously, the same holds true for the Soret coefficient $S_T = D_T/D$. Various experiments in the recent past, however, contradict this general belief and the single-particle or single-chain behavior seems to be inadequate in these cases. In this section, we will mostly discuss about these experimental findings. For convenience, we will discuss the experiments with particles and polymers separately.



Figure 2.8: Variation of the thermophoretic mobility D_T of polyethylene glycol with the chain length N. The datapoints are taken from [6]. Upper solid lines represent the variation of D_T with N for a constant viscosity and the lower curve represent the variation due to change in viscosity resulting from inter-chain interaction. Reprinted with permission from [32].

2.4.1 Experiments on polymers

In case of dilute polymer solutions, the distance between two polymer chains is usually large enough compared to the gyration radius of each chain. Thus there is hardly any overlap between neighbouring chains and one chain remains unaffected by the presence of the other chains. Due to this decoupled state of the chains in a dilute solution, thermophoretic mobility is independent of the molecular weight of the chain. However, for relatively high polymer densities, the interchain interaction becomes relevant and a reduction in the mobility is observed. As an example, Figure (2.8) shows the data reported by Chan *et al* for polyethylene glycol in aqueous solution [6]. In this experiment, when the chain length N is varied at a constant ethyleneoxide concentration of 0.2M/l, a decrease in the mobility for long chains (N > 20) is observed. This decrease is possibly due to the change in viscosity due to increasing chain length [32].

Although this argument can be relevant for solutions which are not dilute or semidilute but certainly does not hold true for dilute cases. However in several experiments a variation of the mobility is observed for dilute solutions. For example, let us consider Duhr and Braun's experiment on DNA [19]. They have measured the thermophoretic mobility for DNA in a 1 mM/l Tris [tris(hydroxymethyl)aminomethane] buffer. Keeping the base pair concentration fixed at 50 μ M/l, when they increased the number of base pairs from 50 to 48 502, a significant decrease in the mobility (by a factor of 5) was observed. The data clearly shows that there is a considerable amount of decrease in the mobility for very short chain length (~ 10²). For such a short chain length, the solution remains sufficiently dilute to fall below the overlap concentration and interaction between nearby chains can not play a role. Thus the variation of D_T due to change in viscosity can be ruled out here.



Figure 2.9: Thermodiffusion coefficient D_T as a function of the DNA chain length. Measurements were done with DNA in a 1 mMl⁻¹ Tris buffer keeping the overall DNA content fixed at 50 μ Ml⁻¹. Data points clearly shows a considerable amount of decrease in the mobility not only at higher lengths but also for relatively smaller chain lengths (~ 10²). Reprinted from [19]. Copyright (2006) National Academy of Sciences, U.S.A.

Similar kind of behavior has been observed by Iacopini *et al* during their experiments on sodium polystyrene sulfonate (NaPSS) [38]. Figure (2.10) shows their data for thermophoretic mobility (D_T) and the Soret coefficient (S_T) of NaPSS in a 100 mMl⁻¹ NaCl solution for varying temperature and molecular weight. Important point to note about their experiment is that, they kept the volume fraction of NaPSS constant (2 gl⁻¹). Now from Figure (2.10a) it can be seen that at any particular temperature D_T decreases with the increasing molecular weight. For example at room temperature T=30°C when they vary molecular weight from $M_w = 15400$ to 74000, the mobility is reduced to a value twothird of its initial value. The same behavior is observed for the span of temperature from $\sim 15^{\circ}$ C to $\sim 35^{\circ}$ C. Figure (2.10b) shows the variation of the Soret coefficient; in this case instead of decreasing S_T increases with increasing molecular weight. These behaviors cannot be explained by the fact of increasing viscosity due to interaction between two chains at higher concentrations. And more interestingly, the Soret coefficient $S_T (= D_T/D)$ does not depend upon the viscosity at all! So a change in viscosity can not change S_T . Thus these experiments certainly indicate towards some discrepancy in the existing theories.



Figure 2.10: (a) Variation of thermophoretic mobility D_T as a function of temperature and molecular weight. At a particular temperature D_T decreases with the increasing molecular weight. Measurements were performed with 2 gl⁻¹ of NaPSS in a 100 mMl⁻¹ NaCl solution by Iacopini *et al.* [38]. (b) Soret coefficient (S_T) as a function of temperature and molecular weight for the same system of NaPSS in NaCl. The circles represent data for molecular weight $M_w = 15\ 200$, triangles for $M_w = 32\ 900$ and the squares for $M_w = 74\ 000$. Data indiates clearly that S_T increases with increasing molecular weight. Reprinted from [38], with permission from Elsevier.

2.4.2 Experiments with colloidal particles

Well, polyelectrolytes are indeed complicated soft matter systems both structurally and from the point of view of physical properties. One can try to think of several effects taking place in these systems. It is therefore reasonable to investigate and discuss comparatively simple systems: to say dispersion of colloidal hard spheres. Being simple, these are one of the best studied soft systems also.



Figure 2.11: (Left) Soret coefficient (S_T) data as a function of volume fraction of silica beads in an aqueous solution of negatively charged dye sulpho-rhodamine B measured by Ghofraniha *et al.* [41]. In the inset, the data shows the variation of diffusion coefficient (D_c) with volume fraction (ϕ) . As the data shows both S_T and D_c varies with ϕ in the range $0 < \phi < 0.1$ and after that both of them becomes constant. (Right) Thermophoretic mobility as a function of volume fraction. It is clear from the data presented that D_T also varies very strongly with ϕ in the range $0 < \phi < 0.1$ and after that attains a constant value. Reprinted (adapted) with permission from [41]. Copyright (2009) American Chemical Society.

As mentioned earlier, in dilute systems all the transport coefficients i.e. thermophoretic mobility D_T , diffusion coefficient D and the Soret coefficient S_T are expected to be independent of colloidal volume fraction. However, several experiments on colloidal particle suspension reveal different behavior where the transport coefficients vary with the colloidal volume fraction. This dependence was explained by considering cooperative diffusion [20]. When the suspensions are not extremely dilute, the interaction of particles take place and affect the particle motion. Interaction between particles can be of different types: potential interaction (e.g. electrostatic repulsion) or hydrodynamic interaction. In case of potential interaction, the dependence of the transport coefficient on various parameters is expressed in terms of virial expansions for various functional forms of the interaction potential. For electrostatic interaction, the diffusion coefficient can be expressed as a function of the colloidal volume fraction by the following relation (upto linear order) [23]:

$$D = D_0 \left(1 + 2B\phi \right)$$

where D_0 is the usual Einstein diffusion coefficient given by Eq. (2.3) for extremely dilute solution, and the factor in the parenthesis is related to the modification for higher concentrations. The coefficient *B* is called the virial coefficient and depends upon the interaction potential. Another kind of interaction, which is called hydrodynamic interaction is related to the fact that migration of a particle generates a velocity field in the surrounding fluid which affects the motion of nearby particles. Due to the short range nature of the hydrodynamic interaction, it is of little significance in the behavior of the transport coefficient. But the effect of electrostatic interaction has been confirmed in various experiments by Piazza, Ning and other workers [20, 18, 42, 43].

So far so good, but the story doesn't end here. Situation becomes complicated while considering one recent experiment by Ghofraniha *et al.* on silica beads in an aqueous solution of negatively charged sulpho-rhodamine B [41]. What they observed in their experiments are striking: all the three transport coefficients D, D_T and S_T seem to vary with the volume fraction of silica beads. If we consider the electrostatic interaction here, then the variation of the diffusion coefficient and the Soret coefficient should cancel each other, ruling out the possibility of change in mobility due to the change in volume fraction. But the right panel of Figure (2.11) clearly shows that D_T also varies very strongly with the increasing volume fraction upto a certain value ($\phi \simeq 0.1$) and above that all the three coefficients become constant.



Figure 2.12: Soret coefficient (S_T) of polystyrene beads with different sizes as a function of the ionic strength of two salts NaCl and CsCl. Data taken from the reference [83]. As shown by these plots, S_T increases initially for lower salinities ($< 2 \times 10^{-3}$) and starts decreasing for relatively higher salinities ($> 2 \times 10^{-3}$). Reprinted from [83], with permission from Elsevier.

Untill now, we have mostly discussed about the experimental studies of variation of the mobility or Soret coefficient with relative colloidal concentration. Let's now discuss about their dependence on the salinity. Eq. (2.12) tells us that thermophoretic mobility D_T depends upon the added salt-ion concentration through the zeta potential. The same is true for S_T (= D_T/D) as the diffusion coefficient D is independent of the salinity. Thus the behavior of D_T or S_T with varying salinity will be determined by the way zeta potential varies with the salinity. In this connection, here we will discuss a very recent experiment by Eslahian and Maskos [83]. In their experiment, they have measured the Soret coefficient for polystyrene beads in NaCl and CsCl solutions, varying the salt concentration from 5×10^{-2} mMl⁻¹ to 10 mMl⁻¹. The obtained data can be seen in Figure (2.12) and it shows that initially the Soret coefficient increases with increasing salinity and above some value of the salinity (~ 1 mMl⁻¹) it starts decreasing. From the corresponding zeta potential values, the decrease in S_T for higher ionic strengths can be explained but this gives no clue about the increase for lower ionic concentrations. This certainly indicates that the mobility does not depend upon the salt-ion concentration only through the surface potential but also in some other ways; there may even be some other interaction mechanism which has been ignored till now.

2.5 Conclusion

In summary, we can say that recent experiments on thrmophoresis indicate surprising dependencies of thermophoretic mobility on various parameters. Several data showing the same behavior make it clear that these experimental findings are not exceptions but there must be some other mechanism which is the root cause of the volume fraction or molecular weight dependence of the thermophoretic mobility. In the remaining part of this thesis we will discuss about a new collective phenomenon (emerging from the thermoelectric response of salt ions as well as the suspended colloid) which can explain these experimental results.

One other aspect will be to discuss the Seebeck effect in different geometries. So far, most of the theories have been developed for one-dimensional geometry where the temperature gradient and consequently, the thermoelectric field are both constant in space. But from experimental point of view, it is very common to generate spatially varying temperature gradients by heating a colloidal particle or a particular liquid spot using laser. Discussing the thermoelectric effect and the nature of the thermoelectric field for these spatially varying thermal gradients will be of particular interest.

Chapter 3

Collective thermoelectrophoresis

3.1 Introduction

Self and cooperative diffusion

Diffusive transport in dispersed systems is usually described by two different diffusion coefficients: the self diffusion coefficient (D_s) or tracer diffusion coefficient and the cooperative diffusion coefficient D_c [23]. They actually correspond to two different measuring techniques for the diffusion coefficient. D_s describes diffusion of one particular particle relative to the surrounding particles whereas D_c describes the motion of a collection of particles in a density gradient. While measuring self diffusion coefficient we tag one particle and track its trajectory for a period of time (Fig. 3.1a). Calculating the mean-square displacement we calculate the self diffusion coefficient for a particular particle (say i^{th}) using

$$D_s^i = \frac{1}{6} \frac{d \langle r_i^2 \rangle}{dt},\tag{3.1}$$

where $\langle r_i^2 \rangle$ is the mean square displacement. Situation is different for cooperative or gradient diffusion. In the presence of a density gradient, the diffusion of all the particles toward low concentration creates a flux of particles. This corresponds to a net current (J_c) which we can write using Fick's law

$$J_c = -D_c \nabla n,$$

where D_c is called the cooperative diffusion coefficient and ∇n is the concentration gradient of the particles. For an infinitely dilute suspension, both D_s and D_c equal the usual Stokes-Einstein diffusion coefficient D_0 . But for semi-dilute or concentrated systems, they depend upon the volume fraction of the particles and differ from D_0 as the interactions between different particles start taking place and modify their individual random walk movement. Mainly two different kinds of interactions exist between such dispersed particles; namely, the hydrodynamic interaction and particle-particle interaction.

Particle-particle interaction can be of different types: it can be electrostatic or excluded volume interaction, which is repulsive in nature. In a colloid-polymer mixture, there exists attractive depletion force also. Due to these interactions, the force or interaction potential



Figure 3.1: (a) Self-diffusion coefficient of a single particle (marked by red colour in the picture) in the homogeneous environment of the surrounding spheres; there is no concentration gradient of the particles are present. (b) Cooperative or gradient diffusion of particles: at $t = t_0$, the number density of particles is more in the central region of the container. As a result the osmotic pressure is also high in this region and to reduce the pressure, particles start diffusing in the outward direction from the central region.

between two dispersed particles changes and results in a modification of the Einstein co-efficient for Brownian motion. Hydrodynamic interactions have different origin. It can be easily understood if we consider the gradient diffusion; see Figure (3.1b). At $t = t_0$, the osmotic pressure is very high in the central region where the number density of the particles is higher than the surroundings. Due to this, particles try to move in the outward direction (to a region where osmotic pressure is low). But the volume of the container being fixed, fluid flows in the opposite direction to occupy the place left by the particles. As a result, the particles have to move against this backflow of fluid. This hindrance offered to the particle motion by the backflow of fluid constitutes the main part of the hydrodynamic interaction. It also includes the velocity field experienced by the neighbouring particles due to the motion of one particle.

Both of these interactions affect the diffusive motion or sedimentation of dispersed particles but usually they appear with different weights and thus D_s and D_c differ from each other. While discussing thermophoresis, we talk about the gradient or cooperative diffusion coefficient mainly as we consider the diffusion of particles in presence of a finite density gradient. By taking into consideration the hydrodynamic and particle-particle interaction, corresponding expression for the cooperative diffusion coefficient reads up to linear order as (note that from now onwards we call the gradient diffusion coefficient D

3.1. INTRODUCTION

instead of D_c)

$$D = D_0 \left[1 + (2B + K_2) n \right], \tag{3.2}$$

where $D_0 = k_B T/6\pi \eta a$ is the diffusion coefficient for a dilute system, n is the number density of dispersed particles, B is the virial coefficient representing the particle-particle interaction and K_2 describes the contribution emerging from the hydrodynamic interaction.

Cooperative diffusion has been studied extensively for sedimentation process of dispersed colloids and diffusion phenomenon. But the scenario is different for the phoretic motion of colloid particles or macromolecules which is mainly driven by interfacial forces. For external force driven motions like sedimentation or Brownian motion, hydrodynamic flow field around a particle varies as 1/r, where r is the distance from the center of the given particle. Whereas, for external force free motion like thermophoresis, it decays more rapidly, with the cube of the inverse distance. Due to this flow pattern, they don't drag the surrounding fluid and correspondingly, there is no backflow. Moreover, the short-range behavior of this flow field implies that the neighboring beads don't get affected by the motion of one particle. Thus the term K_2 in Eq. (3.2) has negligible contribution in case of phoretic transports. Electrostatic pair interaction can't modify the thermophoretic mobility. However it can modify the Soret coefficient $(S_T = D_T/D)$ as it depends upon the diffusion coefficient D. In fact, its importance in the variation of the Soret coefficient has been shown in an experiment by Piazza and Guarino [20], where the change in salinity modifies the diffusion coefficient D and this, in turn, affects the Soret coefficient. Thus themophoretic mobility D_T of a colloidal particle or polyelectrolyte is quite independent of these interaction processes and remain unaffected. As a consequence, their transport velocity is independent of concentration [46]; for the same reason, free-solution electrophoresis of polyelectrolytes does not depend on the molecular weight [47, 48]. Similar results have been obtained for thermal diffusion of high polymers [4, 5, 26, 34].

Recent experiments on thermophoresis in charged colloids, however, address a rather different picture and indicate that the single-particle description fails in several instances: Contrary to expectation, the transport velocity due to a temperature gradient,

$$u = -D_T \nabla T, \tag{3.3}$$

was found to depend on the volume fraction of particle dispersions and on the chain length N of macromolecular solutions: (i) Data on sodium polystyrene sulfonate (NaPSS) [38] and single-stranded DNA [19] at constant polymer content but variable N, reveal that the mobility D_T becomes smaller for larger molecules; e.g., in the range from 50 to 48000 base pairs, that of DNA decreases by a factor of 5. These findings are obtained at low dilution where the molecular mean distance is much larger than the gyration radius. (ii) Regarding particle suspensions, experiments on 70-nanometer silica beads [41] and 26-nm latex spheres [16] in a weak electrolyte, show that at a volume fraction of 2%, D_T is significantly reduced with respect to the zero-dilution value.

In this chapter, we will show that these experimental findings arise from an interaction mechanism that has been overlooked so far, i.e. the collective thermoelectric response of the composite system. By treating the salt ions and the dispersed colloids on an equal footing, we find that both the thermoelectric field and the mobility D_T vary with the colloidal concentration. Depending on the electrolyte strength and the valency of the macroions, collective effects may occur at low dilution, that is, for particle dispersion with negligible pair potential and polymer solutions where neighbor chains don't overlap.

