Thermophoresis for a single charged colloidal particle

S Nader Rasuli and Ramin Golestanian

Institute for Advanced Studies in Basic Sciences, Zanjan 45195-159, Iran

E-mail: rasuli@iasbs.ac.ir and golestan@iasbs.ac.ir

Abstract
The microscopic mechanism for thermodiffusion or the Ludwig–Soret effect is
investigated for a single charged colloidal particle. For the specific example of
a charged permeable membrane, the different forces arising from the interplay
between electrostatic interaction and entropy are identified and their magnitudes
are calculated in both no-salt and salt-saturated limits. The competition between
these forces, which is controlled by the salt density, is shown to decide the
direction of motion for the colloids.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

A temperature gradient applied to a fluid mixture usually causes relative transformation of its
components (i.e. some components become denser in the hotter region and some in the colder
one). This phenomenon, known as thermophoresis or the Ludwig–Soret effect, has been
known of for about 150 years [1, 2]. Although it has been well established in the framework of
non-equilibrium thermodynamics [3] and many observations have been made on it (in binary
fluids, colloidal suspensions etc), its microscopic nature is still unclear [4].

In 1981, Ruckenstein suggested a mechanism for thermophoresis in charged colloidal
solutions [5]. Charged colloids are known to be screened by an ionic double layer around
them. Considering that the free energy stored in this layer could be thought of as a surface
tension, he proposed that this layer could exert a force on the colloid if it is distorted due to the
presence of a temperature gradient. He calculated the velocity of the corresponding motion,
which he found to be always towards the colder side [5]. Recently his idea was tested very
successfully for charged micelles in water with added salt [6]. However, there also exist other
experiments with completely different results. For example, Lenglet *et al* who studied the
Soret effect in magnetic colloids observed charged colloids which went to the hotter side [7].
This observation disagrees with Ruckenstein's prediction not only in value but also in sign.

Here, we attempt to study this phenomenon by explicitly solving the problem in a
simpler geometry. We consider a charged permeable membrane (CPM) and the corresponding
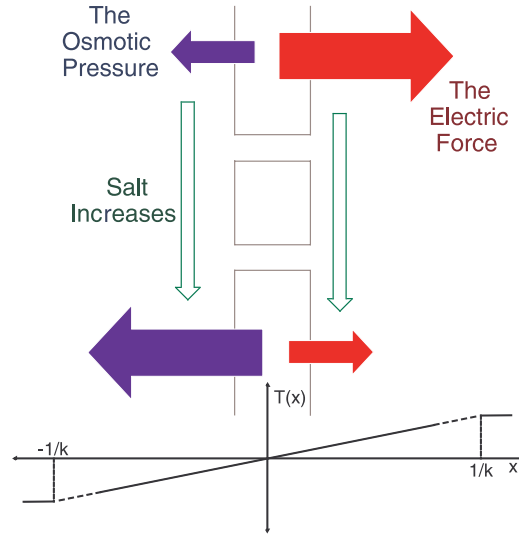
Figure 1. The schematics of the system.

counterions in a temperature gradient, with and without added salt (see figure 1). We find an electric force that is always towards the hotter region and an osmotic stress that is always towards the colder one. The competition between the two decides the direction of the membrane motion. In the no-salt regime, the electric force is found to dominate the osmotic one and pulls the membrane to the hotter region. Addition of salt, however, decreases the electric force and increases the osmotic stress. For a specified salt density the two forces balance each other and the velocity changes sign, as shown in figure 2.

