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Thermometry

- Temperature Measurement, Methods

Thermophoresis

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Synonyms

Thermodiffusion; Thermal diffusion; Soret effect; Ludwig–Soret effect

Definitions

Thermophoresis is defined as the migration of a colloidal particle or large molecule in a solution in response to a macroscopic temperature gradient. The inverse effect, i. e., the formation of a temperature gradient as the result of the mixing of different molecular species, is referred to as the *Dufour effect*. The ► **Soret coefficient** is defined as the ratio of the thermal diffusion coefficient and the normal diffusion coefficient; it is a measure for the degree of separation of the species. These concepts are the same as for a molecular mixture.

Physical Principles

A colloidal particle or large molecule can be driven to move in a gas or a liquid by the application of a non-uniform temperature field. The mass flow rate \mathbf{J}_m of a species or of colloidal particles as the result of a thermal gradient ∇T in a fluid is given in, e. g. [1]:

$$\mathbf{J}_m = -\rho D \nabla c - \rho D_T c (1 - c) \nabla T, \quad (1)$$

where ρ is the fluid density, D the diffusion coefficient, D_T the thermal diffusion coefficient, and c the species or particle concentration in terms of mass fraction. The first term on the right hand side is the Fick diffusion law, while the second term describes the migration due to the thermal gradient.

In a stationary state the mass flux vanishes (i. e., $\mathbf{J}_m = 0$), and the Soret coefficient S_T is given by [5]:

$$S_T \equiv \frac{D_T}{D} = -\frac{1}{c(1-c)} \frac{\nabla c}{\nabla T}. \quad (2)$$

Hence, the effectiveness of the separation is given by the Soret coefficient, while the rate of separation is determined by the diffusivity. In general the thermal diffusion coefficient D_T is a function of temperature and concentration, which complicates the description of thermophoresis.

Thermophoresis as defined above occurs in liquids. For molecular mixtures of gases there is a sound theoretical description [5], but a theory has not been formulated satisfactorily for liquids.

Key Research Findings

For gases thermophoresis can be described using Chapman–Enskog theory [5], assuming a Maxwell–Boltzmann distribution for the velocity of the molecules, with corrections. This approach is only valid when the relative temperature change over the molecular free path is small. Using Onsager’s theorem the transport equation can be derived from the entropy production, which is described by De Groot [5].

For liquids there does not yet exist a satisfactory theoretical description, despite more than 150 years of research since the first description of thermophoresis by Ludwig [6] and Soret [7]. Theoretical descriptions fail to predict correct values of the Soret coefficient, and sometimes even fail to predict the correct sign. Hence, thermophoresis remains an area of active research, both on a theoretical and practical level. Below follows an overview of approaches applicable to large molecules or colloidal particles in suspension.

Thermophoresis of a Particle with a Thin Diffusive Layer

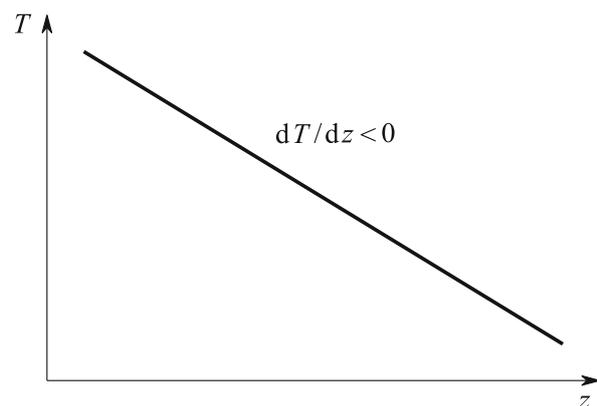
Ruckenstein [8] proposed that thermophoresis, diffusio-phoresis and electrophoresis can be described as the result of a variation of the surface tension (due to a variation in the surface potential; see Fig. 1), so that the motion of a particle is analogous to the Marangoni effect, i. e.:

$$U_T = -\frac{\varepsilon \zeta^2}{32\pi\eta} \frac{d \ln T}{dz} \equiv -\frac{\ell}{\eta} \frac{d\gamma}{dT} \frac{dT}{dz}, \quad (3)$$

where $\ell = \chi^{-1}$ is the Debye length (i. e., the thickness of the diffusive layer), η the dynamic viscosity of the fluid, ζ the surface potential, and $\gamma = \gamma_0 - \frac{1}{8\pi} \varepsilon \chi \zeta^2$ is the interfacial tension (where the second term on the right is related to the total free energy of formation of the diffusive layer) [8].