3.2 Collective thermoelectrophoresis

3.2.1 Where does it originate from?

Thermally driven motion of charged colloids is very sensitive to the solvent composition. From previous works (discussed in the last chapter), it emerges that two rather different mechanisms contribute to the velocity [16, 17],

$$u = -\mu_T \nabla T + \mu E. \tag{3.4}$$

The first term arises from the local particle-solvent interactions in a non-uniform temperature. As first pointed out by Ruckenstein [15], the temperature gradient deforms the electric double layer and induces a pressure gradient opposite to ∇T . The resulting thermoosmotic surface flow toward higher T drives the particle to the cold side; the overall picture is similar to electroosmotic effects in an electric field [32]. The coefficient $\mu_T \propto \varepsilon \zeta^2 / \eta T$ depends on the ζ -potential, and the solvent permittivity ε and viscosity η ; different prefactors occur in the limits of small and large particles [15, 29, 32, 35, 49, 50, 51, 52, 53]. This form agrees rather well with the observed salinity dependence [20], yet fails in view of the strong variation with T reported for various systems [38, 19], thus suggesting the existence of an additional, so far poorly understood contribution to μ_T .

The second term in Eq. (3.4) accounts for the Seebeck effect of the charged solution or, in other words, for electrophoresis in the thermoelectric field E with the mobility $\mu = \varepsilon \zeta / \eta$. We have discussed the origin of this thermoelectric field in the previous chapter. In short, due to their temperature dependent solvation forces, soluted ions migrate along or opposite to the thermal gradient. As a consequence, surface charges develop at the cold and warm boundaries of the vessel and give rise to a macroscopic electric field $E = -\psi \nabla T/T$; see Figure (3.2). The thermopotential parameter ψ is related to the Seebeck coefficient $S = -\psi/T$; for electrolytes S attains values of several 100μ V/K, which is by one to two orders of magnitude larger than in common metals [40].

In the present chapter, we will mainly deal with this second term in (3.4). While discussing the origin of the thermoelectric field, we only consider the salt-ions. But apart from these salt-ions, colloidal macroions are also present in the system. So far all the theories have negleted the contribution of these macroions as their concentration is small compared to the salt-ion concentration. Here we will show that this assumption is not justified always. Even if their concentration is very low, they are not negligible. In fact, they take an active part along with the small ions of the salt and the thermoelectric field E is determined by the combined effect of all of them.

3.2.2 Current equations

We consider a dispersion of negatively charged particles or macromolecules of valency -Z and concentration n, in a monovalent electrolyte solution of ionic strength n_0 with a constant temperature gradient ∇T . Under the application of this temperature gradient, the ions of the electrolyte solution as well as the colloidal macroions start moving and create currents. According to the general formulation of non-linear thermodynamcis these currents of solute and mobile ions are linear functions of generalized forces [22]; the latter can be expressed through thermal and concentration gradients. The current of colloidal macroions is given by

$$J = -D\nabla n + nu, \tag{3.5}$$

where the first term on the right-hand side accounts for normal diffusion and the second one for transport with the drift velocity (3.4). Similarly, the mobile ion currents

$$J_{\pm} = -D_{\pm} \left(\nabla n_{\pm} + 2n_{\pm}\alpha_{\pm} \frac{\nabla T}{T} \mp n_{\pm} \frac{eE}{k_B T} \right)$$
(3.6)

comprise normal diffusion with coefficients D_{\pm} , thermal diffusion with the reduced Soret parameters α_{\pm} , and electrophoresis with the Hückel mobility for monovalent ions. In (3.5) and (3.6) we have added an electric field term; it is important to note that E is not an external field but arises from the kinetics of the mobile charges and is proportional to the applied temperature gradient. A similar phenomenon occurs in a non-uniform electrolyte, where the electric field is proportional to the salinity gradient and to the difference of the ionic diffusion coefficients D_{\pm} [1, 54].

The numbers α_{\pm} describe the drift of positive and negative salt ions in a temperature gradient. Typical values for them vary between 0 to 3 and for most of the common ions they are given in Table 2.1. It is important to mention that the quantities J, J_{\pm}, E and all the gradients are normally vectors. Due to 1-dimensional geometry considered here, they have only one component finite, other components being equal to zero. That's why we have treated them as scalar quantities.

3.2.3 The steady state

Eqs. (3.5) and (3.6) provide the currents as functions of the generalized thermodynamic forces, that is, of the concentration and temperature gradients [22]. We are interested in the steady state characterized by

$$J_{\pm} = 0 = J. \tag{3.7}$$

For later use we give a resulting relation for the electric field. Inserting the drift velocity (3.4) and superposing the three Eqs. (3.7) such that the concentration gradients result in the gradient of the charge density, $\nabla \rho = e \nabla (n_+ - n_- - Zn)$, and collecting terms proportional to E and ∇T , one has

$$E = e \frac{2n_{+}\alpha_{+} - 2n_{-}\alpha_{-} - ZnT\mu_{T}/D}{\varepsilon\kappa^{2}} \frac{\nabla T}{T} + \frac{\nabla\rho}{\varepsilon\kappa^{2}},$$
(3.8)

with the shorthand notation

$$\kappa^2 = \frac{e^2(n_+ + n_- + ZnT\mu_T/D)}{\varepsilon k_B T}.$$

In order to determine the four unknowns ∇n_{\pm} , ∇n , E, the three Eqs. (3.7) need to be completed by a fourth condition; it is provided by Gauss law

$$\nabla E = \rho/\varepsilon \tag{3.9}$$

which relates E and the charge density $\rho = e(n_+ - n_- - Zn)$, and thus closes the above set of equations.

3.2.4 Small-gradient approximation

The above Eqs. (3.7) and (3.9) are non-linear in the concentrations and thus cannot be solved as they stand. The salt and colloid concentrations vary very little through the sample; the relative changes $\delta n/n$ and $\delta n_{\pm}/n_{\pm}$ between the hot and cold boundaries are proportional to the reduced temperature difference $\delta T/T$. Since in experiment, the ratio $\delta T/T$ is much smaller than unity, we may safely replace the concentrations n and n_{\pm} in the coefficients of (3.8) with constants \bar{n} and \bar{n}_{\pm} ; the latter are defined as the colloidal and salt concentrations at $\nabla T = 0$.

Formally, this small-gradient approximations corresponds to neglecting terms that are quadratic in the small quantities ∇n_{\pm} , ∇n , E, and ∇T . This approximation has been used, more or less explicitly, in previous works on the thermoelectric effect [39, 55] and in recent applications in colloidal thermophoresis [16, 17, 18]. Moreover, various works on the osmotic flow driven by externally imposed gradients of charged solutes resorts to the same approximation, albeit with the salinity change ∇n_0 instead of the temperature gradient [1, 3, 54].

3.2.5 Bulk thermoelectric field

The above relations (3.7)-(3.9) describe both the bulk properties of a macroscopic sample and boundary effects such as the surface charges that develop at the hot and cold boundaries; see Figure 3.2. The thickness of the surface layer is given by the Debye length and thus in the range between one and hundred nanometers. This is much smaller than the sample size. Thus we discard surface effects and discuss the bulk behavior only; a full evaluation including surface effects is given in Appendix B.

In a macroscopic sample the net charge density vanishes because of the huge electrostatic energy. With

$$\rho_{\text{bulk}} = 0,$$

Gauss' law (3.9) imposes a constant electric field; its explicit expression is readily obtained from (3.8)

$$E = -\psi \frac{\nabla T}{T},\tag{3.10}$$


Figure 3.2: (a) Thermoelectric effect in a colloidal suspension of charged particles in salt solution. In the example presented, the Soret parameters are such that negative and positive ions accumulate at the cold and warm boundaries, respectively. Vertical dashed lines indicate the thickness of the surface layers of about one Debye length λ . This schematic view exaggerates the surface layers, which are much thinner in real systems. (b) Spatial variation of the net charge density ρ , the thermoelectric field E, and the thermopotential U; dashed lines indicate the zero of the ordinate. Note the non-zero surface charges at the cold and hot boundaries. In the present chapter we have discussed the bulk behavior only, where $\rho = 0$ and where E is constant.

with the shorthand notation for the coefficient of $\nabla T/T$

$$\psi = -e\frac{2\bar{n}_+\alpha_+ - 2\bar{n}_-\alpha_- - Z\bar{n}T\mu_T/D}{\varepsilon\bar{\kappa}^2}$$

and $\bar{\kappa}^2 = e^2(\bar{n}_+ + \bar{n}_- + Z\bar{n}T\mu_T/D)/\varepsilon k_B T$. Note that we have used the small-gradient approximation and replaced the colloidal and ion concentrations with their mean values.

Although it is not always mentioned explicitly, the argument of zero bulk charge density has been used in previous works on the Seebeck effect of electrolytes [39, 55] and, more generally, for colloidal transport in non-equilibrium situations involving thermal or chemical gradients [1, 3, 16, 17, 18, 54].

3.2.6 Zero-dilution limit

We briefly discuss the case of a very dilute suspension where the colloidal charges are negligible for the electrostatic properties. Putting $n \to 0$ in the electric field (3.10) we have $\psi_0 = -(\alpha_+ - \alpha_-) k_B T/e$ and

$$E_0 = (\alpha_+ - \alpha_-) \, \frac{k_B \nabla T}{e}.$$

This expression is exactly similar to the thermoelectric field given by Eq. (2.9) in chapter 2. Note that the parameter κ^{-1} reduces to the usual expression of the Debye screening length.

Inserting the thermoelectric field E in the drift velocity (3.4) and comparing with (3.3) defines the thermophoretic mobility

$$D_T^0 = \mu_T + \frac{\varepsilon \zeta \psi_0}{\eta T}.$$
(3.11)

Not surprisingly it is independent of the colloidal concentration. The parameter ψ_0 and the macroscopic thermopotential $U = \psi_0 \delta T/T$ between the hot and cold vessel boundaries, are given by the steady state of the electrolyte solution. With the numbers of Table 2.1, one finds the values $\psi_0 = -15$ mV and +70 mV for NaCl and NaOH solutions, respectively. Thus one expects D_T^0 to change its sign upon replacing one salt by the other. This is confirmed by a very recent study on sodium dodecylsulfate (SDS) micelles, where the electrolyte composition NaCl_{1-x}OH_x was varied at constant ionic strength [18]; increasing the relative hydroxide content x from 0 to 1 resulted in a linear variation of the Soret coefficient S_T and a change of sign at $x \approx \frac{1}{2}$.

3.3 Collective effects on the electric field E

Having all the necessary tools in hand, now we will proceed to derive the main result of this chapter, that is, the dependence of E and D_T on the colloidal concentration and, in the case of polyelectrolytes, on its molecular weight. As two important parameters we define the ratio of the colloidal charge density and the salinity,

3.4. COLLECTIVE EFFECTS ON THE MOBILITY D_T

$$\phi = \frac{Z\bar{n}}{n_0},\tag{3.12}$$

and the ratio of colloidal electrophoretic mobility μ and diffusion coefficient D,

$$\xi = \frac{k_B T}{e} \frac{|\mu|}{D}.\tag{3.13}$$

To avoid any confusion, it is important to note that in chapter 2 we defined ϕ as a volume fraction. But in this chapter it stands for the charge ratio, not a volume fraction. In the following we assume a negative surface potential. For typical colloidal suspensions, the charge ratio is smaller than unity, $\phi \sim 0.1$, whereas the parameter ξ may exceed 10^2 .

Rewriting the coefficient ψ in (3.10) in terms of the dimensionless quantities ϕ and ξ , we have

$$\psi = -\frac{2(1+\phi)\alpha_{+} - 2\alpha_{-} - \phi T\mu_{T}/D}{2+\phi+\phi\xi}\frac{k_{B}T}{e}.$$
(3.14)

Equation (3.14) shows how the thermoelectric field arises from the competition of the Soret motion of the mobile ions and the colloidal solute. In the low-dilution limit $\phi \to 0$ the first term in the numerator reduces to $(\alpha_+ - \alpha_-)$ which corresponds to the response of the electrolyte solution discussed in previous works [16, 17, 18].

The ϕ -dependent term in the numerator becomes relevant where $\phi \sim D/T\mu_T$ and, in particular, may change the sign of ψ and thus of the thermoelectric field. With typical values $T\mu_T \sim 10^{-9}$ m/s² one has $D/T\mu_T = 10^{-3}$ for micron-size particles (and polyelectrolytes of a gyration radius of 1 μ m), and $D/T\mu_T = 10^{-1}$ for 10-nanometer beads. This means that, at typical colloidal densities, the thermoelectric field is essentially determined by the macroions. The denominator in (3.14) results in an overall decrease when augmenting the colloidal concentration.

3.4 Collective effects on the mobility D_T

Now we determine the steady-state thermophoretic mobility. Plugging the value of the electric field E given in (3.10) into the drift velocity (3.4) and comparing with (3.3), we get

$$D_T = \frac{D_T^0}{1 + \frac{\phi}{2 + \phi} \xi}.$$
 (3.15)

where D_T^0 is defined by Eq. (3.11) albeit with a modified parameter

$$\psi_0 = -\frac{(1+\phi)\alpha_+ - \alpha_-}{1+\phi/2} \frac{k_B T}{e}.$$
(3.16)

According to (3.11), the sign of D_T is determined by the competition of the bare mobility μ_T and the Seebeck term proportional to $\zeta \psi_0$. Since $\phi < 1$ in most cases, the numerator of (3.15) is rather similar to the dilute case discussed below (3.11).

A much more striking variation arises from the denominator of (3.15). For typical values of the charge ratio $\phi \sim 0.1$, collective effects set in where $\frac{1}{2}\phi\xi \sim 1$, in other words

where ξ is of the order of 20. For high polymers $(N = 10^3...10^6)$ and colloidal particles in the range from ten nanometers to a micron, the parameter ξ takes values between 10 and 10^3 . This simple estimate suggests collective effects to occur in many systems. A detailed comparison with experiment is given in the following section.

In the limit of zero dilution $\phi \to 0$ one readily recovers the expression (3.11). The opposite case of a saltfree system leads to

$$D_T = \frac{D_T^0}{1+\xi}, \qquad (\phi \to \infty)$$

with ψ_0 determined by the counterions only. In view of the large values of ξ mentioned above, one expects a strong reduction of the mobility in the salt free case.

3.5 Comparison with experiment

We discuss Eq. (3.15) in view of recent experiments on colloidal suspensions. At relevant values of the charge ratio ($\phi \sim 0.1$) the numerator hardly differs from that of the dilute case. Thus in the following we focus on the reduction of D_T due to the denominator.

3.5.1 Polyelectrolytes

We start with experimental findings on polyelectrolytes at constant volume fraction but variable molecular weight. In their study of 2 g/l of NaPSS in a 100 mM/l NaCl solution, Iacopini *et al.* found a significant variation with the chain length [38]: Fig. (3.3) shows the data measured at 30° C for molecules of 74, 160, and 360 repeat units, with an overall decrease of the mobility by 40 percent. The same factor has been found in the temperature range from 15 to 35° C.

The solid line represents collective effects arising from the denominator of Eq. (3.15). It has been calculated with the double-layer term in the small-bead limit, assuming the monomer to be small as compared to the Debye length $(R < \lambda)$ [51, 52, 35],

$$\mu_T = -\frac{d\varepsilon}{dT} \frac{\zeta^2}{3\eta},$$

and with the Hückel-limit electrophoretic mobility $\mu = \frac{2}{3}\varepsilon\zeta/\eta$. Inserting the diffusion coefficient $D = k_B T/6\pi\eta R$ and the Bjerrum length $\ell_B = e^2/4\pi\varepsilon k_B T$ in (3.13), we have

$$\xi = \frac{e|\zeta|}{k_B T} \frac{R}{\ell_B}.\tag{3.17}$$

The theoretical curve of Fig. (3.3) is calculated with the parameters $\zeta = -27$ meV, nN = 10 mM/l, and $\phi = 0.1$. Its variation arises only from the gyration radius $R = \ell N_K^{1-\nu} N^{\nu}$; we have used the usual exponent $\nu = \frac{3}{5}$, the size of a monomer $\ell = 0.4$ nm, and the number of monomers per segment $N_K = 10$. The dashed line indicates the mobility in the short-chain limit. The theoretical expression (3.15) provides a good description of the reduction of D_T with increasing chain length.



Figure 3.3: Variation of D_T with the chain length N of a polyelectrolyte at fixed volume fraction. The data on 2 g/l NaPSS in a 100 mM/l NaCl solution at 30° C are taken from Iacopini *et al.* [38]. The solid line is calculated from Eq. (3.15) with the parameters as given in the main text. The dependence on N arises from the gyration radius R.

