



# Brownian movement and thermophoresis of nanoparticles in liquids



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## ABSTRACT

Thermophoresis is the realization of the averaged Brownian motion of particles in a fluid, which is subject to a steady temperature gradient. At sufficiently long times, the stronger molecular impulses in the hotter fluid region drive particles towards the colder region, where the molecular impulses are weaker. The effect of the molecular impulses on the particles is described by a stochastic Brownian force. When this force is applied to an ensemble of particles the thermophoretic velocity is the average velocity of the ensemble. In this study the motion of an ensemble of 4000 spherical nanoparticles with the material properties of CNT, aluminum, aluminum oxide, copper and gold was simulated in four base liquids—water, ethyl glycol, engine oil and R134a. The ensemble-averaged results generate the thermophoretic velocity of these particles in the base liquids. It was observed that the computational results agree very well with the few experimental data available for liquids. The computational method is general and may be applied to all heterogeneous systems of nanoparticles in liquids. The numerical results yield very useful information on the process of thermophoresis in liquids as well as values of the thermophoretic coefficients in nanofluids.

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## 1. Historical background and introduction

The predominant philosophical framework of the early 19th Century science accepted the *vis vitalis* theory, that life processes take place because of a nonmaterial “vital force” that cannot be entirely explained by physical forces and science. With the advent of quantitative chemistry and the development of several branches of biology, such as botany and zoology in the early 19th Century, several scientists set upon discovering this “vital force” or at least obtaining enough information to describe its characteristics. One of these scientists was the Scottish botanist and physician Robert Brown, who in 1827 began to make detailed microscopic observations of suspensions of small pollen particles in water. To his surprise, the suspended pollen particles appeared to be in constant and chaotic, movement. Detailed observations by Brown proved that the particle movement was not due to the influence of high temperature or light. Moreover, the movement appeared to be continuous and never slowed down or stopped. The observation was very exciting for Dr. Brown because he first concluded that he had seen the realization of *vis vitalis* and that the pollen particles exhibited the characteristics of life. However, he ruled out this idea after he observed that other particles, composed of inorganic minerals also engaged in the interminable dance we now call Brownian movement. He also observed that the Brownian movement of par-

ticles occurred in several liquids, not only in water, which is the fluids that life manifests itself, but in other fluids, several of which (e.g. acid solutions) are harmful to life. Dr. Brown essentially showed that this incessant movement of small particles was not part of biology, but part of physics [1,2].

The significance of this first observation of the Brownian movement was largely unnoticed until the end of 19th Century when Louis Georges Gouy suggested that the Brownian movement might offer a “natural laboratory” in which to examine directly the recently developed kinetic theory of matter. In particular, he suggested that Brownian movement may be the key to understand and reconcile the reversible framework of kinetic theory with the irreversible nature of the 2nd Law of Thermodynamics [2]. Shortly thereafter, Einstein, who also had an interest in Thermodynamics, realized that micron-size particles that may be seen in a microscope are influenced by the molecular motion. He came to the brilliant conclusion that one could use these particles as an instrument to “see” and draw conclusions about the motion of the invisible atoms and molecules [3]. Einstein showed that the chaotic, incessant movement of the fluid molecules is reflected on the micron-size particles, which undergo a different chaotic movement and disperse in a fluid. He proved that in an isothermal fluid the dispersion coefficient is:

$$D_0 \equiv \frac{d}{2dt} \langle \vec{x} \cdot \vec{x} \rangle = \frac{k_B T}{6\pi\alpha\mu_f}, \quad (1)$$

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where  $k_B$  is the Boltzmann constant;  $T$  is the absolute temperature;  $\alpha$  is the radius of the particle; and  $\mu_f$  is the dynamic viscosity of the fluid. This expression is oftentimes called the Stokes–Einstein diffusion coefficient.

