On thermophoresis modeling in inert nanofluids

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ABSTRACT

Thermophoresis plays an important role in forced and natural convection in channels and enclosures when nanofluids are used instead of pure fluids. One objective of this work, therefore, is to investigate whether reliable expressions exist for the estimation of thermophoresis data. As the second objective of this work we will show similarities between thermophoresis of nanoparticles and macromolecule dispersed in a base fluid with thermodiffusion of species in binary mixtures. To this end, a nonequilibrium thermodynamics-based expression primarily developed for the estimation of thermodiffusion factor in binary mixtures is extended and applied to thermophoresis in nanofluids. A hydrodynamics-based expression and the nonequilibrium thermodynamic-based expression developed here, are used to estimate the thermophoretic velocity in nanofluids. Validation results suggest that the general form of the hydrodynamics-based equation is valid for thermophoresis of nano-sized and even sub-nanometer particles in liquids; however, the correct prediction of the matching parameter is still unresolved. Also, the nonequilibrium thermodynamics combined with the concept of activation energy of viscous is somewhat capable of estimating thermophoresis coefficient of inert particles and macromolecules of about 1 nm or smaller. The agreement, however, is qualitative.

1. Introduction

In addition to a concentration gradient, a temperature gradient can also work as a driving force for mass diffusion in Brownian mixtures of two or more species, in a phenomenon called thermodiffusion (thermal diffusion), or in liquid mixtures Soret (Ludwig–Soret) effect. Temperature-gradient induced motion of macroscopic or non-Brownian particles suspended in a carrier liquid or gas is called thermophoresis. In thermodiffusion, a time-independent temperature gradient (thermal field) is maintained across the mixture, causing all species to become activated and move in response to the thermal field. The thermal field directly or indirectly (via inducing density gradients for instance) exerts forces on all molecules and particles in the mixture, forcing them to move, usually, in the direction of the heat flow, i.e. from the hot side to the cold side. At steady state, however, the molecules reach their final arrangement such that the more thermophobic component is concentrated on the cold side [1]. Predicting which component is more thermophobic, is sometimes a cumbersome modeling task. In thermophoresis of dilute particles, the fluid is assumed unaffected while the particles respond to the temperature gradient. In thermophoresis of a mixture of inert or neutral particles in a fluid, usually the particles move toward the cold side, i.e. particles are more thermophobic compared to the molecules of the carrier. In thermodiffusion of a binary mixture of nonionic, non-associating mixtures, assuming that interfacial forces are insignificant and negligible, the denser component migrates to the cold side. The presence of strong interfacial forces between the mixture components is called the chemical contribution to the Soret effect and makes the analysis and modeling of the problem very difficult [2].

Some workers believe that thermophoresis and thermodiffusion are the same phenomenon observed for different systems. This is true in a sense, because in both processes, a temperature gradient causes activation and movement of the species. But at the present, there is no single theory that can be used to simultaneously simulate and explain it when the size of involved particles/molecules changes. In other words, the range of applicability of existing thermophoresis and thermodiffusion theories is limited. In this context, some scientists have substantiated the differences between thermophoresis and thermodiffusion, e.g., Brenner and coworkers [3,4]. Thermophoresis is more a macroscopic phenomenon concerning motion of non-Brownian particles of sizes much greater than the

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Nomenclature

A	solvent-particle Hamaker constant
c_p	specific heat capacity of the fluid at constant pressure
C_s	a constant in Eq. (3)
D	diffusion coefficient
D_T	thermophoresis or thermodiffusion coefficient also called particle mobility
D_T^H	hydrodynamic-based thermodiffusion coefficient
D_T^{LNET}	linear non-equilibrium thermodynamics based thermodiffusion coefficient
$D_T^{Semenov}$	Semenov's thermodiffusion coefficient
E_i^{vis}	activation energy of viscous flow of component i
k, k_p	thermal conductivities of fluid and particle, respectively
Kn	Knudsen number
N_A	Avogadro's number

Pr	Prandtl number
Q_i^*	net heat of transport of component i
r_0	molecular radius of the solvent molecules
R	gas constant
T	mixture average temperature
U_T	thermophoresis velocity
v	specific volume
V	solvent molar volume
x_i	molar fraction of component i

Greek letters

α	thermodiffusion factor
β	liquid volume expansion coefficient
μ_i	chemical potential of component i
η	liquid viscosity
ρ	liquid density