Thermophoresis, Table 1 Diffusivity and Soret coefficients for different binary liquid mixtures

species	solvent	D [$\times 10^{-12}$ m ² /s]	S _T [K ⁻¹]	Ref.
ethanol	water	1280	0.0056	[1]
DNA(27 bp)	water	36	0.013	[2]
DNA (5.6 kbp)	water	3.4	0.14	[2]
30 nm latex particles	water	15	~2	[3]
490 nm polystyrene particle	water	0.9	~0.5	[4]

**Thermophoresis, Figure 1** The thermophoretic motion of a small particle in a temperature gradient as the result of interfacial tension due to the diffusive layer around the particle; see Ruckenstein [8]

Hydrodynamic Models

Brenner [9] proposes a different description of fluid dynamics. He proposes that ∇v in Newton's rheological law should not be based on the mass based velocity of the fluid, but on its 'volume velocity.' This is a controversial idea. The adapted Navier–Stokes equations provide a hydrodynamic description of thermophoresis and thermal creep. Bedeaux et al. [13] describe how this alternative approach of the transport equations can be validated experimentally by means of thermophoresis.

It would go too far to derive the complete set of equations here so we suffice with the thermophoretic velocity given

by Brenner [9]. The thermophoretic velocity U of a sphere is:

$$U = -\frac{\alpha\beta}{1 + k_p/2k} \nabla T, \quad (4)$$

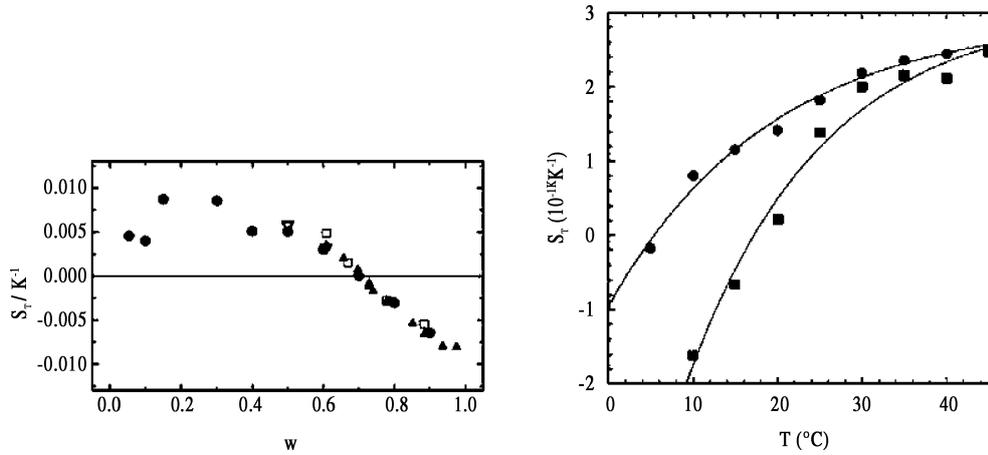
where α is the thermal diffusivity, β the thermal expansion, and k and k_p the thermal conductivity of the solvent and particle respectively.

Solvent Particle Interactions

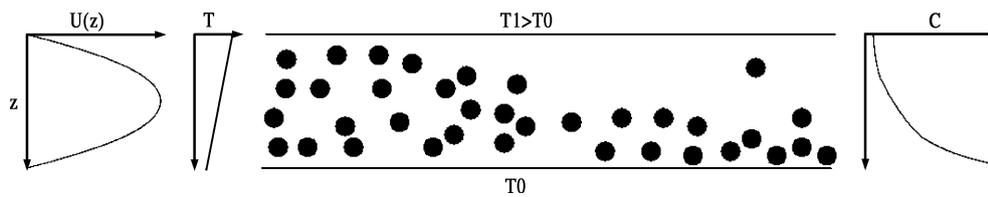
The entropy of particle solvent interactions plays an important role in thermophoresis. The description by [5] of thermophoresis in gases is based on entropy. In complex fluids the entropy of the interaction between molecules or particles and solvent leads to thermophoretic motion. Schimpf & Semenov [10] consider the slip flow caused by a local pressure gradient set up by the temperature dependent properties of the particle and solvent. They find the same thermal expansion proportionality factor as Brenner [9] who does not consider these interactions.

Change of Sign of Soret Coefficient

The Soret coefficient is not a constant; it may vary due to changes in concentration or temperature. A positive Soret coefficient means a thermophobic particle. The Soret coefficient can change sign as a function of concentration [1] or temperature [3] (see Fig. 2). The inversion temperature for latex particles, which only have electrostatic interactions with water, lies close to the maximum density of the solvent at 4 °C. Iacopini et al. [3] conclude based on empirical findings that the thermal expansivity is the major factor in thermophoresis. They claim that this effect can be added to the Soret coefficient caused by the entropy production of particle solvent interactions. The similarity between the results of Brenner [9] and Schimpf & Semenov [10] suggests that this may be valid. For molecular mixtures, Haase [14], Kempers [15] and Rousseau et al. [16], have given important contributions.