As a second example, DNA in 1 mM/l Tris buffer shows a similar behavior; its mobility decreases by a factor of 5 over the range from N = 50 to 48500 base pairs per molecule [19]. The overall DNA content was kept constant, $Nn = 50 \mu$ M/l, with a charge ratio $\phi = 0.05$. Eqs. (3.15) and (3.17) provide a good fit to these data, albeit with a somewhat too small exponent $\nu \approx 0.4$; see Figure (3.4). In view of this discrepancy one should keep in mind the rather complex electrostatic properties of polyelectrolytes.

The reduction observed for both NaPSS and DNA cannot be explained by hydrodynamic effects. Interchain interactions are of little significance because of the low dilution. Indeed, the effective volume fraction of the polymer coils hardly attains a few percent, $nR^3 \sim 10^{-2}$; thus nearby chains don't overlap and leave both the viscosity and the diffusion coefficient unchanged. Regarding hydrodynamic interactions of beads of the same molecule, it is known that they enhance the electrophoretic mobility in (3.4) and (3.11) with increasing chain length. Yet this effect occurs for short polyelectrolytes and saturates for chains longer than the size of the screening cloud [57]; for the examples studied here,



Figure 3.4: Variation of the thermophoretic mobility with length of DNA in 1mM/l Tris buffer solution. Throughout the experiment DNA content was kept constant at 50μ M/l. Data-points taken from [19]. The solid line represents the fit for these data using the expression given by Eq. (3.15).

it would enhance D_T in the range N < 40. We conclude that hydrodynamic effects may be ruled out as an explanation for the reduction shown in Figures (3.3) and (3.4). Finally we discuss electrostatic single-particle effects. The electrophoretic mobility in saltfree solution has been found to decrease slightly at higher concentration, because of the increase of the overall ionic strength and the shorter screening length [58, 59]. In the present case, however, the weight fraction of the polyelectrolyte is constant, and so is the overall charge density. Thus the electrostatic properties of the solution are the same for different chain lengths.

3.5.2 Colloidal particles

Now we discuss the concentration dependent mobility D_T that has been reported for dispersions of solid particles in weak electrolytes. Ghofraniha *et al.* studied silica particles (R = 35 nm) in a 30 μ M/l solution of the negatively charged dye sulpho-rhodamine B [41]. The data shown in Fig. (3.5) reveal a significant decrease with the colloidal volume fraction; at 3% D_T is reduced to less than half of the zero-dilution value. The negative sign of the measured D_T indicates that the thermoelectric contribution $\varepsilon \psi_0 \zeta / \eta T$ to (3.11) overtakes the Ruckenstein term [17]

$$\mu_T = \frac{\varepsilon \zeta^2}{3\eta T}.$$

The negative surface potential ζ implies that the thermopotential parameter of the sulphorhodamine solution is positive, $\psi_0 > 0$.

The curves in Fig. (3.5) are calculated from (3.13) and (3.15) with $\psi_0 = 10$ mV, which is comparable to common salts and weaker than the values of NaOH and tetraethylammonium [16, 18]. The rather small D_T suggests that the particles are weakly charged; we use Z = 30 and $\zeta = -10$ meV. The dashed line gives the mobility D_T^0 in the zero-dilution limit, whereas the solid lines are given by (3.15).

In addition to the explicit concentration dependence in terms of the parameter ϕ , one has to take into account that, even at moderate colloidal volume fraction, the Einstein coefficient D is not constant. Indeed, cooperative diffusion of charged particles arises from the electrostatic pair potential $\Phi(\mathbf{r})$ and, to a lesser extent, from hydrodynamic interactions [23]. To linear order in the concentration, the virial expansion for the Einstein coefficient reads as

$$D = D_0(1 + 2nB), (3.18)$$

with the parameter

$$B = \frac{1}{2} \int dV \left(1 - e^{-\Phi/k_B T} \right).$$

For hard spheres the virial coefficient is given by the particle volume, B = 4V with $V = \frac{4}{3}\pi R^3$. The electrostatic pair potential results in an effective interaction volume $V = \frac{4}{3}\pi (R + \frac{\chi}{2}\lambda)^3$, where λ is the Debye length and χ a numerical factor [20, 56, 18]; for small and highly charged particles in a weak electrolyte, the repulsive forces may enhance the virial coefficient by one or two orders of magnitude. On the other hand, hydrodynamic interactions contribute a negative term $B/V \sim -6.5$ and reduce the Einstein coefficient accordingly [23]. Our discussion of the data of Ref. [41] is restricted to volume fractions up to 3%; at higher concentration the measured D saturates and the linear approximation ceases to be valid. In units of the particle volume V, the measured virial coefficient reads B/V = 20 [41]; the best fit of the mobility data is obtained with B/V = 14. This value is much larger than that of hard spheres and thus indicates the importance of electrostatic repulsion. The concentration of mobile charge carriers $n_0 = 30\mu$ M/l leads to a screening length of about 50 nm. With $\chi \sim 2$ in the above expression for the effective volume, one finds a virial coefficient close to the measured value. As an illustration of the effect of collective diffusion on D_T , we plot Eq. (3.15) for these three values: Though the variation



Figure 3.5: Volume fraction dependence of D_T of a dispersion of 70-nm silica beads in a solution of 30μ M/l sulpho-rhodamine B. The data are from Ghofraniha *et al.* [41]; the fit curves are obtained from (3.15) and (3.18), with different values of the reduced virial coefficient B/V, where $V = \frac{4}{3}\pi R^3$ is the particle volume.

of D_T with B is not neglegible, it is significantly weaker than that of the thermoelectric effect.

As a second experiment we mention data by Putnam and Cahill on latex beads of radius R = 13 nm in an electrolyte solution of 2mM/l ionic strength [16]; varying the volume fractions from 0.7 to 2.2 wt%, these authors observed a reduction of D_T by about 10 percent. With a valency of $Z \sim 50$ one finds that, at the highest particle concentration $n = 4\mu$ M/l, the charge ratio ϕ does not exceed 10 percent.

Finally we address the concentration dependence observed by Guarino and Piazza for the Soret coefficient $S_T = D_T/D$ of SDS micelles [20]. Its decrease with the SDS content, is well described by collective diffusion according to (3.18). In a very recent measurement, Vigolo et al. vary the electrolyte composition NaCl_{1-x}OH_x and thus the thermal diffusion parameter of the anion in (3.16), $\alpha_- = (1 - x)\alpha_{Cl} + x\alpha_{OH}$ [18]. The observed linear dependence of S_T on x confirms the crucial role of the thermopotential. Unfortunately there are no mobility data for micelles; thus at present it is not possible to determine whether their D_T is subject to collective effects similar to those of polyelectrolytes and solid beads.

3.6 Salinity dependence of D_T

If we look at Eq. (3.15), the mobility D_T depends upon the colloidal concentration through the parameter ϕ . Now apart from depending upon the colloidal concentration (\bar{n}) , ϕ depends upon the salinity also (consider Eq. 3.12). So it is equally interesting to see whether Eq. (3.15) can explain the salinity dependence of the mobility or not. Apart from the charge ratio ϕ , there is also one parameter in Eq. (3.15) which depends upon the salinity: that is the zeta potential ζ . It is important to mention here that both D_T^0 and ξ depend upon ζ . So the salinity dependence of the mobility comes from two different contributions: (i) through the zeta potential and (ii) through the charge ratio ϕ .

In a recent experiment, Eslahian and Maskos have measured the Soret coefficient of polystyrene beads of different sizes in a NaCl solution by changing the salt-concentration of NaCl [83]. In Figure (3.6b), we have plotted their data for the Soret coefficient with increasing salt-ion concentration (denoted by black circles). Corresponding zeta potential values were also measured which we have plotted in Figure (3.6a). What their data shows is that at low salinities, the Soret coefficient increases with increasing salt-ion concentration, reaches a maximum value at $n_0 \sim 5 \times 10^{-3}$ M/l and beyond that decreases with increasing salinity. Corresponding zeta potential values can't explain this behavior of S_T completely. As shown in Figure (3.6a), ζ remains almost constant upto $n_0 \sim$ 5×10^{-3} M/l and then decreases sharply. If we consider only the variation due to ζ potential, S_T should remain constant for lower concentrations and then decrease at higher salinities $(n_0 > 5 \times 10^{-3} \text{M/l})$. Therefore, the initial increase of S_T with increasing salinity clearly indicates some other effect. We tried to check whether this can be explained by the collective thermoelectrophoretic effect. In Figure (3.6b), the red line shows the variation of S_T due to only collective effect and it is clear that it fits very well the data for lower salinities. With increasing n_0 , ϕ decreases and this in turn increases the Soret coefficient. In Figure (3.6b), the red line corresponds to the variation of S_T due to only collective effect and the blue squares indicate the variation of S_T due to the change in zeta potential (in the absence of collective effect). If we consider these two effect together, we get the exactly same variation indicated by the measured data [black circles in Figure (3.6b)].

What is striking with this data is that the collective effect starts taking place at the salt concentration $n_0 \sim 5 \times 10^{-3}$ M/l and at this point, the product $\phi \xi \simeq 0.05$ which is much less than 1. This indicates the importance of collective effect at a relatively very low colloidal concentration. One may still think whether electrostatic interaction is at the origin of the observed increase of S_T . Indeed electrostatic interaction gives rise to the Soret coefficient with increasing salt-ion concentration. But for this experiment, with the concentration of polystyrene and salinity used, we found that $2Bn \ll 1$ in Eq. (3.18). This indicates that the effect of electrostatic interaction is much weaker and can't increase the Soret coefficient significantly.



Figure 3.6: (a) Variational of the ζ potential with salinity n_0 . With increasing salt concentration zeta potential remains constant initially and then decreases sharply. (b) Soret coefficient as a function of the salt-ion concentration. Black circles indicate the experimentally measured data, blue squares represent the variation due to the change in zeta potential and the red line correspond to the variation due to collective effect. This line is plotted using Eq. (3.15) for a constant $\zeta = -40$ mV.

3.7 Summary and conclusion

In summary, charged colloids in a non-uniform temperature show collective transport behavior mediated by the Seebeck effect of both colloidal and salt ions. For large particles and macromolecules, cooperative effects set in at rather low concentration, where hydrodynamic interactions are absent and where the charge ratio ϕ is much smaller than unity. The criterion for the onset of collective behavior, $\phi \xi \sim 1$ in (3.15), involves the ratio of the electrophoretic mobility and the Einstein coefficient; by contrast, the criterion for cooperative diffusion, $Bn \sim 1$, depends on the pair potential of the solute particles. The discussed examples suggest that the collective thermoelectric effect is generic for colloids at ordinary concentrations. This issue could be relevant for microfluidic applications of thermophoresis.

If we consider the thermoelectric field given in Eq. (3.14), both its magnitude and sign can be tuned by chosing the appropriate electrolyte and adjusting the charge ratio. With a thermal gradient of less than one Kelvin per micron, E may attain values of 100 V/m. Thus the thermoelectric effect could be used for applying electric fields in microfluidic devices. Local laser heating would permit to realize almost any desired spatiotemporal electric-field pattern.

Chapter 4 Thermocharging colloid particles

4.1 Introduction

Selective transport and controlled pattern formation are of fundamental interest in microfluidics and biotechnology [44]. Particle focussing devices [3, 61, 62] and macromolecular traps [19, 63, 64] have been designed by applying chemical or thermal gradients. In "active colloids" there is no external symmetry breaking field: Thermodynamic forces arise from an embarked chemical reactor [65, 66] or from non-uniform laser heating of Janus particles [21]. In both cases the colloid self-propels in an anisotropic environment that is created by the concentration or temperature variation along its surface. The interplay of self-propulsion and Brownian motion leads to a complex diffusion behavior [65, 66, 21, 67].

Locally modifying material properties by heating a single nanoparticle or molecule in a focussed laser beam is by now a standard technique. The temperature dependent refractive index was used for the photothermal detection of a single non-fluorescent chromophore [68]. Heating an isotropic nanoparticle induces a radial temperature profile in the surrounding fluid and, because of the viscosity change, an enhancement of the Einstein coefficient [69]. The non-uniform laser absorption of half-metal coated particles leads to a temperature variation along its surface; the resulting self-propulsion adds a ballistic velocity component and thus increases the effective mean-square displacement [21].

In this chapter, however we will discuss about a novel actuation mechanism for colloids, which is based on the Seebeck effect of the electrolyte solution: Laser heating of a nonionic particle accumulates in it's vicinity a net charge Q, which is proportional to the excess temperature at the particle surface. The corresponding long-range thermoelectric field provides a tool for controlled interaction with nearby beads or with additional molecular solutes. Moreover, the presence of the charge Q around the particle can be used for selective transport of the colloids. At first, we will discuss briefly the case of a constant temperature gradient which we have mentioned in chapter 2. Then we will discuss how one can create thermocharge around a particle, derive its expression and the electric field associated with this charge. At the end of the chapter, we will discuss a few possible applications of this phenomenon which include aggregation or depletion of a molecular solute in the vicinity of a hot particle, colloidal separation through velocity differentiation etc.

4.2 Seebeck effect in a 1-D system

Here we briefly summarise the basic principle of Seebeck effect in an one dimensional system where the temperature gradient is constant. If the temperature of the hot boundary is T_2 and that of the cold boundary is T_1 , then the resulting temperature gradient present in the system is given by

$$\nabla T = \frac{T_2 - T_1}{L},$$

where L is the length of the system. The response of a salt solution to this constant thermal gradient ∇T is illustrated in the upper panel of Figure (4.1). Because of their temperature dependent solvation energy, positive and negative salt ions migrate along the gradient. In general one of the species moves more rapidly, resulting in a thermopotential between the cold and hot boundaries of the sample [70] and a macroscopic electric field

$$E = S\nabla T$$

which is proportional to the thermal gradient and to the Seebeck coefficient S [39, 71]. The bulk solution is neutral; yet opposite charges accumulate at the boundaries and screen the electric field in a layer of one Debye length. In the last years it has become clear that colloidal motion in a temperature gradient is to a large extent determined by the Seebeck effect of the electrolyte solution [16]: The field E and thus the colloidal velocity depend strongly on the salt composition and are particularly sensitive to the presence of molecular ions containing hydrogen [17, 32, 72]; this thermo-electrophoretic driving has been confirmed for SDS micelles in a NaCl_{1-x}OH_x solution, where a change of sign of the drift velocity has been observed upon varying the parameter x [18].

4.3 Seebeck effect in a 3-D system

Now we consider the Seebeck effect in the vicinity of a heated particle, as shown in the lower panel of Figure (4.1). The qualitative features are readily obtained by wrapping the hot boundary of the one-dimensional case (upper panel) onto a sphere of radius a. Its excess temperature δT results in a radial temperature gradient. Under this temperature gradient, the ions of the salt solution move which gives rise to a charge separation. One kind of charge is present in excess near the hot region i.e. near the hot particle surface and the counter ions go to the cold region (the wall of the container). This charge separation corresponds to a thermoelectric field which is given by $\mathbf{E} = S \nabla T$ at distances well beyond the Debye length. Its complete expression, in particular close to the particle surface, is obtained from the stationary electro-osmotic equations for the ion currents.



Figure 4.1: Upper panel: Seebeck effect in an electrolyte solution that is cooled at the left side and heated at the right. We show the case of a positive Seebeck coefficient S, where cations and anions accumulate at the cold and hot boundaries, respectively. The thermoelectric field E is constant in the bulk and vanishes at the boundaries [72]. The corresponding surface charges are confined in a layer of about one Debye length (dashed lines). Lower panel: Seebeck effect in the vicinity of a hot particle with excess temperature δT . Due to the radial temperature gradient, a net charge Q accumulates within one Debye length from the particle surface. The charge density and the radial electric field are shown in Figure (4.3) below. The counterions are at the vessel boundary.

4.3.1 Mobile ion currents and steady state

In case of a colloid particle dispersed in a monovalent electrolyte solution of ionic strength n_0 , the currents for positive and negative ions are given by

$$\mathbf{J}_{\pm} = -D_{\pm} \left(\boldsymbol{\nabla} n_{\pm} \mp n_{\pm} \frac{e \mathbf{E}}{k_B T} + 2n_{\pm} \alpha_{\pm} \frac{\boldsymbol{\nabla} T}{T} \right), \tag{4.1}$$

which comprise normal diffusion with coefficients D_{\pm} , electrophoresis in the electric field **E** with the Hückel mobility for monovalent ions, and thermal diffusion with reduced Soret parameters α_{\pm} . The latter are reduced values of the ionic entropy of transfer $S_{\pm}^* = 2\alpha_{\pm}k_B$, introduced by Eastman as a measure for the electromotive force of an electrolyte thermocouple [70]. We emphasize that \mathbf{J}_{\pm} , ∇n_{\pm} , ∇T , **E** are vector quantities. Because of the spherical symmetry considered here, only their radial components are finite. In the following these quantities are taken as radial vectors.

