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Fluid Phase Equilibria 243 (2006) 161–165
FLUID PHASE EQUILIBRIA
www.elsevier.com/locate/fluid

Non-equilibrium molecular dynamics calculation of thermal diffusion factor in binary mixtures of hard spheres

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Received 4 October 2005; received in revised form 26 February 2006; accepted 26 February 2006

Abstract

The thermal diffusion factor for binary mixtures of hard spheres was calculated by a direct non-equilibrium molecular dynamics simulation method. The results obtained showed that for equimolar isotopic binary mixtures of hard spheres, the thermal diffusion factor (TDF) increases with density at fixed mass ratios and increases with mass ratio at fixed packing fractions. The dependence of TDF on diameter ratio was also investigated and it was found that if the mass ratio is equal to 1 then larger species are accumulated in the warm region. The reciprocal of the thermal diffusion factor as a function of the mole fraction of the heavier component in two packing fractions was studied as well. The results obtained showed that inverse of thermal diffusion factor 1/TDF tends to be more linear when the mass ratio significantly differ from 1 and the diameter ratio is close to 1. These results are in good agreement with revised Enskog theory (RET). It was also found that those low density results continue to apply at higher densities too.

Keywords: Non-equilibrium molecular dynamics simulation; Hard sphere; Thermal diffusion factor; Soret effect

1. Introduction

Thermal diffusion or Ludwig–Soret effect is caused by the relative motion of components of a mixture due to the presence of a temperature gradient. As a result of this motion, composition gradient subsequently appears in the mixture, which produces ordinary diffusion that tends to eliminate the concentration gradient. A steady state is finally reached in which the separating effect arising from thermal diffusion is balanced by the remixing effect of ordinary diffusion [1]. A partial separation is then usually observed with heavy component in the colder region and light component in the hotter region. The magnitude of separation in thermal diffusion is described by phenomenological coefficients, the thermal diffusion factor (TDF) or Soret coefficient. This phenomenon was first observed in liquids by Ludwig [2] and later by Soret [3] and now is known as the Soret effect. Although the existence of thermal diffusion in gases had been suspected by Feddersen [4] in 1873, it was predicted theoretically by Chapman [5] and Enskog [6] simultaneously and later was confirmed in the experiments by Chapman and Dootson [7]. Thermal diffusion in dilute gas mixtures is well accounted for by the Chapman–Enskog theory of Boltzmann equation. The key applications are the investigation of the nature of intermolecular forces and the separation of mixtures.

The situation is less favourable in dense gases and liquid mixtures. Since the first approximate kinetic theory for hard sphere dense fluids, Enskog theories, many developments for binary and multicomponent mixtures of hard spheres have been proposed. In a series of four papers, Lopez de Haro, Cohen and Kincaid [8–11], have derived and discussed expressions for transport coefficients in dense fluid mixtures of hard spheres based on a consistent generalization of the classical Enskog theory to multicomponent hard sphere mixtures called the revised Enskog theory (RET). They have shown that the sign of thermal diffusion factor for hard sphere mixtures depends on the fluid density, composition, particle mass and diameter ratios. Some general trends for thermal diffusion factor in hard sphere mixtures are: (i) in mixtures of different mass species, the heavier component diffuses towards the cooler region; (ii) if the species have roughly equal masses, then the larger species diffuses into the cooler region. These trends are no longer valid if soft interactions are involved.

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doi:10.1016/j.fluid.2006.02.024

In the recent years, there has been a renewed interest in the thermal diffusion effect for liquid mixtures. Recently thermal diffusion forced Raleigh scattering (TDFRS) [12] have been used to measure the Soret coefficients in liquid mixtures. Debuschewitz and Köhler [13] have shown that the Soret coefficient can be split into independent contribution, a mass effect which is independent of composition, and a so-called chemical effect which is depends on the composition. The attempt to reveal the nature of thermal diffusion in soft sphere mixtures leads to the result that heavier species, smaller species and species with larger interaction strengths, tend to accumulate at the cold side [14–16]. The size dependence of thermal diffusion effect is so far not understood. Studies on the dependence of thermal diffusion on the molecular parameters [15,17,18] confirmed that the larger species move to the warm side. It is interesting that all studies on thermal diffusion by simulation methods have been carried out on the mixtures with soft interactions [19] and we have not found any molecular simulations of thermal diffusion in the mixtures of hard spheres in literature.