Thermophoresis, Figure 2 Inversion of the Soret coefficient. Left: Soret coefficient measurement of water ethanol mixtures, compiled from results obtained by different groups, which shows an inversion of the Soret coefficient for increasing ethanol weight fraction (from Wiegand [1]). Right: Soret coefficient measurement of latex particles (circles) and pMD31 DNA (squares), which shows an inversion of the Soret coefficient with decreasing temperature (from Iacopini et al. [3])



Thermophoresis, Figure 3 Thermophoresis of particles in a microchannel. The top wall has a higher temperature and repulses the particles for thermophobic particles (i. e., a positive Soret coefficient). An exponential concentration profile is established at the channel outlet

Examples of Application

Thermophoresis is applied in industry for the separation of (large) molecules or small particles from their solvent in so-called *thermal field flow fractionation* (TFFF) [11]. A down-scaled version of this process to microscopic scales demonstrated thermophoretic separation on microscopic scales [4, 12]. The advantage of using the very small confinement in a microfluidic device is that the separation times can be reduced, so that thermophoretic separation can be used. Braun & Libchaber [2] use a combination of thermophoresis and convection to concentrate DNA samples. The disadvantage of this approach is that it is a batch process.

As an example we estimate the timescales required to continuously separate a species in a microchannel (see Fig. 3). Consider a two-dimensional channel, e. g., a fluid between two parallel plates separated by a distance h . For low concentrations (i. e., $c \ll 1$) one finds the following stationary solution (i. e., $J_m = 0$) for the concentration:

$$c = c_0 \exp[-S_T(T - T_0)] \quad (5)$$

where c_0 and T_0 are a reference concentration and temperature respectively. The effectiveness of the separation is essentially given by the Soret coefficient. The time scale τ to reach the steady state is given by:

$$\tau = \frac{h^2}{\pi^2 D} \quad (6)$$

For a colloidal particle with a diameter d that is suspended in a fluid with a dynamic viscosity η , the diffusion constant is given by:

$$D = \frac{kT}{3\pi\eta d}, \quad (7)$$

where k is the Boltzmann constant ($k = 1.38 \times 10^{-23}$ J/K). A typical particle diffusion coefficient is $D \sim 0.9 \times 10^{-12}$ m²/s (e. g., $T \sim 300$ K, $\eta \sim 10^{-3}$ Pa s, $d \sim 490$ nm). For a micro-channel (with a typical channel width of $h \sim 10 - 100$ μ m) the time scale τ is typically of the order of $10 - 10^3$ seconds. This means that one has to use long microchannels in combination with low flow rates to establish a high separation ratio.

Another advantage of implementing thermophoretic separation at a microscopic scale is that one can reach very large temperature gradients without applying large temperature differences. For example, a 5 K temperature difference over a 50 μm channel implies a temperature gradient of $\sim 10^5 \text{K/m}$, while the absolute variation of temperature is limited. This is beneficial in the case of biological samples (cells, proteins, DNA) where large variations in temperature can disintegrate the samples. However, the difficulty lies in establishing and maintaining a temperature difference in a microfluidic device, which is complicated by the high conductivity and small dimensions at small scales. A design of a microfluidic device for thermophoretic separation is given by Geelhoed et al. [4].

Cross References

- ▶ Diffusiophoresis
- ▶ Electrophoresis

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Thermopneumatic Membrane Valve

- ▶ Thermopneumatic Valve

Thermopneumatic Valve

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Synonyms

Thermopneumatic membrane valve

Definition

A thermopneumatic valve is a type of micromachined active valve operated by the volumetric thermal expansion of a heated gas or heated liquid in a sealed chamber [1].

Overview

The rapid development of new methods of fabrication and microfluidic components enables the desired control and manipulation of small amounts of fluids. The microvalves in microelectromechanical systems (MEMS) are essential elements of a micro total analysis system. Typically, there are two types of microvalve: one is the passive valve the operation of which is dependent upon its surrounding pressure conditions; the other is the active valve, which can be controlled actively. Active valves are categorized in three major ways: initial working state, control pattern, and actuation principle. Each microvalve has advantages and disadvantages from the viewpoint of power consumption, integration method, response time, operation frequency and voltage, fabrication process, and actuation efficiency. Among the various types of microvalves, thermopneumatic actuation provides a large achievable volume stroke and simple fabrication process relative to other actuation methods for microvalves [1].

A thermopneumatic valve typically consists of a moveable valve diaphragm, a valve seat, and a resistive heater in a sealed cavity. While electrical power is applied to the resistive heater, the initial volume of gas in the sealed chamber expands. Using the volumetric change of the heated gas in the cavity, the diaphragm structure