The mobile ion currents break the uniformity of the electrolyte solution. In a while, the diffusion current cancels the thermal current and we achieve a steady-state where both the diffusion current and thermal current remain finite but the total current due to each kind of ion becomes zero. Thus in this steady-state we have

$$J_{\pm}=0.$$

We will discuss the behavior of all parameters (like electric field or the charge density) in this steady-state. The relation between electric field E and the charge density ρ given by Gauss' law (div $E = \rho/\varepsilon$) also remain valid in this stationary state.

4.3.2 Equation satisfied by the electric field

In order to obtain an equation for the field E and the charge density $\rho = e (n_+ - n_-)$, we evaluate the quantity

$$\frac{eJ_{+}}{D_{+}} - \frac{eJ_{-}}{D_{-}} = \nabla\rho + 2e\left(n_{+}\alpha_{+} - n_{-}\alpha_{-}\right)\frac{\nabla T}{T} - (n_{+} + n_{-})\frac{e^{2}E}{k_{B}T} = 0.$$
 (4.2)

It turns out convenient to define the thermally induced deviation of the salinity from its mean value n_0 ,

$$\delta n = \frac{n_+ + n_-}{2} - n_0.$$

Then the prefactor of ∇T in Eq. (4.2) reads

$$n_{+}\alpha_{+} - n_{-}\alpha_{-} = n_{0}(\alpha_{+} - \alpha_{-}) + \delta n(\alpha_{+} - \alpha_{-}) + \frac{\rho}{e} \frac{\alpha_{+} + \alpha_{-}}{2}.$$
 (4.3)

Throughout this chapter we assume that ion densities n_{\pm} deviate only weakly from their mean value n_0 , that is

$$\delta n \ll n_0, \qquad \rho/e \ll n_0.$$

Discarding small contributions in (4.3) we have $n_+\alpha_+ - n_-\alpha_- = n_0(\alpha_+ - \alpha_-)$ and similarly $n_+ + n_- = 2n_0$ in the last term of Eq. (4.2). Using these, Eq. (4.2) simplifies to

$$\nabla \rho + 2en_0(\alpha_+ - \alpha_-)\frac{\nabla T}{T} - 2n_0\frac{e^2E}{k_BT} = 0.$$
(4.4)

We keep the gradient of the charge density since small ρ does not imply that $\nabla \rho$ is small too. Indeed, we will see that close to the boundaries, $\nabla \rho$ is by much larger than the neglected terms $\rho \nabla T/T$ and $e \delta n \nabla T/T$, more precisely by the ratio a/ℓ_B of particle radius and Bjerrum length.

Equation (4.4) has two unknowns present in it: electric field E and the charge density ρ . This relation between the charge density and the thermoelectric field E is closed by the second equation provided by Gauss' law

$$\operatorname{div} E = \rho/\varepsilon. \tag{4.5}$$

Eliminating the charge density we obtain the inhomogeneous second-order differential equation for the thermoelectric field

$$\nabla^2 E - \frac{1}{\lambda^2} E + \frac{S}{\lambda^2} \frac{\nabla T}{T} = 0.$$
(4.6)

where $\lambda^2 = \varepsilon k_B T/2e^2 n_0$ is the usual Debye length and $S = (\alpha_+ - \alpha_-)k_B/e$ is the Seebeck coefficient.

4.3.3 Temperature profile

To solve Eq. (4.6), we need to know the temperature gradient, which causes the inhomogenity to this equation. The temperature profile can be found by solving the heat flux equation

$$\nabla^2 T = \frac{T}{\alpha_T} - \frac{q}{\kappa_T}$$

where q is the heating power, κ_T is the thermal conductivity, α_T is called the thermal diffusivity and T denotes the time derivative of the temperature. Now in the steady-state, temperature remains constant and its time derivative becomes zero. This can be understood if we compare the time scale for heat diffusion and the diffusion of mobile ions. Charecteristic time scale for heat diffusion (τ_{heat}) and the time scale for ionic diffusion (τ_{ion}) is given by

$$au_{heat} \sim rac{a^2}{lpha_T}$$
 $au_{ion} \sim rac{a^2}{D_i}$

and

respectively. Here D_i is the diffusion coefficient for different ions. Usually heat diffuses much faster than the ions and α_T is of the order of 10^{-6} m²/s whereas D_i is of the order



Figure 4.2: Temperature profile as a function of the distance from the particle center for $T_0 = 300$ K, $a = 1\mu$ m and $\delta T = 10$ K. (Inset) Temperature gradient as a function of the distance from the center for same values of a and δT .

of 10^{-9} m²/s [88]. Thus $\tau_{heat} \ll \tau_{ion}$ and temperature attains a stationary state more quickly and remains constant when the ionic diffusion takes place. In this state, heat flux equation simplifies to

$$\nabla^2 T = -q/\kappa_T. \tag{4.7}$$

When we heat a particle by using focused laser beam, there is no direct heating present for the region outside the particle and the heating power outside the heated particle is zero. With q = 0, the solution of Eq. (4.7) is given by

$$T = T_0 + \frac{\delta T a}{r},$$

where T_0 is the temperature as $r \to \infty$, δT is the excess temperature at the particle surface, r is the distance from the particle center and a is the radius of the particle. Taking the gradient we get

$$\nabla T = -\frac{\delta T a}{r^2}.\tag{4.8}$$

We have plotted the temperature profile and the temperature gradient as a function of the distance from the particle center in Figure (4.2).

4.3.4 Thermoelectric field

Using the expression for ∇T given by Eq. (4.8), we can write Eq. (4.6) in the following way

$$\nabla^2 E - \frac{1}{\lambda^2} E - \frac{S}{\lambda^2} \frac{\delta T}{T} \frac{a}{r^2} = 0.$$
(4.9)

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It is important to note that $\nabla^2 E$ is the vector Laplacian, that is, the gradient of the divergence not the divergence of a gradient. The complete expression for this operator is quite complicated [87]. Since the radial component E is a function of r only, the Laplacian simplifies to

$$\nabla^2 E = \frac{d^2 E}{dr^2} + \frac{1}{r} \frac{dE}{dr} - \frac{E}{r^2}.$$

The usual electrostatic boundary conditions require that the thermoelectric field vanishes at large distances and at the particle surface, $E \to 0$ for $r \to \infty$ and E = 0 for r = a. (We recall that we consider an uncharged particle.) Then the above differential equation is solved by

$$E = S\nabla T \left(1 - \frac{r+\lambda}{a+\lambda} e^{(a-r)/\lambda} \right), \qquad (4.10)$$

where $S = (\alpha_+ - \alpha_-)k_B/e$ is the Seebeck coefficient and the temperature gradient is given by $\nabla T = -\delta T a/r^2$. One can readily verify that E is solution of (4.9) satisfying the boundary conditions. The above linearization approximation implies that quanities such as the Debye and Bjerrum lengths are constant. At distances well beyond $(a + \lambda)$ the exponential factor vanishes; the remaining long-range contribution $E = S\nabla T$ varies with the inverse square of the distance r.

4.3.5 Thermocharge of a hot colloid

From Gauss' law $\rho = \varepsilon \operatorname{div} E$, one obtains the charge density

$$\rho = -2n_0 e^2 \frac{S}{k_B} \frac{\delta T}{T} \frac{a}{r} \frac{\lambda}{a+\lambda} e^{(a-r)/\lambda}$$

Inserting the Bjerrum length ℓ_B and the definition of the Seebek co-efficient S, we can write it as

$$\rho = -e\delta\alpha \frac{a}{\ell_B} \frac{\delta T}{T} \frac{e^{(a-r)/\lambda}}{4\pi(a+\lambda)\lambda r}.$$
(4.11)

It is easy to verify the validity of the approximations made in (4.4) and that the gradient $\nabla \rho$ is much larger than the neglected terms. In particular one finds that the maximum value of the charge density, which occurs at r = a, is of the order $\rho/e \sim (\delta T/T)\lambda/(a+\lambda)n_0$. The reduced excess temperature $\delta T/T$ is typically of the order of ten percent, and $\lambda/(a+\lambda)$ is significantly smaller than unity. Thus the thermocharging does not significantly alter the salt ion densities, $\rho/e \ll n_0$. This validates the linearization of the differential Eq. (4.4).

It turns out convenient to express ρ through the total thermocharge

$$Q = \int dV \rho = 4\pi \int_{a}^{\infty} dr r^{2} \rho.$$

Integration gives

$$Q = -e(\alpha_+ - \alpha_-)\frac{a}{\ell_B}\frac{\delta T}{T},\tag{4.12}$$



Figure 4.3: Thermoelectric field E and charge density ρ as a function of the distance r from the particle centre for different values of the Debye length λ and fixed particle size $a = 1 \mu \text{m}$ [60]. We have used the parameters $\alpha_{+} - \alpha_{-} = -10$ and $\delta T = 30$ K. The dashed line gives the bulk law $E = S \nabla T$.

Table 4.1: Seebeck coefficient S for NaCl, HCl and NaOH in aqueous solution [39, 73], and for tetrabutylammonium nitrate (TBAN) in water (w) and dodecanol (d) [74]. For comparison, S of most simple metals is of the order of a few $\mu V/K$. The Seebeck coefficient is related to Eastman's ionic entropy of transfer $S_{\pm}^* = 2k_B\alpha_{\pm}$ through $S = (k_B/e)(\alpha_+ - \alpha_-)$ [32]. Experimental values for S_{\pm}^* of various ions are given in Refs. [39, 70, 71, 73, 74].

Salt/solvent	NaCl/w	NaOH/w	HCl/w	TBAN/w	TBAN/d
S (mV/K)	0.05	-0.22	0.21	1.0	7.2
$\alpha_+ - \alpha$	0.6	-2.7	2.6	12	86

which is the net thermocharge carried by an otherwise non-ionic particle. Important point to note is that, Q depends on the radius of the particle in units of the Bjerrum length $\ell_B = 7$ Å, the ratio of excess and absolute temperature, and the reduced Seebeck parameter $\alpha_+ - \alpha_-$. Inserting this expression in (4.11) we have

$$\rho = \frac{Qe^{(a-r)/\lambda}}{4\pi(a+\lambda)\lambda r}.$$
(4.13)

which is concentrated within about one Debye length from the particle surface. Figure (4.3) illustrates the variation of E and ρ with distance for different values of λ ; the former is long-range whereas the latter decays exponentially.

We can also find the thermocharge directly from the electric field and the integral form of Gauss' law. For large r, the second term present in the Eq. (4.10) becomes negligible due to the presence of the exponentially decreasing factor. The first term goes like $1/r^2$ and confirms the presence of a net charge Q near the particle surface. Comparing this with the usual expression for the electric field at a distance r due to a charge Q we can readily obtain the amount of thermocharge as given in Eq. (4.12) above.

In physical terms the charge Q arises from the difference in thermo-osmotic pressure of positive and negative ions, which in turn is related to their entropy of transfer $2\alpha_{\pm}k_B$. For $\alpha_+ > \alpha_-$ the anions show thermal diffusion toward higher temperature, thus accumulating a negative charge at the particle surface. The corresponding cations are located at the vessel boundary. Numerical values for the Seebeck coefficient of several electrolytes are given in Table 4.1. For small ions the numbers α_{\pm} are of the order of unity; higher values occur for molecules containing hydrogen. For a 100 nm-bead in NaOH or HCl solution with $\delta T = 30$ K, one finds that Q corresponds to about 40 elementary charges; much higher values occur for protonated salts in water or alcohol solution.

4.3.6 Thermoelectric response time

As an overall feature, it is important to estimate the thermoelectric response time. As discussed in section (4.3.3) heat diffuses much faster than the ions, heat diffusivity α_T (~ 10⁻⁶ m²/s) being much higher than the diffusivity of ions D_i (~ 10⁻⁹m²/s). Because of the fast equilibration of heat flow and temperature, thermocharging occurs on the time scale of thermal diffusion of salt ions over one Debye length. With the above mentioned parameters, one finds a relaxation time of the order of microseconds. Whereas the thermal

diffusion coefficient for colloidal particles is usually of the order of 10^{-12} m²/Ks.Thus colloids move much slower than the mobile ions and on the scale of colloidal motion, thermocharging is an almost instantaneous process.

4.4 Applications

Now as we have already derived the expressions for thermoelectric field and the net thermocharge, in the next part of this chapter we will discuss how the thermocharge allows to actuate colloidal motility and interactions, and how the thermoelectric field can be used for locally controlling an additional charged molecular solute.

4.4.1 Colloid-colloid interaction

We start with the electric force between two hot particles at a distance R. Assuming $R \gg \lambda$, the force experienced by one particle carrying thermocharge Q in the presence of the electric field E due to other hot particle is

$$F = \frac{Q^2}{4\pi\varepsilon R^2}.\tag{4.14}$$

Due to this repulsive force F, in an electrolyte with finite Seebeck coefficient, heating disperses colloidal aggregates and strongly affects collective effects due to thermophoretic or hydrodynamic interactions [75]. So far we have considered non-ionic colloids. A particle carrying a proper charge Q_p gives rise to an additional electric field $E_p = Q_p e^{-(r-a)/\lambda}/(4\pi\varepsilon\lambda r)$. Depending on the sign of Q and Q_p , the superposition $E + E_p$ shows a complex spatial variation. It is important to understand that unlike E_p , E is not screened.

4.4.2 Thermo-electrophoresis

Thermocharging provides a unique tool for creating a radial electric field in an electrolyte solution. For a micron-size bead with an excess temperature $\delta T = 30$ K, the field E may attain 10⁴ V/m in its immediate vicinity, and a few V/m at a distance of 100 microns. The electrophoretic velocity of a molecular solute with zeta potential ζ ,

$$u = \frac{2}{3} \frac{\varepsilon \zeta}{\eta} E, \tag{4.15}$$

varies between 10 μ m/s and 10 nm/s. Depending on the sign of the zeta potential ζ and of the Seebeck coefficient, molecular ions are attracted or repelled by the thermocharge. As illustrated in Figure (4.4a), this can be used for accumulating or depleting a molecular solute in the vicinity of the particle.

More complex patterns are realized by superposing E with the screened field E_p of a proper charge. In addition to thermo-electrophoresis (4.15), the radial temperature

4.4. APPLICATIONS

profile results in thermal diffusion of the solute molecules, due to both double-layer and dispersion forces [32, 76]. Finally we mention that the thermoelectric field E of Janus particles comprises a strongly anisotropic short-range component.

4.4.3 Selective transport

Sorting molecular or colloidal solutes by size is of interest for various applications. The sedimentation potential being rather ineffective for submicron particles, common methods are based on electrophoresis or on motion driven by thermodynamic forces. Since the free-solution mobilities are in general independent of size and molecular weight, velocity differentiation is achieved only after adding a molecular solute as in gel electrophoresis [48, 77], or by spatial flow or field modulation [78, 79, 80].

However, thermocharging in the presence of an applied electric field E_{ext} , provides an efficient means for separating particles by size. The force density ρE_{ext} exerted by the external field on the charged fluid results in a drift velocity u_{ext} of the particle; from the stationary Stokes equation one finds (Appendix D)

$$u_{\rm ext} = \frac{QE_{\rm ext}}{6\pi\eta(a+\lambda)}.$$
(4.16)

Contrary to the Helmholtz-Smoluchowski mobility, this depends explicitly on the particle radius a. In view of the thermocharge (4.12), the most interesting dependencies arise from the excess temperature δT . Assuming a constant volume absorption coefficient β , one finds that the excess temperature varies with the square of the radius,

$$\delta T = \frac{a^2 \beta I}{3\kappa_T},\tag{4.17}$$

where I is the laser intensity and κ_T the thermal conductivity of the solvent.

According to (4.17) the excess temperture increases with the square of the bead size; thus the drift velocity u_{ext} varies with the particle surface in the Hückel limit $(a > \lambda)$ and with its volume in the case $a < \lambda$, as illustrated in Figure (4.4b). As an estimate of the order of magnitude, heating the beads by $\delta T = 30$ K and applying a field $E_{\text{ext}} \sim 10^4$ V/m results in a velocity of about 10 μ m/s. The above argument holds true for non-spherical solute particles, albeit with different geometrical factors. The excess temperature of metalcoated polystyrene beads is linear in the radius. For polymers the charge Q is proportional to the chain length or number N of monomers, whereas the friction coefficient varies with the gyration radius $R \propto N^{\nu}$, resulting in a velocity $u \propto N^{1-\nu}$. In aqueous solution most colloids carry a proper charge with surface potential ζ_p , resulting in an additional velocity $u_p = (\varepsilon \zeta_p / \eta) E_{\text{ext}}$. Still, the thermocharge leads to a significant dispersion of the total velocity $u_{\text{ext}} + u_p$.