There are two categories in molecular dynamics of simulation method for studying thermal diffusion in mixtures, namely equilibrium molecular dynamics (EMD) and non-equilibrium molecular dynamics (NEMD) techniques. By using the EMD method, the transport coefficients can be obtained via Green–Kubo (GK) integrals over the relevant equilibrium correlation functions [20,21] or using the Einstein relation [22]. The NEMD methods generally impose a perturbing field on the system, the analysis of systems not in equilibrium, generated by molecular dynamics, provides a mean for determining the transport coefficients of dense fluid system in both linear and non-linear regimes. The method can in principle, yield new information about non-equilibrium states that cannot be obtained from the Green–Kubo method that has been used extensively.

The transport coefficients of the hard sphere fluid also are of key importance in understanding the dynamics and transport coefficients of real liquids [22]. The hard sphere fluid was the first kind of model molecular system to be simulated by Alder and Wainwright [23] by molecular dynamics method. Recently Sigurgeirsson and Heyes [22] studied systematically the transport coefficients of hard sphere fluid using equilibrium molecular dynamics simulation. The only study on thermal diffusion in mixtures of hard spheres by simulation methods was by Erpenbeck [24] for one diameter and mass ratio. The hard sphere model which implies only two parameters to define a molecule; its atomic mass and diameter, is particularly adopted to study the dependence of TDF on the mass and diameter of the fluid particles. The dependence of thermal diffusion to the molecular parameters in hard sphere mixtures was not studied by simulation methods. The influence of the molar fraction has been analyzed and compared with the results of the revised Enskog theory (RET) of the Kincaid et al. [11].

In this paper also we have calculated the thermal diffusion factor for binary mixtures of hard spheres by a modified non-equilibrium molecular dynamics simulation method known as heat exchange algorithm [14]. Finally, we have studied the thermal diffusion factor of binary mixtures of hard spheres for a wide range of mass ratios, diameter ratios and compositions at different densities.

2. Theory and method

Irreversible thermodynamics provides a framework to describe the transport phenomena in matter. Based on this description the thermodynamic forces and fluxes with appropriate symmetry coupled to each other. For example for a mixture in mechanical equilibrium, mass flux can arise from both mass and temperature gradients The mass flux of species 1 in a binary mixture in a mechanical equilibrium under a thermal gradient is [25]:

$$J_1 = -\rho D_{12}\nabla w_1 - \rho w_1 w_2 D_T \nabla T, \tag{1}$$

where T is the temperature, ρ the density, ∇T and $\nabla \rho$ the temperature and density gradients, respectively, of the mixture, w_i the mass fraction of component i, D the mutual diffusion coefficient, and D_T is the thermal diffusion coefficient. At the stationary state in a closed system due to the counterbalance of two contributions to the mass flux, the mutual diffusion and the thermal diffusion, the mass flux vanish ($J_1 = 0$). The thermal diffusion factor is then defined as

$$\alpha_T = T\frac{D_T}{D_{12}} = -\left(\frac{1}{w_1 w_2}\frac{\nabla w_1}{\nabla T}\right)_{J_1=0} = -\left(\frac{1}{x_1 x_2}\frac{\nabla x_1}{\nabla T}\right)_{J_1=0}. \tag{2}$$

Here x_i ($i = 1, 2$) is the mole fraction of component i and conventionally component 1 is the heaver or the larger one.

Although thermal diffusion effect can be characterized by other transport coefficients (e.g., the thermal diffusion coefficient) we chose α_T because its definition does not depend on any particular choice of fluxes and forces that are used to model heat and mass transport [21,22]. In experiments the sign of the thermal diffusion factor is arbitrary chosen so that if component 1 chosen as the heavier or larger component, the thermal diffusion factor is positive when the heavier or larger species (component 1) tends to move toward the cooler region and the lighter or smaller species (component 2) accumulates in the hotter region at stationary state [1,19]. The kinetic theory of dilute gases [1] also shows that the thermal diffusion factor is larger than zero, when the heavier component tends to move toward colder. Eq. (2) is a straight way to calculate thermal diffusion factor by computer simulations.

The hard sphere potential is

$$\phi(r) = \begin{cases} \infty, & r \le \sigma \\ 0, & r > \sigma \end{cases}, \tag{3}$$

where $\phi(r)$ and σ are the intermolecular interaction potential and diameter of one atom, respectively. This intermolecular potential is discontinuous and non-differentiable, and consequently in general the Green–Kubo formula cannot be used here [22,26] to calculate the transport coefficients as is performed for soft potentials.