2. The model

The membrane is assumed to have a surface charge uniformly distributed on its surfaces, with a surface charge number density of σ. To make it permeable, we assumed channels that connect the two sides. For evaluating the different forces, we need to know the density profiles of the different ion types in the presence of temperature gradient. Let us denote the number density and valence of the ion of type i by C_i and z_i, respectively. These profiles can be calculated by solving the Poisson equation $-\epsilon \nabla^2 \Phi = -4\pi e \sum_i z_i C_i$ for the electrostatic potential Φ, together with the continuity equation $\partial_t C_i + \nabla \cdot \mathbf{J}_i = 0$, where the current is defined as

$$\mathbf{J}_i = -D_i \nabla C_i - \mu_i e z_i C_i \nabla \Phi. \tag{1}$$

Here, D_i is the diffusion constant and μ_i is the mobility of the ion type i, ϵ is the dielectric constant of water and e is the electron charge. We use the Einstein relation $D_i(\mathbf{r}) = \mu_i k_B T(\mathbf{r})$ to relate the position dependence of the diffusion constant to that of temperature. It is also customary to define the so-called Bjerrum length $\ell_B = e^2/(\epsilon k_B T)$.

3. Thermophoretic forces

For a fixed CPM, the steady state means that water cannot flow in its channels, which requires that the water pressures on the two sides of the membrane are equal. Consequently, the
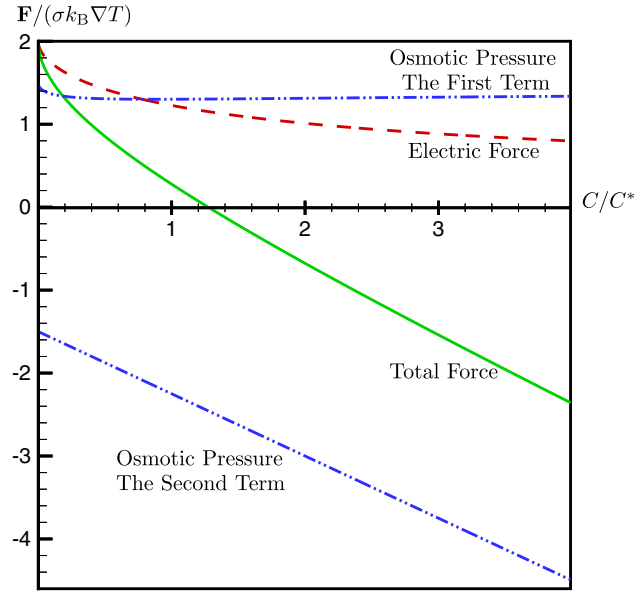
Figure 2. Various contributions to the force per unit area of the CPM as a function of the salt concentration. The total force (solid curve) is composed of two contributions corresponding to the osmotic stress (dash–dotted curves) and the electric force (dashed curve). The total force changes sign upon increasing the salt concentration, as a result of the competition between the two contributions. Here, $C^* = 1/(8\pi\ell_B\lambda_{GC}^2)$ and we have assumed $\lambda_{GC} = 6$ nm, CPM thickness $d = 9$ nm and the Bjerrum length $\ell_B = 0.7$ nm.

membrane will experience two major forces, namely, the electric force and the osmotic force, the origins of which are discussed below.

3.1. The electric force

A fixed CPM in a temperature gradient feels an electric force as a result of migration of mostly oppositely charged ions from the colder to the hotter region. Since most of the migrated ions have a charge opposite to that of the membrane, they attract the membrane towards themselves, which means towards the hotter region.

A simple example helps us to understand this better. Imagine an infinitely thin membrane in a salt free solution, i.e. the only existing ions are negatively charged monovalent counterions. In the uniform temperature case, the counterion density is (see the inset of figure 3)