Last of all, one possible application could be the separation of carbon nanotubes by their wrapping structure [79, 81]. The electronic and optical properties of single-wall nanotubes depend crucially on their "chiral vector" (n, m) that describes the orientation of the graphene structure with respect to the tube axis. Depending on the values of these



Figure 4.4: Pattern formation and selective transport due to thermocharging. a) The thermoelectric field of a hot particle induces electrophoretic motion (4.15) of a charged molecular solute. Depending on the sign of the electrolyte Seebeck coefficient S and the molecular zeta potential ζ , the colloidal thermocharge results in depletion or accumulation of the solute. b) In an external electric field E_{ext} heated particles of radius a_1 and a_2 differ in their excess temperature (4.17) and thus acquire a size-dependent velocity (4.16). c) Because of their different optical absorption properties, metallic and semiconducting carbon nanotubes differ in their thermocharge and in their response to an electric field.

indices, one has metallic or semiconducting nanotubes with a characteristic bandstructure and a particular optical spectrum. The excess temperature $\delta T = a\bar{\beta}I/\kappa_T$ of a nanotube depends on the absorption per unit area $\bar{\beta}$ of its graphene sheet, and so does the drift velocity u_{ext} . As illustrated in Figure (4.4c), by chosing an appropriate laser wave length, one could selectively heat nanotubes with a given chiral vector and separate them through thermocharged induced electrophoresis.

Chapter 5 Heating a liquid spot

5.1 Introduction

Modern optical techniques have made it easy to investigate and study thermophoresis in colloidal suspensions. Heating a particular liquid spot by focussed laser beam is a standard technique to create temperature gradient within an electrolyte solution and probe thermophoretic experiments [19, 29, 63, 84, 85, 86]. In general, thermophoresis deplets particles from a heated liquid spot along the temperature gradient. In an experiment, Braun and Libchaber have shown that DNA can be trapped near a heated liquid spot inside a thin chamber by using the simultaneous effects of thermophoresis and convection flows; leading to a huge increase of the local DNA concentration [84]. Jiang *et al.* has reported the trapping of a colloid particle in an electrolyte by modifying the temperature gradient and the added polymer concentration [63]. A DNA trap was realized through a thermal barrier in a microchannel [29].

The underlying thermal forces depend on the applied temperature gradient through various mechanisms that are not always easily separated [32, 76]. The common physical picture relies on local effects such as thermoosmosis around solute particles [15], or Marangoni forces along fluid interfaces [89]. Yet in recent years it has become clear that, for charged systems in an electrolyte solution, the thermoelectric or Seebeck effect provides a nonlocal driving force that presents surprising properties. Here in this chapter, we will discuss about the effect of thermoelectric response of the electrolyte on thermophoresis due to heating a specific liquid spot.

Suppose we have an electrolyte solution in a container and we are heating a small region of this solution by a focused laser beam (Figure 5.1c & 5.1d). Now due to this increase of local temperature, there will be a temperature gradient in the surrounding liquid which is not constant in space. As a consequence of this temperature gradient, the mobile ions of the electrolyte solution will start moving. In general the transport velocity for different ions differ from each other in magnitude and in some cases in direction also. Due to such motion of mobile ions, there is a separation of charge and we hope to observe charges inside and near the heated spot and near the boundary of the vessel. Now in this chapter we will show that this is indeed the case and we get charges inside the heated



Figure 5.1: (a) Usual experimental setup for heating a particular liquid spot confined in a thin channel by laser heating. The height of the chamber remains very small (of the order of a few tens of micrometer) and thus the temperature gradient is essentially observed in a 2-D surface (X-Y plane in the picture; see Figure (b)). (c) the case we consider here: the chamber has finite width and thus the temperature gradient is formed in all direction. Due to the heating of a spherical region, temperature gradient also has a spherical symmetry. (d) 2-D cross section of the geometry described in Figure (c).

spot. Moreover this corresponds to a radial electric field (\mathbf{E}) which is very close to the macroscopic Seebeck field except at the boundary of the heated spot. When we heat a given spot of liquid in a thin chamber, the problem is essentially 2-dimensional; due to very small thickness of the chamber used in the experiments (Figure 5.1a & 5.1b). But, here we will not impose the condition of small thickness of the chamber and consider the problem in a 3-dimensional space.

5.2 Mobile ion currents

We consider a monovalent electrolyte solution of ionic strength n_0 . According to the general formulation of non-linear thermodynamics the currents of mobile ions are linear functions of generalized forces which can be expressed through the thermal and concentration gradients (as discussed in section 2.3). Ultimately the mobile ion currents are

5.3. THE STEADY-STATE

given by

$$\mathbf{J}_{\pm} = -D_{\pm} \left(\boldsymbol{\nabla} n_{\pm} + 2n_{\pm} \alpha_{\pm} \frac{\boldsymbol{\nabla} T}{T_0} \mp n_{\pm} \frac{e\mathbf{E}}{k_B T_0} \right)$$
(5.1)

where the first term corresponds to normal diffusion with Einstein coefficients D_{\pm} , second term accounts for thermal diffusion with the reduced Soret parameters α_{\pm} , and the last term describes the electrophoresis in the electric field **E** with the Hückel mobility for monovalent ions. Important point to be noted in Eq. (5.1) is that the electric field **E** present is not an external electric field but arises due to the charge separation occuring in the electrolyte solution. The reduced Soret parameters α_{\pm} are related to Agar's "heat of transport" Q_{\pm}^* through the relation $\alpha_{\pm} = Q_{\pm}^*/2k_BT$. From definition it is clear that α 's are dimensionless number and their values were measured by Agar. For most of the common ions α varies from 0 to 3 and are listed in Table 2.1.

5.3 The Steady-state

Due to the non-uniform temperature the ions move and form the currents given by Eqs. (5.1). In a while, although being finite independently, the diffusion current ($\propto \nabla n$) equilibriates the thermal current ($\propto \nabla T$) and we observe a *steady state* where current due to each ionic species becomes individually zero and the fundamental relation between charge density and the electric field remains valid. So this steady state can be described by the following set of equations:

$$\mathbf{J}_{\pm} = \mathbf{0},\tag{5.2}$$

and

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon}$$
 (Gauss' law). (5.3)

We will calculate all the parameters (i.e. electric field, potential and charge density) in this steady state using these three conditions given by equations (5.2) and (5.3). There are three unknown quantities in this problem which are ∇n_{\pm} and **E** and we have three equations given by two Eqs. in (5.2) and one in (5.3). Thus these three equations form a complete set of equations and possible to solve for finding out the three variables.

5.4 Equation satisfied by the electric field

In the steady-state ($\mathbf{J}_{\pm} = 0$), condition (5.2) gives us two equations. Subtracting one from the other and using the gradient of charge density $\nabla \rho$ instead of $e\nabla (n_+ - n_-)$ we get

$$\boldsymbol{\nabla}\rho + 2en_0\delta\alpha \frac{\boldsymbol{\nabla}T}{T_0} - 2n_0 \frac{e^2 \mathbf{E}}{k_B T_0} = 0, \qquad (5.4)$$

where n_0 is the salinity and $\delta \alpha$ is the weighted average of α 's. For a binary electrolyte solution $n_0 = n_+ = n_-$ and $\delta \alpha = (\alpha_+ - \alpha_-)$. Rearranging the terms of this equation, we obtain an expression for the electric field **E** as:

$$\mathbf{E} = \lambda^2 \frac{\boldsymbol{\nabla}\rho}{\varepsilon} + S \boldsymbol{\nabla} T,$$

where $\lambda = \left(\frac{\varepsilon k_B T}{2n_0 e^2}\right)^{1/2}$ is the usual Debye length and $S = \delta \alpha \frac{k_B}{e}$ is the Seebeck coefficient. This shows that the electric field has two contributions in it : one is proportional to the gradient of the charge density which gives the homogeneous solution for the electric field and the other one proportional to the temperature gradient causes an inhomogeneity. Instead of the charge density, the homogeneous term can be expressed in terms of the electric field by using Gauss' law. By doing so, we get a resulting equation for the electric field:

$$\boldsymbol{\nabla}^2 \mathbf{E} - \frac{1}{\lambda^2} \mathbf{E} + \frac{S}{\lambda^2} \boldsymbol{\nabla} T = 0$$
(5.5)

Important point to note in this equation is that the Laplacian (∇^2) present is not a scalar Laplacian, it is a vector Laplacian and acts on a vector quantity (the electric field **E**). It is the gradient of a divergence instead of the divergence of a gradient. The complete expression for this operator is quite complicated [87]. But due to the spherical symmetry of the problem, only the radial component for all the vector quantities are finite; other components equal to zero. Thus for the Laplacian also we need only the radial component which is given by

$$\nabla_r^2 = \left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{2}{r^2}\right)$$

In the rest part of this chapter, we will consider all the vectors as radial vectors and denote them by normal indices instead of bold ones. Thus, for this radially symmetric system, Eq. (5.5) takes the form

$$\nabla_r^2 E - \frac{1}{\lambda^2} E + \frac{S}{\lambda^2} \nabla T = 0.$$
(5.6)

To solve Eq. (5.6) explicitly, we need to know the temperature gradient, which causes the inhomogeneity to this equation. The temperature profile can be found by solving the heat flux equation

$$\nabla^2 T = \frac{T}{\alpha_T} - \frac{q}{\kappa_T},$$

where q is the heating power, κ_T is the thermal conductivity, α_T is called the thermal diffusivity and T denotes the time derivative of the temperature. As already discussed in section (4.3.3), in general heat diffuses much faster than the ions; typical diffusivities being of the order of 10^{-6} m²/s for heat diffusion and 10^{-9} m²/s for ionic diffusion [88]. This can be well understood if we compare the time scale for heat diffusion and the diffusion of mobile ions. Charecteristic time scale for heat diffusion (τ_{heat}) and the time scale for ionic diffusion (τ_{ion}) is given by

$$au_{\text{heat}} \sim \frac{a^2}{\alpha_T}$$
 $au_{\text{ion}} \sim \frac{a^2}{D_i}$

and

respectively. Here D_i is the diffusion coefficient for different ions or ionic diffusivity. As $\alpha_T >> D_i$, $\tau_{\text{heat}} << \tau_{\text{ion}}$. On the basis of this time scale separation, we can consider that

the temperature attains a stationary state sufficiently quickly to remain at a constant value when the ionic diffusion takes place. Therefore, in this state, the time derivative of temperature becomes zero and the heat flux equation simplifies to

$$\nabla^2 T = -q/\kappa_T. \tag{5.7}$$

We get different solutions for Eq. (5.6) depending upon the nature of the temperature profile. In the following we consider two types of temperature profile: (i) caused by the square shaped laser heating and (ii) caused by Gaussian laser heating. (One other type of heating profile will be discussed in Appendix F)

5.5 Square heating profile

In this section, we consider a square heating profile given by

$$q(r) = q_0 \Theta \left(r - a \right),$$

where $\Theta(r-a)$ is called a Heaviside step function and defined as

$$\Theta(r-a) = 1 \quad (r < a)$$
$$= 0 \quad (r > a).$$

Thus q(r) is constant $(= q_0)$ inside the heated spot and outside the spot there is no heating (q = 0); see Figure (5.2). With this form for the heating profile and using the boundary conditions that both temperature and its gradient are continuous at the boundary of the heated spot, the solution for Eq. (5.7) reads as

$$T_{\rm in} = T_0 + \frac{3}{2}\delta T - \frac{\delta T}{2}\frac{r^2}{a^2} \qquad (0 < r < a), \qquad (5.8a)$$

$$T_{\text{out}} = T_0 + \delta T \frac{a}{r} \qquad (a < r < \infty), \tag{5.8b}$$

where r is the distance from the centre of the spot, a is the dimension of the region being heated and δT is the increase in the temperature of the heated spot at r = a. The resulting temperature profile is shown in Figure (5.2); it decreases with r^2 inside the spot and outside it falls with 1/r. In case of an experiment, δT usually remains of the order of unity. Thus the increase of the temperature of the spot is very small compared to its ambient temperature (T_0) which usually is the normal room temperature. The constant heating power q_0 is related to the increase in temperature by the relation

$$q_0 = \frac{6\kappa_T \delta T}{a^2}.$$

Taking the gradient of Eqs. (5.8a) and (5.8b), we get

$$\nabla T_{\rm in} = -\delta T \frac{r}{a^2} \qquad (0 < r < a), \qquad (5.9)$$

$$\nabla T_{\text{out}} = -\delta T \frac{a}{r^2} \qquad (a < r < \infty), \tag{5.10}$$

with δT , a and r defined above.



Figure 5.2: (Left) Heating profile: constant heating inside the spot $(r < 1\mu m)$ and outside the spot $(r > 1\mu m)$ there is no heating. (Right) Temperature profile throughout the electrolyte solution. At the centre of the spot (r = 0) the temperature is $T_0 + \frac{3}{2}\delta T$; at the boundary of the spot it equals $T_0 + \delta T$ and then it decreases as $\sim 1/r$ with the increasing r to become $T = T_0$ as $r \to \infty$.

5.5.1 Potential and the thermoelectric field

We can solve Eq. (5.6) to find out E, the resulting electric field has two parts $E = E_{\rm h} + E_{\rm inh}$, where $E_{\rm h}$ is the solution of the homogeneous equation $\nabla^2 E_{\rm h} - \frac{1}{\lambda^2} E_{\rm h} = 0$ and $E_{\rm inh} = S\nabla T$. This is justified as $\nabla^2 T$ is either constant or zero throughout the entire space. Now it would be much more easier to find the homogeneous solution if we start from the equation satisfied by the potential which is related to the eletric field by the relation $E_{\rm h} = -\nabla \phi_{\rm h}$. Potential satisfies the usual Debye-Huckel equation $\nabla^2 \phi_{\rm h} - \frac{1}{\lambda^2} \phi_{\rm h} = 0$, with the Laplacian present is a scalar Laplacian and has the form $\nabla^2 \equiv \left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right)$.

The general solution for ϕ_h looks like:

$$\phi_{\rm h}(r) = A_1 \frac{e^{-r/\lambda}}{r} + A_2 \frac{e^{r/\lambda}}{r} \quad (0 < r < a),$$

and

$$\phi_{\rm h}(r) = A_3 \frac{e^{-r/\lambda}}{r} \quad (a < r < \infty),$$

where we have discarded the exponentially increasing term outside the spot, otherwise it will blow up as $r \to \infty$. The corresponding homogeneous electric fields can be found by

5.5. SQUARE HEATING PROFILE

using the relation $E = -\nabla \phi$ and this gives

$$E_{\rm h} = A_1 \left(\frac{1}{r^2} + \frac{1}{\lambda r} \right) e^{-r/\lambda} - A_2 \left(\frac{1}{r^2} - \frac{1}{\lambda r} \right) e^{r/\lambda} \quad (0 < r < a),$$

and

$$E_{\rm h} = A_3 \left(\frac{1}{r^2} + \frac{1}{\lambda r} \right) e^{-r/\lambda} \quad (a < r < \infty).$$

This, along with $E_{inh} = S\nabla T$ gives the complete expression for the electric field both inside and outside the heated spot:

$$E_{\rm in}(r) = A_1 \left(\frac{1}{r^2} + \frac{1}{\lambda r}\right) e^{-r/\lambda} - A_2 \left(\frac{1}{r^2} - \frac{1}{\lambda r}\right) e^{r/\lambda} - S\delta T \frac{r}{a^2} \quad (0 < r < a),$$

and

$$E_{\text{out}}(r) = A_3 \left(\frac{1}{r^2} + \frac{1}{\lambda r}\right) e^{-r/\lambda} - S\delta T \frac{r}{a^2} \quad (a < r < \infty)$$

The three constants A_1 , A_2 and A_3 can be found out using the three boundary conditions:

$$E_{\rm in}(0) = 0, \tag{5.11}$$

$$E_{\rm in}(a) = E_{\rm out}(a), \qquad (5.12)$$

and due to the continuity in charge density

$$\nabla \cdot E_{\rm in} \mid_{r=a} = \nabla \cdot E_{\rm out} \mid_{r=a} . \tag{5.13}$$

Condition (5.11) gives $A_2 = -A_1$. Using the other two conditions we arrive at the final result:

$$E_{\rm in}(r) = S\nabla T_{\rm in}\left(1 - 3e^{-a/\lambda}\frac{a+\lambda}{r}i_1(r/\lambda)\right) \qquad (r < a), \tag{5.14}$$

and

$$E_{\rm out}(r) = S\nabla T_{\rm out} \left(1 - 3e^{-r/\lambda} \frac{r+\lambda}{a} i_1(a/\lambda) \right) \qquad (r > a), \tag{5.15}$$

where

$$i_1(x) = \cosh(x)/x - \sinh(x)/x^2$$

is a modified spherical Bessel function of the first kind. Expressions for $\nabla T_{\rm in}$ and $\nabla T_{\rm out}$ given by Eqs. (5.9) and (5.10) ensure that the electric field inside the liquid spot goes to zero linearly with r. For large distances, the second term in the expression for $E_{\rm out}$ vanishes exponentially and the field becomes proportional to $1/r^2$.

