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# A microscopic approach to thermophoresis in colloidal suspensions

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## Abstract

We present a general description of thermophoretic phenomena in dilute suspensions of spherical colloids which lie at the basis of the Ludwig/Soret effect. We first consider how a thermal gradient affects a homogeneous fluid showing that, to linear order, no momentum flux is generated in the bulk. The presence of a colloidal particle, however, modifies the pressure tensor of the fluid, thereby creating a velocity field in the neighbourhood of the surface of the colloid, which can be calculated by use of the Navier–Stokes equation. As a consequence, momentum transfer to the colloid takes place. When this effective force is substituted into a Smoluchowski equation for the particle motion, we arrive at a simple and general expression of the Soret coefficient in terms of the colloid–liquid surface tension.

## 1. Introduction

Thermophoretic phenomena are known to be ubiquitous in soft matter physics [1] and recent experiments also suggest that they are likely to underlie physical mechanisms of considerable biological relevance [2]. One of the simplest instances where thermophoresis occurs is a dilute colloidal suspension in a thermal gradient: after an equilibration time (which depends on the specific system) the colloidal particles acquire a non-uniform profile described by the phenomenological equation:

$$\frac{dc}{dz} = -cS_T \frac{dT}{dz} \quad (1)$$

where  $c$  is the colloid concentration,  $S_T$  is the Soret coefficient and the thermal gradient is placed in the  $\hat{z}$  direction. Positive (negative) values of  $S_T$  mean that colloids accumulate toward the cold (hot) region of the sample. Despite the apparent simplicity of the phenomenon, systematic experimental investigations of thermophoresis in colloidal suspensions have been attempted only recently [3, 4], while studies of the same effect in rarefied gases have been performed

since the 19th century [5]. Therefore, it is not surprising that while a convincing theoretical explanation of the thermophoretic phenomena in gases was achieved a long time ago, the microscopic understanding of the Soret effect in colloidal suspensions is still controversial, and many puzzling features (like the absolute magnitude and the temperature dependence of the Soret coefficient) are still unexplained, despite the long lasting theoretical effort on the subject.

This contribution aims at clarifying some basic theoretical problems in the description of thermophoretic phenomena in colloidal suspensions. In particular, we attempt to develop a general formalism which, in the case of gases, is able to reproduce the known results obtained via the kinetic theory but can, at the same time, be applied to denser systems. Here, we deal with the simplest model exhibiting the thermophoretic phenomenon: an extremely dilute suspension of hard spheres floating in a liquid, subject to a given temperature gradient.

## 2. Distribution function in a thermal gradient

As a first step we ask how the phase space distribution function of the molecules of a simple fluid (i.e. of the solvent) is modified by the presence of a thermal gradient. This problem has been extensively investigated in the special case of rarefied gases, starting from the seminal works by Reynolds and Maxwell [5]. An approach based on the kinetic theory of gases shows that, to linear order in the thermal gradient, the single-particle momentum distribution function acquires a further contribution besides the known equilibrium result  $f_0(p) = Z^{-1} \exp(-\beta p^2/(2m))$ :

$$f(\mathbf{p}) = f_0(p) \left[ 1 + C \left( \frac{5}{2} - \beta \frac{p^2}{2m} \right) \mathbf{p} \cdot \nabla T \right] \quad (2)$$

where the constant  $C$  depends on the particle collision rate [5]. Starting from this result, it is easy to show that no off-diagonal momentum flux is present and the full pressure tensor is *unaffected by the presence of the thermal gradient*. Remarkably, the same conclusion also holds for a dense liquid, where the analysis based on the Boltzmann equation does not hold. The correct way to tackle this difficult problem is the linear response theory in the Green–Kubo formalism, subsequently generalized by Mori to deal with the thermal transport coefficients [6]. According to this theory, the full, phase space distribution function of a fluid in a thermal gradient  $F(q, p)$  differs from its equilibrium result at the average temperature  $F_0(q, p)$  in two distinct ways. The first is based on a natural generalization of the concept of thermodynamical equilibrium: the *local thermal equilibrium* (LTE) described by a distribution function  $F^{\text{LTE}}(q, p)$  formally identical to the equilibrium one, evaluated at the local temperature. However, a further correction to LTE is also present in the form of a time dependent contribution originating from the natural tendency of the system to achieve thermal equilibrium. The final expression for  $F(q, p)$  can be written as

