



Thermodiffusion of rigid particles in pure liquids

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ABSTRACT

Thermodiffusion of particles suspended in a pure liquid is a thorny problem which has not yet received a solution admitted by all the different communities interested in. We approach the subject with macroscopic tools exclusively, hydrodynamics and irreversible thermodynamics. These tools have proved their relevance for molecular mixtures and the Soret effect, and we here extend them to suspensions of particles with supra-molecular size. In particular, we obtain the momentum balance of the particulate phase from which are deduced all the physical phenomena inducing a migration of the particles relative to the carrier fluid. Focussing on thermodiffusion, we show that the osmotic pressure is irrelevant and that thermodiffusion cannot have but two distinct origins : the temperature dependence of the stress associated with the distorted particle microstructure and a fluid–particle interaction force involving the temperature gradient. For deformable particles, it is well known that the origin of the fluid–particle temperature gradient force is the temperature dependence of the surface tension. For rigid particles, we suggest it stems from the temperature dependence of the small density jump, the carrier liquid displays close to the particle's surface.

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1. Suspensions of particles vs. molecular mixtures

The main differences between suspension of particles in a carrier fluid and mixture of solute molecules in a solvent stem from the supra-molecular size of the solute. If the size of the solute exceeds about $0.1 \mu\text{m}$, it is called a particle and the particles can be considered as pieces of a first continuous medium. If the carrier fluid is not a rarefied gas, it can be considered as a second continuous medium embedding the particles. Hence, a suspension is made of two juxtaposed continuous media. However, it is clear that the transformation of wet air (a molecular mixture) into fog (a suspension) does not occur abruptly for a particular drop size and that the above-mentioned size is an order of magnitude only, suggesting an approximate condition for considering a new type of mixture. That mixture of two juxtaposed continuous media is then transformed into a single continuum of two interpenetrating media by means of averaging. The averaging process has far-reaching consequences. While the concept of sharing the total mass (associated with mass fractions) is clear for both molecular mixtures and suspensions, the concept of sharing the total volume (witnessed by volume fractions) is justified for suspensions but not for molecular mixtures because the true volume of a molecule is not defined unambiguously contrary to the true volume of a particle. As an example, the total mass ρ per unit volume can be written in all cases as

$$\rho = n_p m_p + n_f m_f \quad (1)$$

with n_k , the molecular number density and m_k , the molecular mass. But it is only when dealing with a suspension that one can write

$$\rho = \phi \rho_p + (1 - \phi) \rho_f, \quad (2)$$

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where $\phi = n_p \theta_p$ is the particle volume fraction, θ_p the mean particle volume, $1 - \phi$ the fluid volume fraction and ρ_k the mass per unit volume of pure phase k . Another remarkable difference between suspensions and molecular mixtures concerns the averaged velocity. Common to both suspensions and molecular mixtures is the mass-averaged velocity \mathbf{v} defined as

$$\mathbf{v} = c\mathbf{v}_p + (1 - c)\mathbf{v}_f, \quad (3)$$

where $c = n_p m_p / \rho$ is the mass fraction of the particles (or solute) while \mathbf{v}_k is the velocity of phase k . There is a second mean velocity, which is volume-weighted and unambiguously defined for suspensions only

$$\mathbf{u} = \phi\mathbf{v}_p + (1 - \phi)\mathbf{v}_f. \quad (4)$$

The role played by \mathbf{u} in suspensions is best seen when considering mass conservation which is expressed for both molecular mixtures and suspensions as

$$\frac{\partial n_k m_k}{\partial t} + \nabla \cdot (n_k m_k \mathbf{v}_k) = 0. \quad (5)$$

For a suspension of rigid particles suspended in an incompressible fluid mass conservation transforms into volume conservation expressed as

$$\frac{\partial \phi_k}{\partial t} + \nabla \cdot (\phi_k \mathbf{v}_k) = 0. \quad (6)$$

Because $\phi_p + \phi_f = 1$ an immediate consequence is $\nabla \cdot \mathbf{u} = 0$ while in general $\nabla \cdot \mathbf{v} \neq 0$.

Despite ϕ is relevant to suspensions only, one must acknowledge the existence, for molecular mixtures, of quantities *looking like* volume fractions. De Groot and Mazur [1] introduced $\bar{\theta}_p$ and $\bar{\theta}_f$ which have the dimension of a volume and are related to the pressure-derivative of the chemical potentials. Because of the Gibbs–Duhem relation these two quantities are such that $n_p \bar{\theta}_p + n_f \bar{\theta}_f = 1$ which is quite similar to the relation obeyed by the volume fractions. But as was suggested by Felderhof [2] it is only when the size of a solute molecule far exceeds that of a solvent molecule (in other words for suspensions) that $\bar{\theta}_p \approx \theta_p$ and consequently $n_p \bar{\theta}_p \approx \phi$.

Besides the relevance of quantities like ϕ and \mathbf{u} , suspensions of particles differ from molecular mixtures by the relative ease with which

- (a) the microstructure of the particles is distorted by non-uniform flows,
- (b) the relative motion between fluid and particles is created.

For a suspension of deformable particles what is meant by microstructure is mainly the particle shape while in case of rigid particles the microstructure is represented by the *relative position* of the particles characterized by the probability $g(\mathbf{R})$ of observing a particle at position \mathbf{R} when another particle is known to be located at the origin. For the solute molecules in a molecular mixture, that probability is so to say frozen at its equilibrium value while in suspensions that probability can be modified by any non-uniform flow, even a weak one. In case there exists direct inter-particle forces (Van der Waals or DLVO forces for example) the flow-induced deformation of the microstructure will have far-reaching consequences on the modeling of the stress associated with these colloidal forces and, as a consequence, on the relative motion induced by this inter-particle stress.

More generally, there will be many reasons for observing a relative motion in a suspension. In molecular mixtures the relative velocity occurs in the diffusion flux $\mathbf{J} = n_p m_p (\mathbf{v}_p - \mathbf{v})$ only and its role is neglected everywhere else. In suspensions the relative velocity is upgraded to the status of an *internal variable* (a variable which vanishes at equilibrium but plays a role out of equilibrium because of its long equilibration time) and one introduces a momentum balance for the particulate phase besides the momentum conservation for the whole suspension. The momentum exchange between the particles and the carrier fluid is linked to the relative velocity. Similarly one can introduce heat exchanges linked to a temperature difference between the two phases and a volume exchange linked to a pressure difference. However to simplify the issue we will assume in what follows that the suspension is depicted by a single temperature T and a single pressure p . That simplified description is justified for rather small and almost incompressible particles (say with a size less than 10 μm) because they have a very small equilibration time for pressure and temperature. Within this simplified model we will emphasize on the various forces exerted on the particles, and in particular the forces associated with a temperature gradient.

The paper is organized as follows: Section 2 details how the new status of the relative velocity and the presence of a non-equilibrium microstructure have an influence on the thermodynamics and the hydrodynamics of a suspension. Section 3 gives a general presentation of the two main origins of thermodiffusion in suspensions with due account for previous works while Section 4 presents a new approach of thermodiffusion in the special case of rigid particles suspended in a pure liquid.

2. Thermo-hydrodynamics of a suspension

2.1. Thermo-statics of suspensions

The materials from which the particles and the carrier fluid are made of have a free-enthalpy (or Gibbs potential or chemical potential) which per unit mass is given by $\mu_p^0(p, T)$ and $\mu_f^0(p, T)$ respectively. Upon mixing together the particles

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