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Kinetic theory of colloid thermodiffusion

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Abstract

The Kramers' equation of Brownian motion is applied to investigate the motion of a colloidal particle in a medium subjected to a temperature gradient. The equation is generalized in two ways. First, a chemical force is included in order to account for the non-ideality of the colloidal solution, in the thermodynamic sense. Second, the local disequilibrium of the medium gives rise to a force proportional to the temperature gradient, known as the thermophoretic force in the physics of gases. It is found that the latter force dominates in a rarefied gas, while the chemical force is a good candidate in liquid solutions. The description of the cross-over regime is still unsatisfactory. Next, given the force undergone by a colloidal particle, regardless of its physicochemical origin(s), we determine the velocity response. It is demonstrated that the velocity is *not* proportional to the applied force, in variance with the Stokes' law of viscous drag invoked in many works and valid in thermally homogeneous media. An additional effective force tends to drive the particle toward places of higher mobility; that effective force is also proportional to the temperature gradient and can be of the same order of magnitude as the applied force. This conclusion is reached in two different ways, using either a transport equation or statistical-dynamical relations akin to the Ehrenfest theorem in quantum dynamics. Finally, the theoretical formula for the Soret coefficient shows that it is neither proportional to the velocity nor to the force.

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1. Purpose and scope

The motion of a colloidal particle in a medium held at a uniform temperature has been thoroughly investigated. In the absence of an external force such as gravity, the particle undergoes a Brownian motion characterized by a diffusivity D entering Fick's diffusion law. In the presence of an external force $\mathbf{F}$, a drift superimposes onto the diffusion. The drift mobility μ is related to the diffusivity D through the Nernst–Einstein relation $D = kT\mu$ if the colloidal solution is ideal in the thermodynamic sense (k is the

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Boltzmann's constant and T the temperature). The comprehensive theory of Brownian motion is based upon the Kramers' equation and is successful in explaining many properties of colloidal solutions [1,2]. When the solution is the seat of a temperature gradient, the motion of a colloidal particle no longer reduces to Brownian motion. In the absence of **F**, it is observed that the particles tend to congregate near the colder or warmer boundary, and this is phenomenologically described by writing the particle current density as

$$\mathbf{j} = -D\,\mathbf{grad}\,n - DS^{*}n\,\mathbf{grad}\,T, \tag{1}$$

where n is the particle number density and S^{*} is called the Soret coefficient. Various equivalent expressions exist where **j** is a linear combination of $\mathbf{grad}\,x$ and $\mathbf{grad}\,T$, and x is either the mole [3] or mass [4] or volume [5] fraction of the solute, i.e. the colloid. The solution is taken to be isobaric, so that **j** is a function of $\mathbf{grad}\,n$ and $\mathbf{grad}\,T$ only, with no barodiffusion current proportional to the gradient of pressure. In (1), Fick's diffusion current is supplemented with a thermodiffusion current proportional to $\mathbf{grad}\,T$. Thermodiffusion is also named the Soret or Ludwig–Soret effect, after the discoverers of that effect in liquids [6,7]; it was later observed in gases [8]. Formally, the thermodiffusion current looks like a drift current caused by an effective force $-\alpha\,\mathbf{grad}(kT)$ with D/kT as the mobility, where

$$\alpha = TS^{*}, \tag{2}$$

will be called the dimensionless Soret coefficient in this paper.

Thermodiffusion has been discovered 150 years ago and studied independently in distinct areas. When the solute is a macromolecule, it is usual to call *thermophoresis* its motion in a temperature gradient [9–12], in analogy with electrophoresis, which is the motion of a charged solute in an electric field. Thermophoresis refers to a particle velocity (in $\mathrm{m\,s^{-1}}$) while thermodiffusion refers to a current density (in $\mathrm{m^{-2}\,s^{-1}}$). The latter concept explicitly involves ordinary (Fick's) diffusion, whereas thermophoresis is only concerned with the directed motion, with no attention being payed to fluctuations. The reader is warned about the frequent confusion between motion (thermophoresis) and transport (thermodiffusion) [13]. Practically speaking, the effect for small molecules, or for gaseous or liquid mixtures, is more often referred to as thermodiffusion, while for suspensions of large particles in gases or in liquids, it is more often referred to as thermophoresis. This work is restricted to strongly asymmetric binary systems of colloidal particles in a solvent.

A recent review [14], devoted to both ordinary and colloidal solutions, shows that several theoretical approaches exist that generally do not offer a microscopic view of thermodiffusive transport. Since then, other theoretical proposals have appeared [15–18]. Dhont's approach [19] is concerned with thermodiffusion due to interaction between the colloidal particles, and has been applied to concentrated solutions [20]. However, thermodiffusion can be strong in dilute solutions as well, and does not need an intercolloidal interaction for its existence. The present paper seeks an explanation of thermodiffusion that does not rely on an intercolloidal interaction, and is able to account for thermodiffusion in dilute colloidal solutions.

Given that thermodiffusion of colloidal particles is a perturbation of the Brownian motion, it is natural to reformulate the Kramers theory of Brownian motion in an inhomogeneous temperature field. This has been done by van Kampen [21] who obtained Eq. (1) with $TS^{*} = 1$. Experiments performed on colloids with a core of γ-$\mathrm{Fe_2O_3}$ give values of TS^{*} ranging between -75 and $+51$, depending on the coating (ionic or surfacted) and on the solvent (organic or aqueous), including the pH of the aqueous solvent; this has been confirmed by several independent experimental techniques which give consistent values of S^{*} [5,22,23]. Other colloidal systems [14] exhibit $|\alpha| \gg 1$ as well. The problem is to account for a factor of typically ± 50 between the observed and expected values of α. Now there are two notable assumptions in the original Kramers' equation: (i) thermodynamically speaking, the solution is an ideal binary mixture of colloid and solvent [24], and (ii) the solvent is in thermal equilibrium. Regarding assumption (i), since thermodynamic non-ideality is known to affect diffusion [3,25], it might affect thermodiffusion as well. Regarding assumption (ii), the solvent is not in equilibrium although it is at rest, because it is traversed by a heat current directed against $\mathbf{grad}\,T$. The simple device of plugging temperature-dependent coefficients in the Kramers' equation implicitly assumes that equilibrium continues to hold when temperature depends on position; but that is not true because a heat current is flowing. Similarly, van Kampen [26] had shown that plugging position-dependent coefficients in a Smoluchowski's equation originally devised to describe transport in a homogeneous medium is often incorrect