$$F = F^{\text{LTE}} + \beta F_0 \int d\mathbf{x} \left[ \mathbf{j}(q, p, \mathbf{x}) \cdot \mathbf{v}(\mathbf{x}) - \beta \int_0^t d\tau U(\tau) \mathbf{J}_H(q, p, \mathbf{x}) \cdot \nabla T \right] \quad (3)$$

where the dependence of the distribution functions on the phase space variables  $(q, p)$  is understood.  $U(t) = \exp(t\mathcal{L})$  is the exact many-body evolution operator, while  $\mathbf{j}(q, p, \mathbf{x})$  and  $\mathbf{J}_H(q, p, \mathbf{x})$  are the local mass and energy flux respectively, whose microscopic definition can be found in [6]. By use of the non-equilibrium distribution function (3) it is (formally) possible to calculate averages of any local microscopic observable: the physical result corresponds to the limit  $t \rightarrow \infty$ . Finally, the auxiliary function  $\mathbf{v}(\mathbf{r})$  appearing in (3) is implicitly defined by the condition that the average mass flux coincides with the product of the average mass density  $\rho(\mathbf{r})$  times the average velocity  $\mathbf{u}(\mathbf{r})$ , i.e. by  $\langle \mathbf{j}(q, p, \mathbf{r}) \rangle = \rho(\mathbf{r}) \mathbf{u}(\mathbf{r})$ .

Interestingly, the symmetry properties of the distribution functions  $F_0$  and  $F^{\text{LTE}}$  have important consequences for the momentum transport in the fluid and lead to simple and general results. In a homogeneous and isotropic system described by the distribution function  $F_0$  no privileged vector can be defined. As a consequence, the equilibrium averages of the rank three tensors appearing in the calculation of the pressure tensor  $\langle J^{\alpha\beta}(\mathbf{r}) \rangle$  via equation (3) must vanish identically:

$$\int d\mathbf{x} \langle J^{\alpha\beta}(\mathbf{r}) j^\gamma(\mathbf{x}) \rangle_0 = 0; \quad \int d\mathbf{x} \langle J^{\alpha\beta}(\mathbf{r}) U(\tau) J_H^\gamma(\mathbf{x}) \rangle_0 = 0. \quad (4)$$

Only the local thermal equilibrium part contributes to the pressure tensor, which, due to the isotropy of the momentum distribution  $F^{\text{LTE}}$ , reduces to diagonal form:

$$\langle J^{\alpha\beta}(\mathbf{r}) \rangle = \langle J^{\alpha\beta}(\mathbf{r}) \rangle_{\text{LTE}} = p \delta_{\alpha\beta}. \quad (5)$$

The last equality in (5) then follows from the hypothesis that the pressure is uniform throughout the sample, due to the requirement of mechanical stability of the system.

If the fluid remains static even in the presence of the thermal gradient, the condition of vanishing mass flux reads

$$\langle \mathbf{j}(\mathbf{r}) \rangle = \rho_0 \mathbf{v} - \frac{\beta^2}{3} \nabla T \int_0^\infty d\tau \int d\mathbf{x} \langle \mathbf{j}(\mathbf{0}, \tau) \cdot \mathbf{J}_H(\mathbf{x}) \rangle_0 = 0 \quad (6)$$

which defines the parameter  $\mathbf{v}$ .

In the limiting case of extremely rarefied gases (ideal limit) equation (3) together with (6) reproduces the results of kinetic theory (2). However, even in the presence of strong interactions between the molecules, Mori's linear response theory shows that a temperature gradient *in a homogeneous fluid* does not affect the pressure tensor.