We have plotted the electric field inside as well as outside the spot for $a = 1\mu m$, $\lambda = 0.1\mu m$, S = 0.05 mV/K and $\delta T = 10 K$ in Figure (5.3). Electric field is zero at the center of the spot and goes to zero as we approach $r \to \infty$. It turns out that the homogeneous part of the electric field is very small compared to the inhomogeneous part originating from the temperature gradient and it hardly modifies the macroscopic



Figure 5.3: Electric field as a function of the reduced distance (r/a) from the spot for $\lambda = 0.1 \mu \text{m}$. The field is continuous at the boundary of the heated region and becomes zero at r = 0 as well as at $r \to \infty$.

Seebeck field. To compare the homogeneous and the inhomogeneous part of the electric field, we have plotted the total electric field E_{tot} (containing both the homogeneous and the inhomogeneous part) and the inhomogeneous electric field only in the same plot for two different values of λ (=100nm and 30nm); see Figure (5.4). It is clear from the plots that except very close to the boundary of the heated spot homogeneous electric field is very small and consequently the electric field remains similar to the macroscopic Seebeck field.

5.5.2 Charge density ρ and total charge Q

As we know the electric field, we can now find the charge density ρ using the relation $\rho = \varepsilon \operatorname{div} E$ where the del operator has the form $\nabla \equiv \left(\frac{d}{dr} + \frac{2}{r}\right)$ and ε is the permittivity. Taking the gradient of Eqs. (5.14) and (5.15), we get



Figure 5.4: Comparison of the total electric field and its inhomogeneous part for $a = 1\mu m$ and two different values of $\lambda = 30 nm$ and 100nm. Plots show that the total electric field and the inhomogeneous part are almost equal everywhere except at the boundary of the spot and that too is very small. So the homogeneous electric field is of very little importance and the total field depends largely on the temperature gradients.

$$\frac{\rho_{\rm in}}{\varepsilon} = \frac{3\varepsilon S\delta T}{a^2} \left[\frac{a+\lambda}{r} \sinh\left(\frac{r}{\lambda}\right) e^{-a/\lambda} - 1 \right],\tag{5.16}$$

and

$$\frac{\rho_{\text{out}}}{\varepsilon} = -\frac{3\varepsilon S\delta T}{\lambda} i_1(a/\lambda) \frac{e^{-r/\lambda}}{r}.$$
(5.17)

We have plotted the charge density as a function of the distance from the center of the spot. It is clear that we observe a finite charge density inside the heated spot ($r < 1\mu$ m) and outside the spot it becomes zero very rapidly. Total charge confined in the spot can be calculated by integrating the charge density:

$$Q = 4\pi \int_{0}^{a} r^{2} \rho_{\rm in} dr + 4\pi \int_{a}^{\infty} r^{2} \rho_{\rm out} dr.$$

Using the expressions for $\rho_{\rm in}$ and $\rho_{\rm out}$ from Eqs. (5.16) and (5.17) respectively, we obtain

$$Q = -\frac{3}{2}e\delta\alpha\frac{a}{\ell_B}\frac{\delta T}{T},$$

where $\ell_B = e^2/4\pi\varepsilon k_B T$ is the Bjerrum length and at room temperature it equals to 7 Å.

5.6 Gaussian heating profile

Now we consider the case of a Gaussian heating profile; see Figure (5.6). For a Gaussian heating profile, the heating power q is given by

$$q = q_0 \exp^{-r^2/a^2}.$$

Using this, the solution of the heat flux Eq. (5.7) gives the temperature profile as

$$T(r) = T_0 + \frac{\delta T a}{r} \operatorname{erf}\left(\frac{r}{a}\right), \qquad (5.18)$$

where r is the distance from the centre of the spot, a is the dimension of the region being heated and erf $\left(\frac{r}{a}\right)$ is known as the Gauss Error functions (for more details on Error function see Appendix A), T_0 is the temperature at distances far away from the heated spot $(r \to \infty)$. The heating profile and the resulting temperature profile is shown in Figure (5.6). Heating is maximum at r = 0 and it equals to q_0 . Maximum heating power is related to the excess temperature δT by the relation

$$q_0 = \frac{4\kappa_T \delta T}{\sqrt{\pi}a^2},$$

where is the κ_T thermal conductivity and a is the radius of the heating spot.


Figure 5.5: Charge density ρ (divided by the permittivity) as a function of the reduced distance (r/a) from the spot for various values of the Debye length. Now usually Debye length is very small in case of an experiment and the plot shows that for small Debye length we get significant amount of charge inside the spot and outside the spot the charge is esentially zero.



Figure 5.6: (a) Plot shows the nature of the Gaussian heating profile (not to scale). (b) Temperature profile throughout the solution for a Gaussian heating $q \sim \exp(-r^2/a^2)$ for $a = 1\mu$ m. The plots show that the temperature is a long-range function whereas the former is a short-range function of distance.

5.6.1 Potential and the electric field

We need to solve Eq. (5.6) in order to get the electric field. However, we can simplify the solution if we start from the equation satisfied by the potential which is related to the eletric field by the relation $E = -\nabla \phi$. Using this and the integral $\int_{\infty}^{r} (\nabla T) dr =$ $T(r) - T(\infty) = T - T_0$, we have a resulting equation for the potential by integrating the previous equation

$$\nabla^2 \phi - \frac{1}{\lambda^2} \phi - \frac{S\delta T}{\lambda^2} \frac{a}{r} \operatorname{erf}\left(\frac{r}{a}\right) = 0.$$
(5.19)

Solution of this equation is given by (for the detailed derivation see Apendix E)

$$\phi(r) = -S\delta T \frac{a}{r} \operatorname{erf}\left(\frac{r}{a}\right) + S\delta T \frac{a}{2r} e^{a^2/4\lambda^2} \sum_{\pm} \mp e^{\pm r/\lambda} \operatorname{erf} c\left(\frac{a}{2\lambda} \pm \frac{r}{a}\right), \quad (5.20)$$

with the complementary error function

$$\operatorname{erf} \operatorname{c}(x) = 1 - \operatorname{erf}(x).$$

Corresponding electric field is readily obtaind by using the relation $E = -\nabla \phi$:

$$E = -S\delta T \frac{a}{r^2} \left[\operatorname{erf}\left(\frac{r}{a}\right) - \frac{1}{2} e^{a^2/4\lambda^2} \sum_{\pm} \left(\frac{r}{\lambda} \mp 1\right) e^{\pm r/\lambda} \operatorname{erf} c\left(\frac{a}{2\lambda} \pm \frac{r}{a}\right) \right].$$
(5.21)

Now the properties of the error function enables us to investigate both the electric field and the potential in two particular limits: large a/λ ratio and small a/λ ratio. Now in case of experiments, the size of the heated spot is usually several microns, whereas

5.6. GAUSSIAN HEATING PROFILE

the Debye length takes values between 1 and 100 nanometers. So from practical point of view, the only interesting limit is where $a >> \lambda$. Then a powers series expansion for $\operatorname{erf}(x)$ provides useful approximation. Below we discuss about this case.

Large a/λ ratio:

For large x, error function $\operatorname{erf}(x)$ can be expanded in the following way (see Appendix A for details):

$$\operatorname{erf}(x) = 1 - \frac{e^{-x^2}}{\sqrt{\pi x}} \left(1 - \frac{1}{2x^2} - \cdots \right) \quad \text{(for large } x)$$

For $a >> \lambda$, we can always expand $\operatorname{erf}\left(\frac{a}{2\lambda} \pm \frac{r}{a}\right)$ using this expression. If we do this we get much simple expressions for both the electric field and the potential (which is valid for any r) as (see Appendix E):

$$\phi(r) = -S\delta T \frac{a}{r} \operatorname{erf}\left(\frac{r}{a}\right), \qquad (5.22)$$

and

$$E(r) = -S\delta T \frac{a}{r^2} \operatorname{erf}\left(\frac{r}{a}\right) + \frac{2S\delta T}{\sqrt{\pi}} \frac{e^{-r^2/a^2}}{r}.$$
(5.23)

Equations (5.22) and (5.23) represent the potential and the electric field respectively at any distance in the large a/λ ratio. To compare we have plotted the actual expressions for potential and the electric field given by Eqs. (5.20) and (5.21) and simplified expressions [Eqs. (5.22) & (5.23)] in the same plot for different values of a/λ ratio (see Figure 5.8 and Figure 5.7). For high a/λ ratio (=100), the two lines coinciding with each other shows the validity of our approximation (Figure 5.8). Whereas in Figure (5.7), for small a/λ ratios (= 0.3, 1, 3, 10), the curves differ in the region of small r showing the importance of the terms we have neglected to arrive at the simplified expressions [Eqs. (5.22) & (5.23)]. Important point to note about Eqs. (5.22) and (5.23) is that both of them are independent of the Debye length λ . That means when the dimension of the the heated region is large compared to the Debye length, the potential or the electric field generated becomes independent of the concentration of the electrolyte solution.

What happens at large distances?

Now the interesting thing is to see how the potential and the electric field behave for large r. For large r (r >> a), erf $\left(\frac{r}{a}\right)$ becomes equal to 1 and the exponential term decreases rapidly. So the potential and the electric field can be written as:

$$\phi(r) = -S\delta T \frac{a}{r},\tag{5.24}$$

and

$$E(r) = -S\delta T \frac{a}{r^2},\tag{5.25}$$

which are exactly similar to the macroscopic Seebeck field and corresponding electric potential. Important point to note is that the erf(r) becomes 1 approximately at r = 2 (see Appendix A). So at nearly r = 2a, Eqs. (5.22) and (5.23) correspond to Eqs. (5.24) and (5.25). This can be seen in Figure (5.9), where we have plotted the potential and the



Figure 5.7: (a) Plot shows the potential as a function of the reduced distance r/a according to Eqs. (5.20) and (5.22) for $\lambda/a = 3, 1, 0.3, 0.1$ and 0. The dashed line indicates the potential for $\lambda/a = 0$. It is clear that as we increase the λ/a value the curves start deviating from the value for $\lambda/a = 0$ which is essentially represented by Eq. (5.22). This shows the importance of the neglected terms in small a/λ ratio. (b) Electric field as a function of the reduced distance according to Eqs. (5.21) and (5.23). Here also the curves for different λ/a ratio differ from the curve corresponding to $\lambda/a = 0$. As we decrease λ/a ratio or equivalently increase a/λ ratio, this difference becomes smaller. All the curves have been drawn using the parameters S = 0.05 mV/K and $\delta T = 10 \text{K}$.



Figure 5.8: (a) Plot shows the potential as a function of the reduced distance (r/a) according to Eqs. (5.20) [red line] and (5.22) [blue dashed line] for $\lambda = 0.01 \mu$ m. The two curves fall exactly on each other and validates the approximation made to arrive at Eq.(5.22) from Eq.(5.20). (b) Electric field as a function of distance according to Eqs. (5.21) [red line] and (5.23) [blue dashed line]. Here also the two curves give exactly same result.



Figure 5.9: (a) Electric potential as a function of the reduced distance r/a according to Eq. (5.22) [solid line] and Eq. (5.24) [dashed line] for $a/\lambda = 100$, S = 0.05 mV/K and $\delta T = 10 \text{K}$. (b) Electric field as a function of the reduced distance according to Eq. (5.23) [solid line] and Eq. (5.25) [dashed line] using the same parameters. From the plot it is clear that for large r, both electric field and potential corresponde to the macroscopic Seebeck field and potential given by Eqs. (5.25) and (5.24). But for small r, the electric field decreases and goes to zero at r = 0.



Figure 5.10: Charge density (ρ) as a function of the reduced distance (r/a) from the center of the spot. This gives an idea about how the charge density varies with the distance but the numbers don't correspond to the actual value of the charge density as it misses an overall multiplicative factor of permittivity (ε). We have used $\delta T = 10$ K and S = 0.05mV/K.

electric field for $a = 1\mu m$ and $\lambda = 0.01\mu m$. Thus $a/\lambda = 100$ here. Other parameters used for this plot are: S = 0.05 mV/K and $\delta T = 10 \text{K}$. The electric field satisfies the boundary conditions also: it becomes zero at r = 0 as well as for $r \to \infty$.

5.6.2 Charge density and the total charge

Taking the divergence of Eq. (5.21), we get the general expression for the charge density as

$$\rho = \frac{S\delta Ta}{2\lambda^2 r^2} e^{a^2/4\lambda^2} \sum_{\pm} \pm e^{\pm r/\lambda} \operatorname{erf} \operatorname{c} \left(\frac{a}{2\lambda} \pm \frac{r}{a}\right)$$

Expanding the error function in the limit $a >> \lambda$, we arrive at the final expression for the charge density as (Appendix E):

$$\rho(r) = -\frac{4\varepsilon S\delta T}{\sqrt{\pi}a^2} e^{-r^2/a^2}.$$
(5.26)

Charge density decays exponentially and becomes zero at a distance very close to the radius of the spot (Figure 5.10). Total charge (Q) accumulated within and very close to the heated region can be calculate by integrating the charge density and this gives

$$Q = -4\pi aS\delta T = -e\delta\alpha \frac{a}{\ell_B} \frac{\delta T}{T},$$
(5.27)

where we have used the definition of Bjerrum length $\ell_B = e^2/4\pi\varepsilon k_B T$ and expressed the Seebeck coefficient in terms of the reduced Soret parameters ($\delta \alpha = \alpha_+ - \alpha_-$). The net charge accumulated is proportional to the ratio of excess and absolute temperature, radius of the heated spot and $\delta \alpha$. It is easy to see that for positive $\delta \alpha$ values, negative charge appears at the heated spot which is expected from the discussions in Chapter 2. The opposite case happens for $\delta \alpha < 0$; positive charges appear at the spot. Corresponding counter-ions go to the sample container and due to the large geometry of the container, the counter-ion density becomes effectively zero.

5.7 Summary and conclusion

In summary, in this chapter we have discussed the role of thermoelectric effect in case of heating a particular liquid spot. We have considered two different types of laser heating profile: one is a square heating profile and the other one is a Gaussian heating profile. In both the cases, we saw the evidence of an accumulation of charges inside the heated spot. This is due to the charge separation taking place due to the motion of the mobile ions in the temperature gradient. Moreover this charge accumulation corresponds to a long range electric field which varies as $1/r^2$ for large distances and equals to the macroscopic Seebeck field. But the most important point is that this charge is proportional to the excess temperature and dimension of the spot and to the reduced Seebeck coefficient of the electrolyte solution. This latter parameter opens up the possibility of changing the type of charge being accumulated in the spot by changing the salt. Correspondingly, the direction of the electric field will also be changed.

Appendix A Error Function

Error functions are defined as the integral of a Gaussian function:

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_{0}^{x} e^{-t^{2}} dt.$$
 (A.1)

The complementary error function, denoted by $\operatorname{erf} c$, is related to the error function in the following way:

$$\operatorname{erf} c(x) = 1 - \operatorname{erf} (x)$$

$$= \frac{2}{\sqrt{\pi}} \int_{x}^{\infty} e^{-t^{2}} dt.$$
(A.2)

From definition it is clear that this is an odd function, $\operatorname{erf}(-x) = -\operatorname{erf}(x)$. We have plotted the error function $\operatorname{erf}(x)$ in Figure (A.1) from r = -4 to 4 and most important property which can be seen from this plot is that the function becomes constant and takes the value of ± 1 for large x in either direction.

In general, error function can be expanded in terms of a Maclaurin series:

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n x^{2n+1}}{n!(2n+1)}$$
$$= \frac{2}{\sqrt{\pi}} \left(x - \frac{x^3}{3} + \frac{x^5}{10} - \frac{x^7}{42} + \cdots \right)$$

For $x \ll 1$, it can be expanded as:

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} e^{-x^2} \left[x + \frac{2x^3}{1 \cdot 3} + \frac{4x^5}{1 \cdot 3 \cdot 5} + \cdots \right]$$
(A.3)



Figure A.1: Error function $\operatorname{erf}(x)$ as a function of x; it shows that for large x, $\operatorname{erf}(x)$ becomes constant and takes the value ± 1 depending upon the sign or x.

