

THERMOPHORESIS AND THE EFFECT OF HYDRODYNAMIC INTERACTIONS IN A LINEAR MODEL FOR COLLOIDS

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Thermal diffusion or Soret effect is the directed motion of colloidal particles in temperature gradient. In this article, by assuming local thermodynamic equilibrium, the drift velocity for a molecular system composed of two connected spheres is calculated. It is shown that for this system the positive Soret coefficient is given by: $S_T = (3/8)(a/l)(1/T)$, where l is the average linear size of the system, a is the radius of spheres and T is the local temperature. To investigate the hydrodynamic coupling in a dilute suspension of diffusers, we calculate the average drift velocity for two far diffusers. It is shown that due to the hydrodynamic interaction, an overall attraction between diffusers can be achieved.

Keywords: Thermophoresis; Soret effect; hydrodynamic interaction.

1. Introduction

Directed motion of suspended colloidal particles induced by temperature gradients is referred to as thermophoresis or Ludwig–Soret effect.^{1,2} Since the early experimental evidences for this effect, there have been many experimental and theoretical efforts to understand its microscopic origin.^{3–12} Soret coefficient quantifies the strength of this phenomena and is defined as the ratio of thermal to self-diffusion coefficients. For a suspension of colloidal particles, the Soret coefficient is positive when the condensation of particle happen in the colder region and it is negative when the particles move to the high temperature region. In most experimental observations the Soret coefficient appears to be positive, but examples of negative sign are also common in charged systems.^{13,14}

In this article, we focus on a simplified picture for the internal structure of a colloidal particle. We model a colloidal particle with two rigid spheres connected by one linear spring. With this modeling, we can include the geometrical and elastic properties of the colloid. In Sec. 2, we briefly review the hydrodynamic equations for the colloidal motion and calculate the positive Soret coefficient for a model colloidal

particle. The effects due to the hydrodynamic interaction in a dilute suspension of particles are presented in Sec. 3. In Sec. 4, we present our conclusions and discussion.

2. Dynamics of a Single Diffuser

To describe the motion of immersed objects in the fluid medium, dynamics of the flow field should be considered. To determine the flow regime, Reynolds has defined a dimensionless number which is the ratio of inertial forces to the viscous forces. In terms of a relevant length scale l , typical velocity U , fluid density ρ and fluid viscosity η , Reynolds number is given by: $Re = (\rho l U / \eta)$. A micron-sized colloidal particle moving with velocity $U = 10 \mu\text{m/s}$ in water ($\rho = 10^3 \text{ Kg/m}^3$, $\eta = 10^{-3} \text{ Pa}\cdot\text{s}$), has a Reynolds number $Re = 10^{-5}$. This extremely low value for Reynolds number suggests that any inertial effect in the colloidal dynamics can be neglected.

In the low Reynolds regime, where the frictional forces dominate over the inertial effects, the Stokes equation governs the dynamics of fluid flow. Denoting the velocity and pressure field by $\mathbf{u}(\mathbf{r})$ and $p(\mathbf{r})$ respectively, the Stokes equation is a linear equation with respect to the velocity field. The Stokes equation relates the flow field to the external force distribution $\mathbf{f}(\mathbf{r})$ by:

$$-\eta \nabla^2 \mathbf{u}(\mathbf{r}) + \nabla p(\mathbf{r}) = \mathbf{f}(\mathbf{r}), \quad \nabla \cdot \mathbf{u}(\mathbf{r}) = 0, \tag{1}$$

where the incompressibility condition is also assumed. Since the Stokes equation is linear, the relation between velocity of solid bodies and viscous forces acting on particles is linear.

Figure 1 shows a schematic view of a linear macro-molecule with a prescribed internal structure, immersed in a fluid medium with temperature gradient. The internal structure of this colloidal particle is modeled by two spheres with radius a

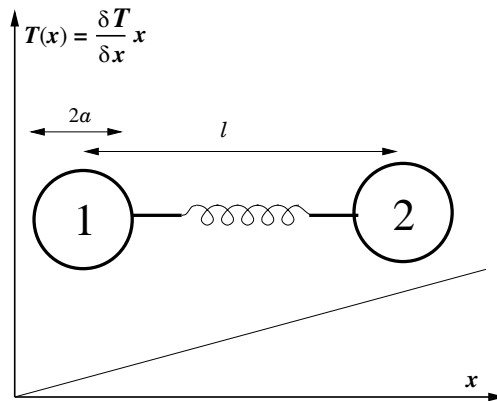


Fig. 1. Schematic view of a microscopic tracer immersed in a viscous fluid medium. Two spheres with radius a are connected by a linear spring with average length l . The system is immersed in a fluid medium with nonuniform temperature field. In the neighborhood of the diffuser, the temperature field is varying linearly with $\nabla T = (\delta T / \delta x) \hat{x}$.

that are connected by a linear spring. The equilibrium length of the spring is denoted by l and its stiffness is given by K . This modeling allows us to investigate the role of hydrodynamic interactions in the motion of colloid. A nonuniform temperature field $T(x)$, is applied to this diffuser. Non-equilibrium nature of the fluctuations make the analysis of this system difficult. For a very slowly varying temperature field, we can use the local equilibrium approximation.

