

Microscopic Interpretation of a Pure Chemical Contribution to the Soret Effect

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(Received 21 November 2006; published 23 March 2007)

In a recent Letter by Köhler [Phys. Rev. Lett. **87**, 055901 (2001)], it has been shown that the Soret effect or thermal diffusion can be split into three different contributions: mass, moment of inertia, and a so-called chemical effect, but only the chemical effect gives rise to a composition dependent contribution. As it is experimentally difficult to deal with the chemical contribution without changing the two others, it has not been studied accurately yet. Our Letter presents both equilibrium and nonequilibrium Molecular Dynamics in simple Lennard-Jones mixtures. By thoroughly changing the strength of direct and cross interaction energies between particles, we show that the composition dependence and the change of sign of the Soret coefficient is driven only by the nature of interactions between unlike particles and propose a microscopic interpretation of the Soret effect.

DOI: [10.1103/PhysRevLett.98.125901](https://doi.org/10.1103/PhysRevLett.98.125901)

PACS numbers: 66.10.Cb, 83.80.Hj

A fluid mixture subjected to a thermal gradient responds with concentration gradients. This is the Soret or Ludwig-Soret effect. In the stationary state, the degree of separation of species 1 for instance is quantified by the Soret coefficient $S_{T,1}$:

$$S_{T,1}x_1(1-x_1)\nabla x_1 = -\nabla T \quad (1)$$

where x_1 is the mole fraction of species 1 and T is the temperature. Separations are usually small: typical $S_{T,1}$ values are in the range 10^{-3} – 10^{-2} K $^{-1}$ although larger effects (by several orders of magnitude) can be seen in soft matter mixtures [1,2]. The sign of the Soret coefficient indicates the direction of separation: $S_{T,1}$ is positive when component “1” goes to the “cold side.” In many mixtures, $S_{T,1}$ does not change significantly with composition, but in some systems, such as associated mixtures, a change of sign of $S_{T,1}$ is observed, correlated with a strong composition dependence of the Soret coefficient [1]. Recently, reliable experimental data have been acquired and validated by different groups on reference mixtures (see, e.g., [3]). Among the existing methods, the thermal diffusion forced Rayleigh scattering (TDFRS) technique [4] has been used to study isotopic effects in benzene-cyclohexane mixtures [5], and a molecular interpretation of the Soret effect has been proposed. It was found that the Soret coefficient can be split into different contributions: a mass and moment of inertia difference between species and one quantifying the “chemical” effect, including the remaining contributions. More importantly, it was shown by Köhler [5] that mass and inertia contributions are roughly independent of the composition for deuterated experiments, whereas the chemical contribution depends on composition. Molecular dynamics simulations in Lennard-Jones mixtures have revealed that differences in molecular mass, diameter, and interaction energies con-

tribute almost additively to the Soret coefficient [6] which corroborate Köhler’s results [5]. However, these studies were performed on equimolar mixtures, and composition dependence was not investigated. Here, we concentrate on the chemical effect and its influence on the composition dependence of the Soret coefficient. Thus, we have studied binary mixtures at different compositions for particles interacting via the Lennard-Jones potential:

$$v_{ij}(r_{ij}) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right],$$

where σ_{ij} and ε_{ij} are, respectively, related to atomic diameter and depth of the potential, and r_{ij} is the distance between i and j . Species 1 is modeled as Argon ($\varepsilon_{11} = 0.99607$ kJ/mol, $\sigma_{11} = 0.3405$ nm, and $m_1 = 40$ g/mol). In order to investigate a purely chemical effect, species 2 has the same mass and size but a different energetic parameter ε_{22} . The interaction energy parameter between unlike species, ε_{12} is obtained using a modified Lorentz-Berthelot (LB) mixing rule: $\varepsilon_{12} = k_{12}\sqrt{\varepsilon_{11}\varepsilon_{22}}$ (the classical LB mixing rule is recovered for $k_{12} = 1.0$ [7]). The chemical effect in our systems depends entirely on two parameters: k_{12} controls the strength of the interaction between unlike species, the cross interaction, and as we will see later, it affects strongly thermodynamic excess properties of the mixture. The second parameter is the energy ratio $\psi_\varepsilon = \varepsilon_{22}/\varepsilon_{11}$. It indicates the difference of thermodynamic properties of the two species, such as the critical point coordinates. In this Letter, three k_{12} values (1.35, 1.50, and 1.75) and five ψ_ε values (from 1.0 to 1.8 with a 0.2 increment) were used.

In order to compare transport coefficients in our different mixtures, we should study them roughly in the same thermodynamic state. We used the Van der Waals one fluid

approximation to prepare all the equimolar mixtures in the same thermodynamic state: a supercritical dense fluid with $T/T_c = 1.5$ and $\rho/\rho_c = 2.0$, where T_c and ρ_c are, respectively, the critical temperature and density of the mixture. The computed pressure for the equimolar mixture is then used for all other molar fractions. This approximation defines an equivalent pure Lennard-Jones fluid for which the critical coordinates are known [8] in terms of the different parameters. However, all simulations were done at constant absolute pressure and average temperature, not at constant reduced density as in previous work [9].