### 3. Thermophoretic force

The case, however, is different when the presence of a surface breaks space homogeneity. This circumstance does indeed occur when a large body (e.g. a colloid) is present in the solvent. In such a case the structure of the pressure tensor predicted by linear response theory is richer and a net momentum transfer between the fluid and the colloid sets in. Instead of using the fully microscopic distribution function (3), valid both for gases and liquids, we adopt a hydrodynamic approximation keeping only the  $F_{\text{LTE}}$  contribution and determining the average velocity profile  $\mathbf{u}(\mathbf{r})$  via the Navier–Stokes equation for an incompressible fluid in the absence of external forces:

$$\eta \nabla^2 u^\alpha(\mathbf{r}) - \partial_\beta \langle J^{\alpha\beta}(\mathbf{r}) \rangle_{\text{LTE}} = 0 \quad (7)$$

where  $\eta$  is the shear viscosity of the solvent. For a spherical colloid of radius  $a$ , the most general pressure tensor depends upon two scalar functions of the radial variable, the normal and the tangential components [7]:

$$\langle J^{\alpha\beta}(\mathbf{r}) \rangle_0 = n^\alpha n^\beta p_N(r) + (\delta_{\alpha\beta} - n^\alpha n^\beta) p_T(r) \quad (8)$$

where  $\mathbf{n}$  is the radial unit vector, and the two components of the pressure satisfy the equilibrium condition  $\partial_\beta \langle J^{\alpha\beta}(\mathbf{r}) \rangle_0 = 0$ . Evaluating the pressure tensor in LTE amounts to considering  $p_N(r)$  and  $p_T(r)$  as functions of the *local* temperature  $T(z)$  (here we assume that the gradient is along the  $\hat{z}$  direction) at fixed bulk pressure  $p$ . By substituting equation (8) into the Navier–Stokes equation (7) we can formally solve (7) for the velocity profile with no slip boundary conditions on the surface of the colloid  $\mathbf{u}(\mathbf{r})|_\Sigma = 0$ . Following the same procedure as developed

in [8], we finally obtain the velocity field  $\mathbf{u}(r, z)$ . The momentum flux transferred to the colloid then yields the net force acting on the particle due to the thermal gradient [8]:

$$\mathbf{f} = -2\pi a \nabla T \left. \frac{\partial}{\partial T} \right|_p \int_a^\infty dr \frac{r^2 - a^2}{r} (p_N(r) - p_T(r)). \quad (9)$$

In the limit of a large colloid, which is often fairly realistic, the planar limit can be used and equation (9) acquires a simple and suggestive form:

$$\mathbf{f} = -4\pi a \nabla T \left. \frac{\partial}{\partial T} \right|_p \int_0^\infty dx x (p - p_T(x)) \quad (10)$$

where use has been made of the mechanical equilibrium condition at planar interfaces  $p_N(x) = p$  [7].

According to the standard jargon of interface physics, the quantity appearing on the right hand side of equation (10) is just the temperature derivative of the product of the surface tension  $\gamma$  times a characteristic length  $\ell$  which measures the size of the liquid layer where the pressure tensor is anisotropic:

$$\begin{aligned} \gamma &= \int_0^\infty dx (p - p_T(x)) \\ \ell &= \gamma^{-1} \int_0^\infty dx x (p - p_T(x)). \end{aligned} \quad (11)$$

#### 4. Smoluchowski equation and the Soret coefficient

Now we can follow the discussion of [8] in order to relate the net ‘thermophoretic force’ (10) on a single colloid to the Soret coefficient in a dilute colloidal suspension under a uniform thermal gradient in the  $\hat{z}$  direction. The starting point is the Smoluchowski equation describing the time evolution of the probability  $P(z, t)$  to find a colloidal particle at height  $z$ :