$$C(x) = \frac{1}{2\pi\ell_B} \frac{1}{(|x| + \lambda_{GC})^2}, \tag{2}$$

where $\lambda_{GC} = 1/(\pi\ell_B\sigma)$ is the so-called Gouy–Chapmann length. Now imagine that the right-hand side temperature is increased to T_+ and the left-hand side temperature is decreased to T_-. As the density close to the membrane surfaces $C(0) = 1/2\pi\ell_B\lambda_{GC}^2 = \pi e^2\sigma^2/2\epsilon k_B T$ depends inversely on the temperature, it increases in the colder side and decreases in the hotter one as compared to the equilibrium value. Since an infinitely thin permeable membrane cannot bear two different densities on its opposite sides, there will be a migration of counterions from left to right. For a temperature profile that varies continuously a similar migration is expected to occur, leading to an excess of counterions in the hotter region as compared to the colder one, which in turn produces an electric field of $E_0 = k_B\nabla T/e$ at the CPM position, which pushes
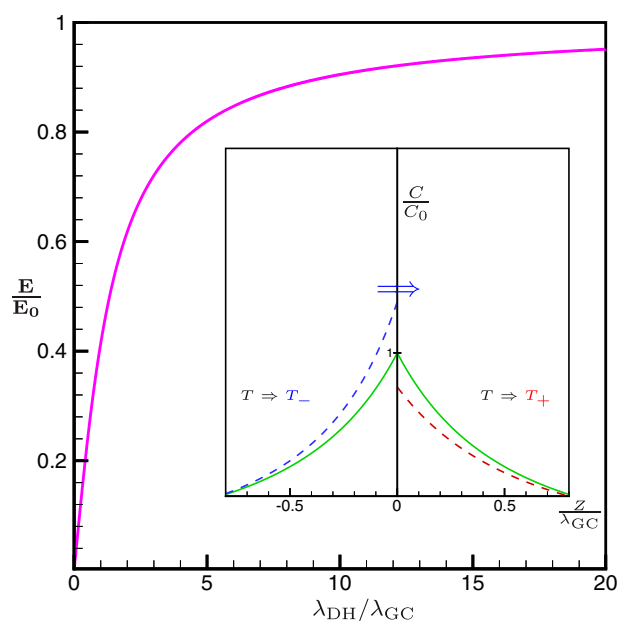
Figure 3. The electric field at the centre in units of its no-salt value $E_0 = k_B \nabla T / e$ is plotted as a function of $\lambda_{DH}/\lambda_{GC}$, a measure of the salt density. Inset: the counterion density profile for the no-salt case. When the temperatures of the two separate regions change, densities in the vicinity of the CPM change as well (dashed curves). To obtain the steady state, some of the ions should go from the higher density region (i.e. the colder side) to the lower density region (i.e. the hotter side).

it to the hotter region. Considering a finite thickness for the membrane does not affect the situation too much—it only introduces a correction factor for the electric field that is between 1 and 2.

Addition of salt, however, can have a drastic effect. The presence of salt weakens the electric field at the CPM, as can be seen from figure 3 where the electric field is plotted as a function of the ratio between the Debye–Hückel length $\lambda_{DH} = 1/\sqrt{8\pi \ell_B C_{Salt}}$ and the Gouy–Chapmann length. In the limit of salt saturation, the field is reduced by a factor proportional to $\lambda_{DH}/\lambda_{GC}$, which is the ratio between the electric field decay length or the double-layer width in the salty regime and its value in the no-salt case. In other words, for each of these two limiting cases the number of migrating ions is proportional to the width of the double layer in that case. We note that the fact that an excess of oppositely charged ions, in the hotter region, attracts colloidal particle was also pointed out by Morozov in his numerical work on thermophoresis of spherical colloids [9].

3.2. The osmotic force

The other important force comes from the difference of the osmotic pressures exerted on the two sides of the membrane. To evaluate the osmotic pressures, we can use the ideal gas equation of state [8]. Then, for each type of ion the difference in pressure will have two contributions coming from the differences in the densities and the temperatures, i.e. $\Delta \Pi = \sum_i k_B T(0) \Delta C_i + \sum_i k_B \Delta T C_i(0)$, in the first order. For a permeable membrane with zero thickness all the ΔC_is and ΔT are zero in the steady state. As we increase the membrane

thickness, however, the channels connecting two sides to each other maintain differences in the concentration and temperature. Solving for the profiles of the ions, we find that the density in the hotter side is smaller than that of the colder side, which means that the term $\sum_i k_B T(0) \Delta C_i$ tends to push the CPM to the hotter region. The second term $\sum_i k_B \Delta T C_i(0)$, however, has the opposite tendency and tends to push the CPM to the colder region. It is interesting to note that the second term always dominates the first one in the high salt concentrations, as can be seen from figure 2. It can be shown that the first contribution $\sum_i k_B T(0) \Delta C_i$ asymptotes to a fixed value as the salt concentration is increased, while the second term $\sum_i k_B \Delta T C_i(0)$ increases with salt content indefinitely.