There exist different ways to compute the Soret coefficient by molecular dynamics. One route is to compute the phenomenological Onsager coefficients [10], related to the direct and cross transport coefficients, using equilibrium molecular dynamics (EMD) and the Green-Kubo formalism [11]. Another route is the so-called synthetic nonequilibrium molecular dynamics method (NEMD) proposed by Evans [12] and Ciccotti [13]. In this Letter, we preferred to use a boundary driven NEMD method to compute the Soret coefficient, based on the HEX (heat exchange) algorithm [14] which gives directly the Soret coefficient [9,15]. The HEX algorithm mimics a thermal diffusion experiment: a thermal gradient is created by a modification of the kinetic energy of particles located at the boundaries of the simulation box. In the stationary state, local composition and temperature are computed in the simulation box. The Soret coefficient is then computed through Eq. (1). This method has proven to be a reliable tool in the study of liquid mixtures [15].

We present the results of our simulations, the Soret coefficient versus composition for different k_{12} for $\psi_\epsilon = 1.0$ and for some ψ_ϵ for $k_{12} = 1.5$ in Figs. 1 and 2, respectively. A clear linear dependence of $S_{T,1}$ is observed in both figures, and a change of sign can be seen, depending on k_{12} and ψ_ϵ values. A major conclusion from Fig. 1 is that the slope of the $S_{T,1}(x)$ is controlled by the value of k_{12} .

The modulus of the slope, and therefore the composition dependence of $S_{T,1}$, is increased for strengthened cross interactions. On the contrary, Fig. 2 shows that ψ_ϵ has almost no effect on the slope, and its effect is rather to shift the Soret coefficient as mass or inertia effects would, the latest of which Köhler noticed [5]. If one examines Fig. 1 in more detail, it appears that the Soret coefficient is equal to zero for equimolar mixtures: as $\psi_\epsilon = 1$ ($\epsilon_{11} = \epsilon_{22}$), all systems are “symmetrical” for a given k_{12} value; consequently, the local environment is the same for both species, and there is, as expected, no separation (i.e., $S_{T,1} = 0$). For small molar fraction, species 1 always goes to the cold side corresponding to a positive Soret coefficient, with a larger separation (i.e., a greater $S_{T,1}$ value) for greater k_{12} values. In the limit $k_{12} \rightarrow 1$, no separation will be observed as the system becomes a pure component. A simple, but relevant, microscopic picture can emerge from this behavior if one looks at the infinite dilution value of the Soret coefficient: consider a single particle of type 1 infinitely diluted in particles of type 2. For all particles, it is energetically more favorable to stay in the more dense region, the cold one. However, the single particle 1 competes with particles 2. In such a simple system of particles with same mass and size, if interactions between unlike species, ϵ_{12} , are larger than interactions between like species, ϵ_{22} , particle 1 will go to the cold side. The driving force for the system at infinite dilution for species 1 is therefore the difference $\epsilon_{12} - \epsilon_{22} \propto (k_{12} - \sqrt{\psi_\epsilon})$. In Fig. 1, k_{12} is always greater than $\sqrt{\psi_\epsilon}$. Accordingly, species 1 goes to the cold side, and this trend increases with an increasing value of $k_{12} - \sqrt{\psi_\epsilon}$. In Fig. 2, on the other hand, k_{12} is constant (1.35), and ψ_ϵ increases from 1.0 to 1.8. If we look at the values at large dilution for species 1, the separation decreases for increasing ψ_ϵ values. In particular, for $\psi_\epsilon = 1.8$, the difference $k_{12} - \sqrt{\psi_\epsilon}$ is very close to zero; there is almost no separation for the smallest molar fraction. Respectively, for the infinite dilu-

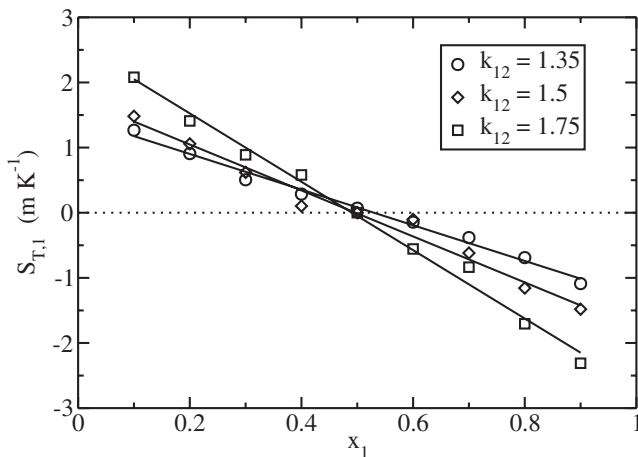


FIG. 1. $S_{T,1}$ versus molar fraction for all k_{12} tested with $\psi_\epsilon = 1$. Symbols are NEMD data and lines are linear fits to NEMD data.