In the other limit x >> 1,

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_{0}^{r} e^{-t^{2}} dt$$
$$= \frac{2}{\sqrt{\pi}} \left(\int_{0}^{\infty} e^{-t^{2}} dt - \int_{x}^{\infty} e^{-t^{2}} dt \right)$$
$$= 1 - \frac{2}{\sqrt{\pi}} \int_{x}^{\infty} e^{-t^{2}} dt$$

Using integration by parts, we get

$$\int_{x}^{\infty} e^{-t^{2}} dt = \frac{e^{-x^{2}}}{2x} - \frac{e^{-x^{2}}}{4x^{3}} - \cdots$$

Thus in the limit x >> 1,

erf
$$(x) = 1 - \frac{e^{-x^2}}{\sqrt{\pi x}} \left(1 - \frac{1}{2x^2} - \cdots \right).$$
 (A.4)

The derivative of an error function can be easily derived from it definition:

$$\frac{d}{dx}\operatorname{erf}\left(x\right) = \frac{2}{\sqrt{\pi}}e^{-x^{2}}.$$
(A.5)

Appendix B Thermoelectric field in 1D systems

The thermoelectric field (3.10) in chapter 3 has been derived by using the charge neutrality of the bulk of a macroscopic sample. Here we give a derivation based on the steady state, Gauss' law, and the electrostatic boundary conditions. Resorting to the small-gradient approximation, we replace the coefficients in (3.8) by their mean values and thus have

$$E = -\psi \frac{\nabla T}{T} + \frac{\nabla \rho}{\varepsilon \ \bar{\kappa}^2}.$$

With Gauss's law (3.9), one has a set of differential equations with a constant inhomogeneity $-(\psi/T)\nabla T$. The resulting thermoelectric field $E = E_{\rm inh} + E_{\rm h}$ consists of two contributions. The inhomogeneous term $E_{\rm inh} = -(\psi/T)\nabla T$ occurs for zero charge density and accounts for the macroscopic Seebeck effect. The second one $E_{\rm h}$ is related to surface charges at the cold and hot boundaries of the sample. The equation for the surface layers are closed by Gauss' law and the resulting homogeneous equation $\nabla^2 E_{\rm h} = \bar{\kappa}^2 E_{\rm h}$ is solved by the exponential function,

$$E_{\rm h} = A_+ e^{\bar{\kappa}z} + A_- e^{-\bar{\kappa}z},$$

where z is the coordinate in the direction of the temperature gradient. Its range is $-\frac{1}{2}L \leq z \leq \frac{1}{2}L$ with the sample size L.

The electrostatic boundary conditions require that the electric field vanishes at $z = \pm \frac{1}{2}L$. Putting E = 0 and solving for the coefficients of $E_{\rm h}$, one readily finds $A_{\pm} = -\frac{1}{2}E_{\rm inh}/\cosh(\bar{\kappa}L/2)$ and the thermoelectric field

$$E = -\frac{\psi}{T} \nabla T \left(1 - \frac{\cosh(\bar{\kappa}z)}{\cosh(\bar{\kappa}L/2)} \right).$$

Corresponding charge density can be calculated using the relation

$$ho = arepsilon \left(\operatorname{div} E
ight)$$
 .

Both E and the charge density ρ are illustrated in Figure (B.1) below. The field vanishes at the boundaries and reaches its constant bulk value (3.10) within a few screening lengths $\bar{\kappa}^{-1}$. The parameter $\bar{\kappa}^{-1}$ takes values in the range between 1 and 100 nanometers and



Figure B.1: Thermoelectric field and the corresponding charge density for an one dimensional systam with constant temperature gradient. The dashed lines indicate the zero of the ordinates.

thus is much smaller than the size of sample L. Even in microfluidic devices, $\bar{\kappa}L$ is in general larger than 10^3 .

In real systems a more complex picture may emerge from the surface roughness of the boundaries, the solute size, and surface charges of other origin. Note that such additional effects do not affect the bulk electric field (3.10) and thus are irrelevant for the results discussed in this chapter.

Appendix C

Thermoelectric field due to a hot particle

In order to find out the electric field E, we have to solve Eq. (4.6) which reads as

$$\nabla^2 E - \frac{1}{\lambda^2} E + \frac{S}{\lambda^2} \nabla T = 0.$$
 (C.1)

We will solve this equation in two different methods, which are: (i) using Green's function and (ii) direct solution using vector Laplacian.

C.1 Method 1: Green function

We can solve Eq. (C.1) directly, but the associated Green function will be a bit complicated as $\nabla T \sim \frac{1}{r^2}$. It can be simplified if we start from the equation satisfied by the potential which is related to the eletric field by the relation $E = -\nabla \phi$. Using this and the integral $\int_{\infty}^{r} (\nabla T) dr = T(r) - T(\infty) = T - T_0$, we have a resulting equation for the potential by integrating the previous equation

$$\nabla^2 \phi - \frac{1}{\lambda^2} \phi - \frac{S}{\lambda^2} \left(T - T_0 \right) = 0.$$

Here the Laplacian present is a scalar Laplacian and has the form $\nabla^2 \equiv \left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right)$. The last term present in the left side of this equation is like a source term, which contains the source of inhomogeneity through the temperature present in it. For simplifying further calculations, we will call this as g(r). Inserting the expression for $(T - T_0)$ and using the definition of the Debye length λ , we get $g(r) = -\frac{S}{\lambda^2} \frac{a\delta T}{r}$. Using this, we have

$$\nabla^2 \phi - \frac{1}{\lambda^2} \phi + g(r) = 0$$

The general solution for this equation is

$$\phi = A \frac{e^{-r/\lambda}}{r} + \frac{\lambda}{2r} e^{-r/\lambda} I_1(r) + \frac{\lambda}{2r} e^{r/\lambda} I_2(r)$$

with $I_1(r) = \int_a^r e^{r'/\lambda} r'g(r')dr'$ and $I_2(r) = \int_r^\infty e^{-r'/\lambda} r'g(r')dr'$ and the constant A which is to be determined using the boundary condition: Electric field E = 0 at the particle surface i.e. at r = a. While writing down this solution, we have discarded the term proportional to $e^{r/\lambda}$ to satisfy the boundary condition $E \to 0$ as $r \to \infty$. We obtain these two boundary conditions by using the Gauss' law, as there is no charge inside the particle and the total charge in the system is also zero. But for using the boundary condition of zero field at the particle surface to find out A we have to calulate the electric field first. Remembering that the electric field $E = -\nabla \phi$, we have

$$E = A\left(\frac{1}{r^2} + \frac{1}{\lambda r}\right)e^{-r/\lambda} + \left(\frac{\lambda}{2r^2} + \frac{1}{2r}\right)e^{-r/\lambda}I_1(r) + \left(\frac{\lambda}{2r^2} - \frac{1}{2r}\right)e^{r/\lambda}I_2(r)$$

with $I_1(r)$ and $I_2(r)$ defined as above. Using the boundary condition of zero electric field at the particle surface and remembering that $g(r) = -\frac{S}{\lambda^2} \frac{a\delta T}{r}$ to find out the integrals $I_1(r)$ and $I_2(r)$, we find

$$A = \frac{S\delta Ta}{2} \frac{\lambda - a}{\lambda + a} e^{a/\lambda}.$$

Plugging back this value of A in the expression for electric field and arranging the terms present, we have finally

$$E = S\nabla T \left[1 - \frac{r+\lambda}{a+\lambda} e^{(a-r)/\lambda} \right].$$

C.2 Method 2: Direct solution with vector Laplacian

The solution of Eq. (C.1) can be written as $E = E_{\rm h} + E_{\rm inh}$, where $E_{\rm h}$ is the homogeneous solution and $E_{\rm inh}$ is the inhomogeneous part. More clearly $E_{\rm h}$ is the solution of the equation

$$\nabla^2 E_{\rm h} - \frac{1}{\lambda^2} E_{\rm h} = 0, \qquad (C.2)$$

and

$$E_{\rm inh} = S\nabla T. \tag{C.3}$$

We can write this as there is no source of heating outside the particle or technically $\nabla^2 T = 0$ everywhere outside the particle. This is easy to check. If we just put $E = E_{\rm h} + E_{\rm inh}$ in the left hand side of Eq. (C.1), it gives

$$\nabla^2 \left(E_{\rm h} + E_{\rm inh} \right) - \frac{1}{\lambda^2} \left(E_{\rm h} + E_{\rm inh} \right) + \frac{S}{\lambda^2} \nabla T$$

= $\nabla^2 E_{\rm h} - \frac{1}{\lambda^2} E_{\rm h} + \nabla^2 E_{\rm inh} - \frac{1}{\lambda^2} E_{\rm inh} + \frac{S}{\lambda^2} \nabla T$
= 0,

where we have used Eqs. (C.2) and (C.3) and the fact that $\nabla^2 T = 0$. This simplifies the whole procedure. Now we have to find $E_{\rm h}$ and if we add $E_{\rm inh}$ to this, we get the complete solution. The solution of Eq. (C.2) is given by

$$E_{\rm h} = \frac{A\left(r+\lambda\right)e^{-r/\lambda}}{\lambda r^2},$$

where we have discarded the exponentially increasing term to ensure the boundary condition of zero electric field as $r \to \infty$. Adding $E_{inh} = S\nabla T$ to this E_h we get the total electric field as

$$E = \frac{A(r+\lambda)e^{-r/\lambda}}{\lambda r^2} - S\frac{a\delta T}{r^2}.$$

The constant A can be found by using the boundary condition of zero electric field at the particle surface i.e. E = 0 at r = a. By doing this, we arrive at the final expression for the electric field as

$$E = S\nabla T \left[1 - \frac{r+\lambda}{a+\lambda} e^{(a-r)/\lambda} \right].$$

78 APPENDIX C. THERMOELECTRIC FIELD DUE TO A HOT PARTICLE

Appendix D

Velocity of a thermocharged particle in external field

Here we derive the expression for the thermo-electrophoretic velocity given in equation (4.16) of chapter 4. An applied external field $\mathbf{E}_{\text{ext}} = \mathbf{e}E_{\text{ext}}$ along the unit vector \mathbf{e} , exerts on the charge density ρ the force per unit volume $\rho \mathbf{E}_{\text{ext}}$. Then the Stokes equation for the velocity field \mathbf{v} of the surrounding fluid reads as

$$\eta \nabla^2 \mathbf{v} = \nabla P - \rho \mathbf{E}_{\text{ext}},$$

where η is the viscosity and P the pressure.

The fluid velocity is given by the formal solution of Stokes' equation,

$$\mathbf{v}(\mathbf{r}) = \int dV' \mathbf{G}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{E}_{\text{ext}} \rho(\mathbf{r}'), \qquad (D.1)$$

in terms of the Green function or Oseen tensor [82]

$$\mathbf{G}(\mathbf{r}) = rac{1}{8\pi\eta r} \left(1 + rac{\mathbf{rr}}{r^2}
ight).$$

The particle velocity is given by $\mathbf{v}(\mathbf{r})$ evaluated at its surface, $\mathbf{u} = \mathbf{v}|_{r=a}$, which is a constant independent of the orientation of \mathbf{r} .

The charge density being isotropic, the integral can the performed analytically. Choosing the z-axis along the external field and the particle velocity, the Oseen tensor in the integrand simplifies to the scalar $G(\mathbf{r}-\mathbf{r}') = 1/6\pi\eta|\mathbf{r}-\mathbf{r}'|$. Because of the spherical symmetry of $\rho(\mathbf{r}') = \rho(r')$, only the isotropic contribution of G contributes, $G(\mathbf{r}-\mathbf{r}') \rightarrow 1/6\pi\eta r_>$, where $r_> = \max(r, r')$; since $\mathbf{v}(\mathbf{r})$ is evaluated at the particle surface, one has $r_> = r'$, resulting in

$$u = \frac{1}{6\pi\eta} \int dV' \frac{\rho(r')}{r'} E_{\text{ext}} = \frac{QE_{\text{ext}}}{6\pi\eta(a+\lambda)}.$$
 (D.2)

This is the result given in equation (4.16). It is important to note that we have not accounted for the deformation of the applied field due to the permittivity jump at the water-particle interface.

80APPENDIX D. VELOCITY OF A THERMOCHARGED PARTICLE IN EXTERNAL FIELD

Appendix E

Thermoelectric field of a hot liquid spot

E.1 Potential

Eq. (5.19) gives the differential equation satisfied by the potential as

$$\nabla^2 \phi - \frac{1}{\lambda^2} \phi - \frac{S\delta T}{\lambda^2} \frac{a}{r} \operatorname{erf}\left(\frac{r}{a}\right) = 0,$$

and its general solution is given by

$$\phi(r) = -S\delta T \frac{a}{r} \operatorname{erf}\left(\frac{r}{a}\right) + C_1 \frac{e^{-r/\lambda}}{r} + C_2 \frac{e^{r/\lambda}}{r} - S\delta T \frac{a}{2r} e^{a^2/4\lambda^2} \left[e^{-r/\lambda} \operatorname{erf}\left(\frac{a}{2\lambda} - \frac{r}{a}\right) - e^{r/\lambda} \operatorname{erf}\left(\frac{a}{2\lambda} + \frac{r}{a}\right)\right].$$
(E.1)

For $a >> \lambda$, erf $\left(\frac{a}{2\lambda} + \frac{r}{a}\right) = 1$, so we can write equation (E.1) as

$$\phi(r) = -S\delta T \frac{a}{r} \operatorname{erf}\left(\frac{r}{a}\right) + C_1 \frac{e^{-r/\lambda}}{r} + C_2 \frac{e^{r/\lambda}}{r} - S\delta T \frac{a}{2r} e^{a^2/4\lambda^2} \left[e^{-r/\lambda} \operatorname{erf}\left(\frac{a}{2\lambda} - \frac{r}{a}\right) - e^{r/\lambda} \right].$$

Now the potential must be finite at large distances. So as $r \to \infty$, the exponentially increasing terms must cancel each other and this gives

$$C_2 = -S\delta T \frac{a}{2} e^{a^2/4\lambda^2}.$$

Similarly for small r, the exponentially decreasing terms cancel out each other and this gives

$$C_1 = S\delta T \frac{a}{2} e^{a^2/4\lambda^2}.$$

Putting these values for C_1 and C_2 in equation (E.1), we get the expression given in (5.20)

$$\phi(r) = -S\delta T \frac{a}{r} \operatorname{erf}\left(\frac{r}{a}\right) - S\delta T \frac{a}{2r} e^{a^2/4\lambda^2} \left[e^{-r/\lambda} \left\{ \operatorname{erf}\left(\frac{a}{2\lambda} - \frac{r}{a}\right) - 1 \right\} - e^{r/\lambda} \left\{ \operatorname{erf}\left(\frac{a}{2\lambda} + \frac{r}{a}\right) - 1 \right\} \right].$$
(E.2)

For $a >> \lambda$, we can expand the error functions present in (E.2) using Eq. (A.4) in the following way:

$$\operatorname{erf}\left(\frac{a}{2\lambda} - \frac{r}{a}\right) = 1 - \frac{e^{-\left(\frac{a}{2\lambda} - \frac{r}{a}\right)^{2}}}{\sqrt{\pi}\left(\frac{a}{2\lambda} - \frac{r}{a}\right)}$$
(E.3)

$$\operatorname{erf}\left(\frac{a}{2\lambda} + \frac{r}{a}\right) = 1 - \frac{e^{-\left(\frac{a}{2\lambda} + \frac{r}{a}\right)^2}}{\sqrt{\pi}\left(\frac{a}{2\lambda} + \frac{r}{a}\right)}$$
(E.4)

Putting these, the second term of Eq. (E.2) can be written as

$$-S\delta T \frac{a}{2r} e^{a^2/4\lambda^2} \left[e^{-r/\lambda} \left\{ \operatorname{erf}\left(\frac{a}{2\lambda} - \frac{r}{a}\right) - 1 \right\} - e^{r/\lambda} \left\{ \operatorname{erf}\left(\frac{a}{2\lambda} + \frac{r}{a}\right) - 1 \right\} \right]$$
$$= -S\delta T \frac{a}{2r} \left[-\frac{1}{\left(\frac{a}{2\lambda} - \frac{r}{a}\right)} + \frac{1}{\left(\frac{a}{2\lambda} + \frac{r}{a}\right)} \right] \frac{e^{-r^2/a^2}}{\sqrt{\pi}}$$
$$= 0 \quad \text{(for } a >> \lambda\text{).}$$

Thus Eq. (E.2) reduces to

$$\phi(r) = -S\delta T \frac{a}{r} \operatorname{erf}\left(\frac{r}{a}\right) \qquad (a >> \lambda).$$

E.2 Electric field

The general expression for the electric field given in Eq. (5.21) is:

$$E(r) = -S\delta T \frac{a}{r^2} \operatorname{erf}\left(\frac{r}{a}\right) - S\delta T \frac{a}{2r^2} e^{a^2/4\lambda^2} \left[\left(1 - \frac{r}{\lambda}\right) e^{r/\lambda} - \left(1 + \frac{r}{\lambda}\right) e^{-r/\lambda} + \left(1 + \frac{r}{\lambda}\right) e^{-r/\lambda} \operatorname{erf}\left(\frac{a}{2\lambda} - \frac{r}{a}\right) - \left(1 - \frac{r}{\lambda}\right) e^{r/\lambda} \operatorname{erf}\left(\frac{a}{2\lambda} + \frac{r}{a}\right) \right]$$
(E.5)

For $a >> \lambda$, we expand the error functions using Eqs. (E.3) and (E.4) and can write

$$\left(1 - \frac{r}{\lambda}\right) e^{r/\lambda} \left[1 - \operatorname{erf}\left(\frac{a}{2\lambda} + \frac{r}{a}\right)\right] + \left(1 + \frac{r}{\lambda}\right) e^{-r/\lambda} \left[\operatorname{erf}\left(\frac{a}{2\lambda} - \frac{r}{a}\right) - 1\right]$$

$$= \left[\frac{\left(1 - \frac{r}{\lambda}\right)}{\left(\frac{a}{2\lambda} + \frac{r}{a}\right)} - \frac{\left(1 + \frac{r}{\lambda}\right)}{\left(\frac{a}{2\lambda} - \frac{r}{a}\right)}\right] \frac{e^{-a^2/4\lambda^2 - r^2/a^2}}{\sqrt{\pi}}$$

$$= -\frac{4r}{a} \frac{e^{-a^2/4\lambda^2 - r^2/a^2}}{\sqrt{\pi}} \quad \text{(for } a >> \lambda\text{).}$$

Putting this in Eq. (E.5), we arrive at the expression for electric field given in Eq. (5.23).