We denote by f_i , the hydrodynamic force acting on the i th spherical particle that is located at position x_i . The forces and velocities of the spheres obey the linear relations:

$$\begin{cases} \frac{dx_1}{dt} = M_{11} \times f_1 + M_{12} \times f_2, \\ \frac{dx_2}{dt} = M_{21} \times f_1 + M_{22} \times f_2, \end{cases} \tag{2}$$

where M_{ij} is the hydrodynamics interaction between i th and j th spheres. The hydrodynamic interaction depends on the sphere radius and also on the distance between them. For the case where the distance between spheres is very larger than the size of sphere, a perturbative result for the hydrodynamic interaction is given by the Oseen tensor.^{15,16} For the present one-dimensional geometry, the Oseen's hydrodynamic interaction is given by:

$$M_{ii} = \frac{1}{6\pi\eta a}, \quad M_{ij} = \frac{1}{8\pi\eta|x_i - x_j|}. \tag{3}$$

Here we should emphasize that this result is a perturbative result which can be systematically extended it for spheres with larger radius. To finish the formulation we should note that, at zero Reynolds number, the hydrodynamic force acting on each sphere should be balanced by the other forces acting on it. Thermal noise and spring force are the forces that should be balanced. Writing the spring force acting on the first sphere as $F = -K(x_2 - x_1 - l)$ and denoting the thermal noise acting on this sphere by ζ_1 , now for the two spheres we will have:

$$f_1 = \zeta_1 + F, \quad f_2 = \zeta_2 - F. \tag{4}$$

In the local thermal equilibrium with local temperature, the stochastic thermal white noise obey the following correlation functions:^{17,18}

$$\begin{cases} \langle \zeta_i(t) \rangle = 0, \\ \langle \zeta_i(t)\zeta_j(t') \rangle = 2M_{ii}^{-1}k_B T(x_i)\delta_{ij}\delta(t - t'), \end{cases} \tag{5}$$

where $k_B T(x_i)$ is the local thermal energy for the i th sphere. For simplicity, we have neglected the hydrodynamic coupling between the noises acting on different spheres. For a diffuser in a temperature gradient with local equilibrium approximation, an instantaneous net drift velocity can be achieved. To simplify the calculations, we assume that the distance between the two spheres can be considered as an average length l and a small deformation around this average value by: $x_2 - x_1 = l + \epsilon(t)$.

Additionally we denote the position of the system’s center by: $R(t) = (1/2)(x_1 + x_2)$. With these new variables and for small amplitude noise and small deformation of the spring, the dynamical equations read:

$$\begin{aligned} \dot{\epsilon}(t) &= A(\zeta_2(t) - \zeta_1(t)) - 2KA\epsilon(t) + \mathcal{O}(\epsilon^2), \\ \dot{R}(t) &= B(\zeta_2(t) + \zeta_1(t)) - C(\zeta_2(t) + \zeta_1(t))\epsilon(t) + \mathcal{O}(\epsilon^2), \end{aligned} \tag{6}$$

where $A = (1/6\pi\eta a - 1/8\pi\eta l)$, $B = (1/6\pi\eta a + 1/8\pi\eta l)$ and $C = 1/8\pi\eta l^2$. We solve these governing equations for very small deformation. After solving these equations and expanding the results for small sphere’s radius limit, we can average the results over a long time to obtain the average drift velocity. For average drift velocity, we will obtain:

$$V = \frac{1}{T} \int_0^T \dot{R}(t) dt = -\frac{k_B}{8\pi\eta l} \nabla T, \tag{7}$$

where $\nabla T = (T(x_2) - T(x_1))/l$. As one can see, the diffuser is moving from hotter to colder region. An interesting observation is the point that, at small $\epsilon(t)$ approximation, the average velocity does not depend on the spring constant and the size of spheres. Equilibrium distance between the two spheres is the relevant length scale that appears in the velocity. The spring constant, the elastic properties of the colloids, can affect the short time behavior of the system.