### 1.1. Continuum description of the Brownian movement

Another way of looking at the Brownian movement in a continuum framework, without the stipulation of the molecular motion, and draw conclusions in a mechanistic, Newtonian framework, is that the particle movement is the consequence of a random force, which continuously acts on the individual particles. This continuum framework is very useful in conducting Monte-Carlo simulations of particles. The random force that causes particle diffusion that is equal to the Stokes–Einstein dispersion is [4]:

$$\vec{F}_{Br} = \vec{R} \sqrt{\frac{12\pi k_B T \alpha \mu_f}{\Delta t}}, \quad (2)$$

where  $\vec{R}$  is a random vector with Gaussian random number components of zero mean and unit variance; and  $\Delta t$  is the time interval of action of the random force. It must be noted that when this random force is integrated over a long time  $t$  ( $t \gg \Delta t$ ) the results of the particle dispersion are independent of the choice of the interval  $\Delta t$  and yield the Stokes–Einstein diffusion coefficient of Eq. (1). This analytical result was tested in the M-C simulations of Section 3 by taking several values of the interval  $\Delta t$  and integrating over times  $t$  of the order of  $1,000,000\Delta t$ , to derive results for the dispersion coefficient  $D_0 \equiv \frac{d}{2dt} (\vec{x} \cdot \vec{x})$ . At these long times, it was observed that the dispersion coefficient,  $D_0$ , was independent of the choice of the time interval,  $\Delta t$ . For this reason, in the simulations of Section 3 the choice  $\Delta t = 0.1\tau_p$  was made (see Eq. (20)) where  $\tau_p$  is the characteristic time of the particle.

Thermophoresis is an interesting consequence of the Brownian movement of particles in fluids with an externally sustained and constant temperature gradient: It becomes apparent from Eqs. (1) and (2) that particle dispersion is higher and the Brownian force is stronger when the local fluid temperature is higher. When there is a temperature gradient in the flow domain of the suspension, small particles disperse faster in hotter regions and slower in colder regions. The collective effect of the differential dispersion of the particles is their migration from hotter to colder parts of the fluid domain. That is, in the presence of a temperature gradient, particles move on the average against this gradient. The averaged motion of the particles has been known as *thermophoresis*. The phenomenon of thermophoresis was first observed by Tyndall, when he saw that aerosol particles in a dust-filled room were driven away from a heated surface [5] but was not studied in detail until the 20th Century. Tyndall did not connect thermophoresis to the molecular impulses on particles [5].

It must be noted that the particles in suspension will not fully accumulate in the colder region. Interparticle collisions in the colder regions, where the particle concentration becomes higher, would disperse the particles stronger than in the hotter regions, where the particle concentration is lower. Thus, in the absence of other dispersion mechanisms – such as turbulence, velocity fluctuations, shear forces, lift forces, etc. – a dynamic equilibrium for the particle concentration will be established, with lower particle concentrations in the hotter regions and higher concentrations in the colder regions [4].

Epstein [6] was the first to perform an analytical, quantitative study on the thermophoresis of particles in gases using a continuum mechanics approach. This approach is valid in the “continuum flow” regime of gas–particle interactions, which is characterized by small Knudsen numbers, less than 0.1 ( $Kn = \lambda/\alpha < 0.1$ , where  $\lambda$  is the mean free path of the gas molecules) [7].

Epstein [6] used a continuum model for the hydrodynamic and thermal gas–particle interactions but allowed velocity and temperature discontinuities at the interface. He derived the following expression for the average thermophoretic velocity and the associated thermophoretic force:

$$\vec{V}_{tp} = -\frac{3}{2} \frac{k_f}{2k_f + k_p} \frac{\mu_f}{\rho_f} \frac{\vec{\nabla}T}{T_\infty}, \quad (3)$$

$$\vec{F}_{tp} = 6\pi\mu_f\alpha\vec{V}_{tp} = -9\pi\alpha \frac{k_f}{2k_f + k_p} \frac{\mu_f^2}{\rho_f} \frac{\vec{\nabla}T}{T_\infty}, \quad (4)$$

where  $k_f$  and  $k_p$  are the thermal conductivities of the fluid and the particles. The thermophoretic force is the steady force that would induce the steady thermophoretic velocity when acting alone on the particles with the Stokesian drag being the resisting force.