E.3 Charge density and the total charge

Taking the divergence of Eq. (E.5) we get the general expression for charge density as

$$\rho(r) = \frac{S\delta T\varepsilon}{2\lambda^2} \frac{a}{r} e^{a^2/4\lambda^2} \left[-e^{-r/\lambda} \left\{ 1 - \operatorname{erf}\left(\frac{a}{2\lambda} - \frac{r}{a}\right) \right\} + e^{r/\lambda} \left\{ 1 - \operatorname{erf}\left(\frac{a}{2\lambda} + \frac{r}{a}\right) \right\} \right]$$

Again expanding the terms in the third bracket by using Eqs. (E.3) and (E.4), we can write

$$\begin{split} \rho(r) &= \frac{S\delta T\varepsilon}{2\lambda^2} \frac{a}{r} e^{a^2/4\lambda^2} \left[-e^{-r/\lambda} \left\{ 1 - \operatorname{erf}\left(\frac{a}{2\lambda} - \frac{r}{a}\right) \right\} + e^{r/\lambda} \left\{ 1 - \operatorname{erf}\left(\frac{a}{2\lambda} + \frac{r}{a}\right) \right\} \right] \\ &= -S\delta T\varepsilon \frac{a}{2r} \left[\frac{1}{\left(\frac{a}{2\lambda} - \frac{r}{a}\right)} - \frac{1}{\left(\frac{a}{2\lambda} + \frac{r}{a}\right)} \right] \frac{e^{-r^2/a^2}}{\sqrt{\pi}} \\ &= -S\delta T\varepsilon \frac{a}{2r} \frac{e^{-r^2/a^2}}{\sqrt{\pi}} \left[\frac{\frac{2r}{a}}{\frac{a^2}{4\lambda^2} - \frac{r^2}{a^2}} \right] \\ &= -4\varepsilon S\delta T \frac{e^{-r^2/a^2}}{a^2\sqrt{\pi}}, \end{split}$$

which is given in Eq. (5.26) and valid in the limit $a >> \lambda$. Total charge contained in the heated region is obtained by integrating the charge density

$$Q = 4\pi \int_{0}^{\infty} r^2 \rho(r) dr = -4\pi a S \delta T.$$

Using the definition of $S = \delta \alpha \frac{k_B}{e}$ and the Bjerrum length $\ell_B = e^2/4\pi \varepsilon k_B T$, we obtain the total charge in the unit of Bjerrum length which is given in Eq. (5.27).

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Appendix F

Hot liquid spot: another temperature profile

F.1 Temperature profile

In chapter 5 we disucssed two kinds of temperature profile: one was square heating profile and another one was Gaussian heating profile. Here we discuss a very simple form for the temperature profile which is valid both inside and outside the spot. We say that the temperature profile looks like

$$T = T_0 + \frac{a\delta T}{(a+r)} \qquad (0 < r < \infty), \qquad (F.1)$$

where r is the distance from the centre of the spot, a is the dimension of the region being heated, T_0 is the temperature as $r \to \infty$ and δT is the difference of temperature between two given point in the space. At the center of the spot the temperature is given by $T = T_0 + \delta T$. Taking the gradient, we have

$$\nabla T = -\frac{a\delta T}{(a+r)^2}.\tag{F.2}$$

So $(T - T_0) \sim \frac{1}{(a+r)}$ (Fig. F.1) & $\nabla T \sim \frac{1}{(a+r)^2}$. Now in case of an experiment, T_0 is usually the room temperature ~ 300 K whereas δT ranges from 10 - 15 K and thus $\delta T \ll T_0$.

F.2 Equation satisfied by the electric field and the potential

To obtain the electric field we have to solve the same differential equation given by Eq. (5.5) with the temperature gradient given by Eq. (F.2). The equation satisfied by the electric field is:

$$\nabla^{2}\mathbf{E} - \frac{1}{\lambda^{2}}\mathbf{E} + \frac{2n_{0}(\delta\alpha)e}{\varepsilon}\frac{\nabla T}{T_{0}} = 0.$$
 (F.3)



Figure F.1: Temperature profile throughout the solution. At the centre of the spot (r = 0) the temperature is $T_0 + \delta T$ and it decreases as $\sim 1/r$ with the increasing r to become T_0 as $r \to \infty$

Important point to note in this equation is that the Laplacian (∇^2) present in this equation is not a scalar Laplacian, it is a vector Laplacian. It is the gradient of a divergence instead of the divergence of a gradient. In a 3-dimensional geometry having spherical symmetry the vector Laplacian has the form

$$\boldsymbol{\nabla}^2 = \left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{2}{r^2}\right)$$

We can solve Eq. (F.3) to find out \mathbf{E} , but for this the associated Green function is complicated as

$$\nabla T \sim \frac{1}{\left(a+r\right)^2}.$$

We can simplify the solution if we start from the equation satisfied by the potential which is related to the electric field by the relation $\mathbf{E} = -\nabla \phi$. Using this and the integral

$$\int_{\infty}^{r} \left(\boldsymbol{\nabla} T \right) dr = T(r) - T(\infty) = T - T_0,$$

we have a resulting equation for the potential by integrating Eq. (F.3)

$$\nabla^2 \phi - \frac{1}{\lambda^2} \phi - \frac{2n_0(\delta \alpha)e}{\varepsilon} \frac{T - T_0}{T_0} = 0.$$
 (F.4)

Here the Laplacian present is a scalar Laplacian and has the form

$$\boldsymbol{\nabla}^2 \equiv \left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right)$$

The last term present in the left side of Eq. (F.4) is like a source term, which contains the source of inhomogeneity through the temperature present in it. For simplifying further calculations, we will call this term as g(r). Inserting the expression for T and using the definition of the Debye length λ , we get $g(r) = -\delta \alpha \frac{k_B \delta T}{e} \frac{a}{\lambda^2} \frac{1}{(a+r)}$. Using this, we have

$$\boldsymbol{\nabla}^2 \phi - \frac{1}{\lambda^2} \phi + g(r) = 0 \tag{F.5}$$

F.3 Potential and the thermoelectric field

Solution of the above Eq. (F.5) gives the potential in the region $0 < r < \infty$. The general solution for this equation is

$$\phi = A \frac{e^{-r/\lambda}}{r} + \frac{\lambda}{2r} e^{-r/\lambda} I_1(r) + \frac{\lambda}{2r} e^{r/\lambda} I_2(r)$$

with

$$I_1(r) = \int_0^r e^{r'/\lambda} r'g(r')dr',$$

$$I_2(r) = \int_r^\infty e^{-r'/\lambda} r'g(r')dr',$$

and the constant A which is to be determined using the boundary condition E = 0 at the centre of the heated spot i.e. at r = 0. While writing down this solution, we have discarded the term proportional to $e^{r/\lambda}$ to satisfy the boundary condition $E \to 0$ as $r \to \infty$. We obtain these boundary conditions by using the Gauss' law, as there is no net charge inside the system, only a charge separation occurs. But for using the boundary condition of zero field at the centre of the spot to find out A we have to calulate the electric field first. Remembering that the electric field $\mathbf{E} = -\nabla \phi$, we have

$$E = A\left(\frac{1}{r^2} + \frac{1}{\lambda r}\right)e^{-r/\lambda} + \left(\frac{\lambda}{2r^2} + \frac{1}{2r}\right)e^{-r/\lambda}I_1(r) + \left(\frac{\lambda}{2r^2} - \frac{1}{2r}\right)e^{r/\lambda}I_2(r)$$

with $I_1(r)$ and $I_2(r)$ defined as above. Important point to note is that E is the radial part of the electric field \mathbf{E} and in this problem we only have the radial component present in \mathbf{E} $\left(\mathbf{E} = E\hat{r}\right)$, the other two components being equal to zero. Using the boundary condition of zero electric field at the particle surface and remembering that $g(r) = -(\delta \alpha) \frac{k_B \delta T}{e} \frac{a}{\lambda^2} \frac{1}{(a+r)}$ to find out the integrals $I_1(r)$ and $I_2(r)$, we find

$$A = \delta \alpha \frac{k_B \delta T}{2e} a \left[1 + \frac{a}{\lambda} e^{a/\lambda} \operatorname{Ei} \left(-\frac{a}{\lambda} \right) \right],$$

where Ei function represents the usual exponential integral which is defined as

$$\operatorname{Ei}(x) = -\int_{-x}^{\infty} \frac{e^{-t}}{t} dt$$
 (for all non-zero values of x)

or equivalently $\int_{-\infty}^{x} \frac{e^{t}}{t} dt$. Plugging back this value of A in the expression for electric field and arranging the terms present, we have finally

$$E = E_0 \frac{a^2}{r^2} \left[1 - E_1(r) e^{-r/\lambda} + E_2(r) \right],$$
 (F.6)

with

$$E_0 = -\delta \alpha \frac{k_B \delta T}{ea},\tag{F.7}$$

$$E_1(r) = 1 + \frac{r}{\lambda} + \frac{a}{2\lambda} \left(1 + \frac{r}{\lambda} \right) \left\{ e^{a/\lambda} \operatorname{Ei} \left(-\frac{a}{\lambda} \right) - e^{-a/\lambda} \operatorname{Ei} \left(\frac{a}{\lambda} \right) \right\}$$
(F.8)

and

$$E_2(r) = \frac{a}{2\lambda} \left(1 - \frac{r}{\lambda} \right) e^{(a+r)/\lambda} \operatorname{Ei}\left(-\frac{a+r}{\lambda} \right) - \frac{a}{2\lambda} \left(1 + \frac{r}{\lambda} \right) e^{-(a+r)/\lambda} \operatorname{Ei}\left(\frac{a+r}{\lambda} \right).$$
(F.9)

Here E_0 has a dimension of the electric field and it is the maximum electric field we can obtain for this system with a given dimension of the heated spot and temperature difference as $\lambda \to 0$. For example, if we heat a spot of radius $a = 1\mu$ m by $\delta T = 10$ K in an electrolyte solution having $\delta \alpha \approx 1$, E_0 is approximately given by 900V/m. In Figure (F.2) we have plotted $\frac{E}{E_0}$ as a function of r, the distance from the centre of the particle for various values of λ . In each cases a and λ are kept constant. This shows that as we decrease λ , we obtain higher and higher electric field near the particle surface and for $\lambda \to 0$ we have $E = E_0$ at r = a.

F.4 Total charge

Let us briefly discuss something about Eq. (F.6) representing the electric field E. There are three terms present in this expression. For large r, the second term essentially becomes negligible due to the presence of the exponentially decreasing factor. Now for large values of x, the exponential integral Ei(x) and Ei(-x) can be approximated well by the following functions:

$$\operatorname{Ei}(x) \sim e^x \log\left(1 + \frac{1}{x}\right),$$

and

$$\operatorname{Ei}(-x) \sim -e^{-x} \log\left(1 + \frac{1}{x}\right)$$

Using these forms, we get, for large r, $E_2(r) \sim \mathcal{O}\left(\frac{1}{a+r}\right)$. So for large r, the third term vanishes sufficiently rapidly compared to the first term present in Eq. (F.6) and we can neglect this term also. Thus for large r, first term goes like $1/r^2$. Due to the presence



Figure F.2: Temperature T, E/E_0 and ρ/ρ_0 as a function of the distance from the particle centre (r) for a fixed particle radius $a = 1\mu m$. In the left panel we have used $\lambda = 0.1\mu m$ and in the right panel $\lambda = 10\mu m$.

of this, for large r the electric field is proportional to $1/r^2$ which confirms the presence of a net charge near the heated spot. Comparing the first term with $\frac{Q}{4\pi\varepsilon r^2}$ (which is the electric field at a distance r due a charge Q present at the origin) we get the total charge within the spot as

$$Q_{tot} = e\delta\alpha \frac{a}{\ell_B} \frac{\delta T}{T_0},\tag{F.10}$$

where $\ell_B = e^2/4\pi\varepsilon k_B T$ is the Bjerrum length. At room-temperature $(T \approx 300K)$, Bjerrum length ℓ_B equals to 0.7nm. From eq. (F.10) it is clear that Q_{tot} is independent of λ . So for large r, the electric field will also be independent of the value of λ .

F.5 Charge density ρ and the total charge

As we know the electric field, we can now calculate the charge density ρ using the relation $\rho = \varepsilon (\text{div}E)$ where the gradient operator has the form $\nabla \equiv \left(\frac{d}{dr} + \frac{2}{r}\right)$. Taking the gradient of Eq.(F.6), we get

$$\rho = \rho_0 \frac{a}{r} \left[\rho_1(r) + \rho_2(r) \right], \tag{F.11}$$

where

$$\rho_0 = -2en_0\delta\alpha \frac{\delta T}{T_0},\tag{F.12}$$

$$\rho_1(r) = \left[1 + \frac{a}{2\lambda} e^{a/\lambda} \operatorname{Ei}\left(-\frac{a}{\lambda}\right) - \frac{a}{2\lambda} e^{-a/\lambda} \operatorname{Ei}\left(\frac{a}{\lambda}\right)\right] e^{-r/\lambda}$$
(F.13)

and

$$\rho_2(r) = -\frac{a}{a+r} - \frac{a}{2\lambda} e^{(a+r)/\lambda} \operatorname{Ei}\left(-\frac{a+r}{\lambda}\right) + \frac{a}{2\lambda} e^{-(a+r)/\lambda} \operatorname{Ei}\left(\frac{a+r}{\lambda}\right).$$
(F.14)

Here ρ_0 has the dimension of the charge density and it is the maximum charge density we have as we approach the centre of the spot (i.e. $r \to 0$). So $\rho(r \to 0) = \rho_0$. It is clear that the charge density decreases exponentially as we go far from the spot and it becomes zero for large distances. This result is quite expected because we are dealing with an infinte dimensional geometry. But the total charge produced at the particle surface and at the boundary of the container is finite. Now if we have a finite amount of charge in a surface of infinite radius, the charge density must be zero. In Fig. (F.2) we have plotted $\frac{\rho}{\rho_0}$ versus r (distance from the particle centre) for different values of λ . For each cases as $r \to 0$, $\rho \to \rho_0$.

We can also calculate the total charge by integrating the charge density over a sphere of infinite radius $(0 < r < \infty)$

$$Q_{tot} = \lim_{R \to \infty} \int_0^R \rho d^3 r = 4\pi \lim_{R \to \infty} \int_0^R r^2 \rho dr$$

and this gives $Q_{tot} = e \delta \alpha \frac{a}{\ell_B} \frac{\delta T}{T_0}$ which is exactly similar to that obtained in Eq. (F.10).

F.6 Summary and conclusion

In this case also we obtain the same behaviors for the electric field and charge density at large distances and clearly see the evidence of accumulation of a net charge Q inside the heated region. Still there is a problem with this particular choice of the heating profile. If we use this temperature profile then $\nabla^2 T$ diverges at the origin of the heated spot (r = 0), so does the heating power of the laser. That's why it's not a good choice for the temperature profile although it gives essentially the same behavior for all the quantities at large ditances.

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