Soret coefficient, which is the most important macroscopic measurable quantity in thermodiffusion phenomena, is defined as the ratio of thermal to self diffusion coefficients as: $S_T = D_T/D$. Thermal diffusion coefficient relates the particle velocity to temperature gradient as: $v = -D_T \nabla T$. Assuming local thermal equilibrium, we can use Einstein’s relation to relate the self diffusion of particle to its mobility μ and local temperature T as: $D = \mu k_B T$ (See Refs. 17 and 18). Regarding the fact that our system consists of two small spheres, we see that the friction coefficient of the colloid in the longitudinal direction is approximately two times the single sphere’s friction.¹⁶ In this case, the mobility of colloidal particle is given approximately by $\mu = 2/6\pi\eta a$. Collecting all these informations we can obtain the Soret coefficient as:

$$S_T = \frac{3}{8} \left(\frac{a}{l}\right) \frac{1}{T}. \tag{8}$$

As one see, a geometrical prefactor a/l appears in the Soret coefficients. This is the influence of hydrodynamic interactions in the Soret phenomena.¹³

Another interesting phenomena which we can consider here, is the effect of temperature gradient in a sedimenting system. In this case, an external gravitational force can be compensated by the Soret force and eventually leads the system to a state with levitating particle. Denoting the strength of external gravitational force acting on a single colloid by f_{ext} , we see that a temperature gradient: $k_B \nabla T = (4/3)(l/a)f_{\text{ext}}$ is sufficient to levitate the particle. In this simplified picture, we have assumed that the external force is applied to the particle in the longitudinal direction, along the two spheres’ linker.

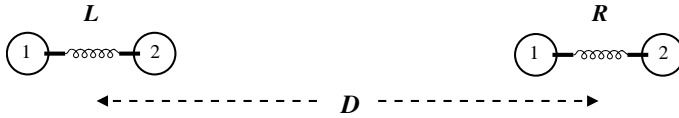


Fig. 2. Two diffusers, L (Left) and R (Right), separated by a distance D are coupled by hydrodynamic interactions.

3. Two Diffusers

In this section, we consider an interacting system of two diffusers moving in a temperature gradient field. The results of this section will be useful in analyzing a very dilute suspension of diffusers.

As shown in Fig. 2, two diffusers, left (L) and right (R), are forced to move along a one-dimensional line. The dynamical equations describing this system read:

$$\frac{dx_i}{dt} = \sum_{j=1}^4 M_{ij} \times f_j, \tag{9}$$

where, as before, f_i stands for the hydrodynamic force acting on the i th sphere and M_{ij} is the hydrodynamic interaction between i th and j th sphere. As before, stochastic forces with strength proportional to the local temperature is acting on each sphere.

For the case where the distance between diffusers is much larger than the average size of each diffuser, we can set up a perturbative expansion for the dynamical equations. Denoting the distance between diffusers by $D = 1/2(x_4 + x_3 - x_1 - x_2)$, we define a small parameter $\lambda = l/D$, where l is the average linear size of each diffuser. In the zeroth order of λ , two diffusers are decoupled and the previous results for each individual diffuser will retain. To investigate the effect of hydrodynamic coupling, we can proceed to the higher-order correcting terms.

Following the method which we used for a single diffuser and for small deformation limit, we can solve the system of two diffusers. Again expanding the final results for small sphere approximations, we will obtain the following approximate average drift velocities for each diffuser:

$$\begin{aligned} V_L &= - \left(\frac{k_B}{8\pi\eta l} \right) \nabla T(L) + \frac{1}{4\eta D^2} \left(1 + \frac{3}{4} \frac{al}{D^2} + \mathcal{O}(l/D)^4 \right) k_B T(R), \\ V_R &= - \left(\frac{k_B}{8\pi\eta l} \right) \nabla T(R) - \frac{1}{4\eta D^2} \left(1 + \frac{3}{4} \frac{al}{D^2} + \mathcal{O}(l/D)^4 \right) k_B T(L). \end{aligned} \tag{10}$$

As one can see, the average drift velocity of each colloid, has a contribution from hydrodynamic interactions with the other particle. The hydrodynamic enhancement of the drift velocity for a diffuser, has appeared to depend on the local temperature at the position of the other diffuser. One should note that this result is valid only in the limit of very slowly varying temperature field. The correction terms in the velocity of each diffuser, show an overall attraction between colloidal particles. This

means that, in nonuniform temperature field, our modeled colloidal particles will eventually condense in the colder region.

4. Discussion and Concluding Remarks

The main purpose of this work is to introduce a simplified model for investigating the phenomena of thermophoresis and also analyzing the role of hydrodynamic interactions in a dilute suspension of colloidal particles. We use a very simplified internal structure for a single colloidal particle and obtain a size-dependent Soret Coefficient. The model system which we use, is able to capture the geometrical as well as elastic properties of the particles. As we have shown, in the small deformation limit and for the long time experiments, the elastic properties may not have a relevant manifestation in Soret coefficients.

The D^{-2} dependence of the interaction term in the velocity, is related to the absence of net body force in the motion of colloid. In the first approximation, the far field distribution for a force-free, translating particle, should behave like D^{-2} , that is the characteristic velocity profile of a force dipole at low Reynolds regime.

It will be interesting to use the simplified model proposed here, for more realistic cases. Inspired by the drift motion of charged colloidal particles, we are extending our model to investigate the electrostatic effects for charged colloidal particles.

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