In the no-salt regime, the magnitudes of the two osmotic contributions are nearly equal and the total osmotic force becomes much weaker than the electric force. Since the electric force dominates, the CPM feels a net force towards the hotter region in this case. Addition of salt, however, changes the situation, as in a characteristic salt concentration the osmotic force dominates and the membrane feels a net force towards the colder region. The crossover salt concentration is given by $C \simeq C^*$, which corresponds to $\lambda_{DH} \simeq \lambda_{GC}$.

4. Concluding remarks

To complete the discussion and calculate the thermophoretic velocity of the CPM, we should balance the net force induced by the gradient of temperature by the friction. While at small forces or low velocities this could be easily achieved by considering a constant friction coefficient caused by the viscous drag of the membrane itself, the contribution due to the drag of the *comoving* counterions may complicate matters at higher velocities [10]. We expect, however, that this effect will not change the overall tendency of the CPM to move towards the colder or the hotter regions.

The above treatment has been within the mean-field scheme, and the effect of ionic correlations fluctuations has been neglected. Including the fluctuations can be shown to result in an additional force, whose magnitude per unit area goes like $-k_B \nabla T / a^2$, where a is a cut-off representing the smallest length scale in the system [11], which can be identified as λ_{GC} in the no-salt case and λ_{DH} in the high salt one. In both of these limits, the correction term is negligible with respect to the other forces described above, so we can safely ignore the correlations.

One may question the validity of the form of the current as given in equation (1), in the case of nonuniform temperature. To address this question one can begin with the Langevin equation for the ions and try to derive the corresponding Fokker–Planck equation for nonuniform temperature. One can show that the form of the current will be modified as $\mathbf{J} = -D \nabla C - \mu e z C \nabla \Phi - \alpha C \nabla D$, although the choice of α is ambiguous. In fact, α can be related to the thermodiffusion coefficient of the ions. Carrying out the calculations as before yields similar forms for the electric and osmotic forces, except that they are both multiplied by $1 - \alpha$.

Finally, in our treatment we have neglected the temperature dependence of the dielectric constant of water, which should be taken into consideration for a full understanding of the problem. This effect, together with other extensions of the present scheme, will be addressed elsewhere.

In conclusion, we have presented an analysis of the motion of a charged permeable membrane due to the gradient of temperature. In this one-particle model, we have provided a clear picture of the phenomenon of sign change for the thermodiffusion coefficient by identifying two competing contributions to the force, coming from charge migration and osmosis.

Acknowledgments

References

[1] Ludwig C 1856 *Sitz. ber. Akad. Wiss. Wien Math.-Nat. wiss. Kl.* **20** 539
[2] Soret C 1879 *Arch. Geneve* **3** 48
[3] de Groot S R and Mazur P 1984 *Non-Equilibrium Thermodynamics* (New York: Dover)
[4] Debuschewitz C and Köhler W 2001 *Phys. Rev. Lett.* **87** 055901
[5] Ruckenstein E 1981 *J. Colloid Interface Sci.* **83** 77
[6] Piazza R and Guarino A 2002 *Phys. Rev. Lett.* **88** 208302
[7] Lenglet J, Bourdon A, Bacri J C and Demouchy G 2002 *Phys. Rev.* E **65** 031408
[8] Wennerström H, Jönsson B and Linse P 1982 *J. Chem. Phys.* **76** 4665
[9] Morozov K I 1999 *JETP* **88** 944
[10] Golestanian R 2000 *Europhys. Lett.* **52** 47
[11] Najafi A and Golestanian R 2004 *Europhys. Lett.* at press