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size of the molecules of the carrier liquid and therefore may be handled using the hydrodynamic theory with satisfactory results. Thermodiffusion, on the other hand, is a molecular phenomenon and is described by a variety of theories such as nonequilibrium thermodynamics and kinetics, although hydrodynamics theory has been used as well. In binary thermodiffusion, the two constituent substances are usually fluid at room temperature, are of comparable molecular sizes and are mixed or dissolved. We believe that despite the distinction, there are similarities between the two phenomena in the asymptotic limit, i.e. when the particle size in thermophoresis approaches the molecular size of the carrier fluid (~ 1 nm), the thermophoresis problem may be treated as a thermodiffusion problem and vice versa. As an example, Soret effect in polymer solutions (the order of magnitude of polymer molecules radius is about 1 nm) is sometimes called thermodiffusion, e.g. Refs. [5–7], and sometimes as thermophoresis, e.g. Refs. [8,9]. In DNA solutions, which are very similar to polymer solutions, the term thermophoresis is used for temperature gradient manipulation of DNA molecules [10,11]. As mentioned earlier, the hydrodynamics approach, which is more applicable to thermophoresis of non-Brownian particles, has been used to model thermodiffusion of binary mixtures [12] as well, showing the fine boundary between thermophoresis and thermodiffusion when particles are small enough. Therefore, the dual thermophoresis/thermodiffusion modeling may be applicable to nanoparticle mixtures (nanofluids) as well [13]. Thus, the focus of this work is to study the phenomenon that falls between the definition of thermophoresis and thermodiffusion. This is of particular importance given that thermophoresis/thermodiffusion is present in the heat transfer phenomenon in microchannels and enclosures when liquid nanofluids are used instead of pure liquids, to augment the heat transfer rate [14].

The nanofluids literature is currently overwhelmed with erroneous interpretation regarding the role of thermophoresis in nanofluids heat transfer. We limit our analysis to thermophoresis of inert or neutral particles in which the interfacial and electrical forces between the liquid and particle surface are absent or minimized.

2. Theoretical background

Bringuier [15] studied the similarity between the physics of binary mixtures and suspensions in a liquid under a temperature gradient. Bringuier has mathematically shown that the unary diffusion coefficient of particles in the liquid in thermophoresis (D) is almost identical with the binary diffusion coefficient in thermodiffusion in a binary mixture. Bringuier [15] also derived the following equation that links the thermophoresis velocity of guest particles in a fluid U_T to the binary thermodiffusion coefficient of a dilute mixture of two species D_T:

$$U_T = \left(-D_T + \frac{\partial D}{\partial T} - \beta D \right) \nabla T \qquad (1)$$

where β is the liquid volumetric expansion coefficient. Note that the quantity U_T has units of velocity but it has been debated that it may not be necessarily identical with the velocity of particles [4]. Brenner [4] believes that the particle velocities in thermophoresis cannot be measured adequately, due to the presence of convection and other uncertainties. For instance, in an analysis performed by Brenner, it was revealed that the particle velocities measured by McNab and Meisen [16] may not be due to thermophoresis only. Brenner refers to U_T as thermodiffusion velocity to emphasize that it is an imaginary or virtual velocity rather than a velocity that can be actually measured [4]. In thermodiffusion, on the other hand, it may not be even experimentally possible to measure species transport velocities. Also, in steady state, species are at rest and there is no motion. This indicates that even if an actual velocity can be attributed to the species or particles, that velocity would be the initial particle velocity once a temperature gradient is applied on a homogenous mixture. Whether or not the particle or species transport velocity can be measured adequately, the unit of U_T is identical to that of the unit of velocity and it is called the thermodiffusion or thermophoretic velocity.

According to the Stokes–Einstein equation, Brownian diffusion coefficient (D) is related to fluid viscosity (η), mixture temperature (T) and particle radius (r) ($D = k_B T / 6\pi \eta r$, k_B being the Boltzmann constant). Assuming that for small temperature changes experienced in thermophoresis, fluid viscosity does not change significantly, and the rate of change of Brownian diffusion coefficient with respect to temperature is equal to $k_B / 6\pi \eta r$, for 1 nm size particles in water at 20 °C, $k_B / 6\pi \eta r$ is about 7×10^{-13} m²/s. Given that thermodiffusion coefficient (or thermal diffusivity) D_T is usually at least one order of magnitude greater than this number and the product of βD is a small number as well (smaller that D_T), to estimate thermophoresis velocity, it is justified to use the following equation, which is the simplified version of Eq. (1).

$$U_T = -D_T \nabla T \qquad (2)$$

Eq. (2) has been already used in the thermophoresis and thermophoresis literature, e.g. Refs. [3,4,8]. It correlates the