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial z} \left[ -\frac{P}{\gamma} f_z + D \frac{\partial P}{\partial z} \right] \quad (12)$$

where the friction coefficient  $\gamma$  is linked to  $D$  by the Einstein relation:  $\gamma D = kT$ . At stationarity, the time derivative vanishes, leading to

$$kT \frac{dP}{dz} = P f_z. \quad (13)$$

The concentration profile of a suspension of  $N$  non-interacting particles is then given by equation (13) for the variable  $c = NP$ :

$$kT \frac{dc}{dz} = c f_z, \quad (14)$$

which, together with equation (10) and compared with equation (1), provides the required explicit expression for the Soret coefficient (in the planar approximation):

$$S_T = 4\pi\beta a \left. \frac{\partial}{\partial T} \right|_p \int_0^\infty dx x (p - p_T(x)). \quad (15)$$

This expression, derived here in a rather general framework, closely resembles the phenomenological ansatz put forward by Ruckenstein [9], which helped the interpretation of experiment in SDS micelles [3]. For hard particles and thin solvent inhomogeneous layers, equation (15) predicts the Soret coefficient to scale linearly with  $a$ , and therefore

the thermophoretic velocity  $u_T = -nS_T D\nabla T$ , where  $n$  is the particle number density, to be independent of the particle size. Such a behaviour was actually observed back in 1973 in a seminal paper on thermophoresis of large colloidal particles [10]. In the presence of specific particle–solvent interactions, the situation may be different. For instance, the explicit expression for charged colloids in the linear DH limit derived in [8],

$$S_T = \frac{\epsilon a}{k_B T^2} \psi_s^2 \quad (16)$$

yields a different scaling on  $a$  depending on whether the particle surface potential  $\psi$  or the surface charge is kept fixed when  $a$  is varied. In the latter case, it is interesting to note that  $\psi$  depends on  $a$  even in the quasi-planar limit, so that  $S_T$  scales as  $a^{-3}$ .

Further insight on the state dependence of the Soret coefficient can be obtained by recalling the microscopic expression of the pressure tensor of a fluid interacting via a two-body potential  $v(r)$  [6]:

$$\langle J^{\alpha\beta}(\mathbf{x}) \rangle_0 = \left\langle \sum_n \delta(\mathbf{r}_n - \mathbf{x}) \left[ \frac{P_n^\alpha P_n^\beta}{m} - \frac{1}{2} \sum_{m \neq n} \frac{r_{nm}^\alpha r_{nm}^\beta}{r_{nm}} \frac{\partial v(r_{nm})}{\partial r_{nm}} \right] \right\rangle_0 \quad (17)$$

where  $r_{nm} = |\mathbf{r}_n - \mathbf{r}_m|$ . By modelling the *structure* of the fluid as that of a hard sphere liquid, it is easy to show that the difference between the normal and the transverse contribution to the pressure tensor comes entirely from the second term in equation (17) and then it just depends on density (while the first term provides the huge ideal gas contribution to the bulk pressure which is linear in temperature). In this case, the surface tension  $\gamma$  and the length  $\ell$  (11) depend on temperature only through the number density of the liquid  $n(p, T)$  leading to a Soret coefficient (15) proportional to the thermal expansion coefficient of the fluid  $\alpha = -n^{-1}(\partial n/\partial T)_p$ .

## 5. Conclusions

In this note, we briefly discussed the basic concepts of a microscopic approach for the interpretation of thermophoresis in colloidal suspensions. Starting from the general formalism of linear response, we showed that thermophoretic phenomena are basically surface effects, originating from the breaking of the translational and rotational invariance of the host fluid (solvent) induced by the presence of the colloidal particle. This formalism, when specialized to rarefied gases in an external thermal gradient, reproduces the known results obtained by use of the Boltzmann equation. If local thermal equilibrium is attained in the solvent, the Soret coefficient can be expressed in terms of the pressure tensor of the fluid and is closely related to the temperature derivative of the tension of the colloid–solvent interface.

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