Brock [8] and later Talbot et al. [9] performed more detailed analytical derivations of thermophoresis in gases, also in the continuum flow regime ( $Kn < 0.1$ ). Brock used thermal slip at the interface and Basset’s expression [10] for the velocity slip. He derived the following expressions for the thermophoretic velocity and the corresponding force:

$$\vec{V}_{tp} = -\frac{2C_s(k_f + k_p)Kn}{(1 + 3C_m)Kn(2k_f + k_p + 2k_s C_t)Kn} \frac{\mu_f}{\rho_f} \frac{\vec{\nabla}T}{T_\infty} \quad (5)$$

$$\vec{F}_{tp} = -\frac{2C_s(k_f + k_p)Kn}{(1 + 3C_m)Kn(2k_f + k_p + 2k_p C_t)Kn} 6\pi\mu_f^2\alpha \frac{\vec{\nabla}T}{\rho_f T_\infty}.$$

The parameters  $C_s$ ,  $C_m$  and  $C_t$ , were determined empirically from the flow field around the particles and the discontinuities on the gas–particle interface. The original suggestion by Brock is:  $C_s = 0.75$ ,  $C_m = 1.14$  and  $C_t = 2.18$ . Talbot et al. [9] performed a very similar analysis, but used the velocity slip expression that was recommended by Millikan for a droplet in air [11]. Their expressions for the thermophoretic velocity and force are as follows:

$$\vec{V}_{tp} = -\frac{2C_s(k_f + k_p)Kn[1 + Kn(1.2 + 0.41 \exp(-0.88/Kn))]}{(1 + 3C_m)Kn(2k_f + k_p + 2k_p C_t)Kn} \frac{\mu_f}{\rho_f} \frac{\vec{\nabla}T}{T_\infty}$$

$$\vec{F}_{tp} = -\frac{2C_s(k_f + k_p)Kn[1 + Kn(1.2 + 0.41 \exp(-0.88/Kn))]}{(1 + 3C_m)Kn(2k_f + k_p + 2k_p C_t)Kn} 6\pi\mu_f^2\alpha \frac{\vec{\nabla}T}{\rho_f T_\infty}. \quad (6)$$

They determined that the best fit with experimental data is with  $C_s = 1.17$ ,  $C_m = 1.14$  and  $C_t = 2.18$  in the range  $Kn = \lambda/\alpha < 0.1$ . The higher value of the constant  $C_s$  than the one proposed by Brock yields more accurate results for the thermophoretic velocity in gases [7,12]. The thermophoretic velocity and force of Eqs. (5) and (6) reduce to the expressions obtained by Epstein [6] Eqs. (3) and (4) when  $Kn = 0$ .

Derjaguin and Yalamov [13] adopted a different analytical approach and determined the thermophoretic velocity using the theory of non-equilibrium thermodynamics. The latter provides a methodology to determine the transport coefficients in coupled processes at near-equilibrium states. As a consequence, the results of the methodology may not be extended to high non-equilibrium states, e.g. at very high temperature gradients. Derjaguin and Yalamov obtained a slightly different formula for the thermophoretic velocity of relatively large aerosol particles allowing for the effects of the temperature slip at the fluid–particle interface. The functional form of this relationship is similar to Eq. (5). Actually, the two equations give identical results with a suitable choice of the three constants  $C_s$ ,  $C_m$ , and  $C_t$ .

Most of the analytical and experimental studies on thermophoresis were performed with fine particles in gases. The case of thermophoresis of particles in liquids is quantitatively different because of the following reasons:

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