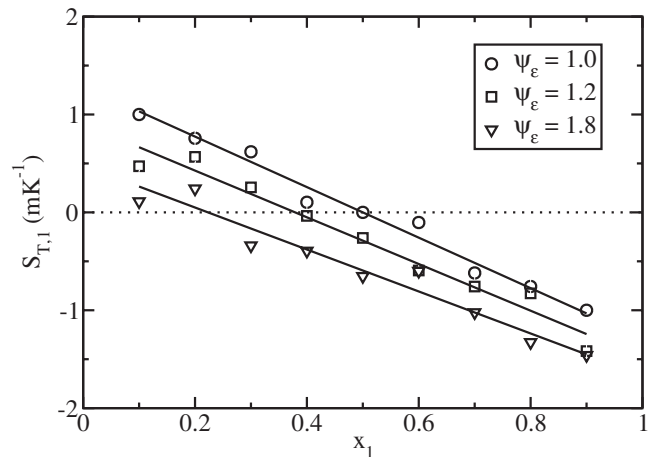


FIG. 2. $S_{T,1}$ versus molar fraction for three different values of ψ_ϵ : 1.0, 1.2, and 1.8 for $k_{12} = 1.35$. Symbols are NEMD results; lines are linear fits to the data.

tion of species 2, the same argument can be called upon although the relevant energetic terms are now ε_{12} and ε_{11} . Particle 2 will preferentially go to the cold side for positive values of $\varepsilon_{12} - \varepsilon_{11} \propto (k_{12} - \sqrt{1/\psi_\varepsilon})$. This microscopic interpretation explains qualitatively the behavior of the Soret coefficient at large molar fraction.

Furthermore, our work elucidates some experimental results (see for instance [1]): the temperature can affect the dependence of the Soret coefficient with the molar fraction. As we show, this dependence is governed by the nature of the cross interactions. If the slope changes with temperature, that means the nature of cross interactions between particles changes too.

The approach followed here gives a microscopic interpretation of the pure chemical contribution to the Soret effect, based on direct and cross interactions. On a macroscopic scale, excess properties, which quantify the non-ideality of a mixture, reflect the nature of intermolecular interactions. In order to make a link between microscopic quantities describing molecular interactions in our systems (k_{12} and ψ_ε) and macroscopic properties, we have performed a thermodynamics study of our systems. We have used the difference method introduced by Sindzingre *et al.* [16] in which fictitious swaps between particles of different species are realized at constant total number of particles, pressure, and temperature. Using this EMD method, we have been able to compute, with a good accuracy [17], differences between partial molar quantities such as chemical potential $\Delta\mu = \mu_1 - \mu_2$, partial molar enthalpies Δh , and partial molar volumes Δv .

Figures 3 and 4 present, respectively, Δh versus mole fraction for different k_{12} at constant $\psi_\varepsilon = 1.4$ and for different ψ_ε at constant $k_{12} = 1.5$. We recall here that the modulus of the slope of Δh versus x is an indication of the degree of nonideality: the larger the modulus, the larger the nonideality. Figure 3 clearly indicates that the nonideal behavior of our systems increases on increasing k_{12} . In the

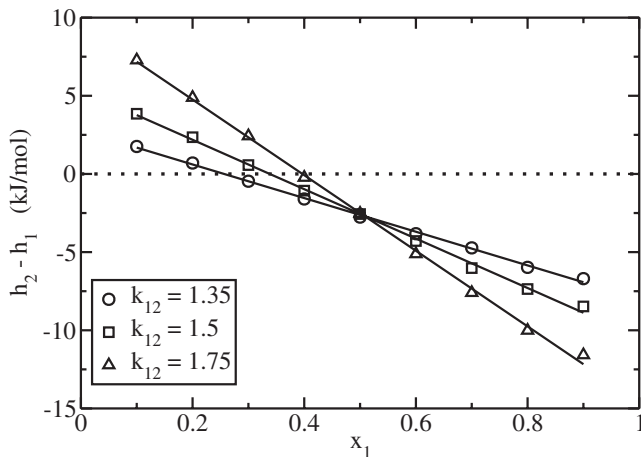


FIG. 3. Difference between partial molar enthalpies $h_2 - h_1 = -\Delta h$, versus molar fraction for all k_{12} values tested at $\psi_\varepsilon = 1.4$. Symbols are EMD results.

limit of k_{12} close to 1, an almost constant Δh is expected (this corresponds to a standard Lennard-Jones Lorentz-Berthelot mixture, i.e., an almost ideal mixture). From Fig. 4, it can be seen that the modulus of the slope of Δh versus x is almost independent of ψ_ε . Indeed, by changing ψ_ε , the enthalpies of the pure components are changed, but this only shifts Δh values and does not quantitatively alter the slope. These results show an obvious correlation between the behavior of Δh and $S_{T,1}$ versus x_1 with changes of k_{12} and ψ_ε . Quantitatively, we have been able to show that the composition at which $S_{T,1}$ and Δh cross the 0 value is the same. This behavior has an important implication from a thermodynamic point of view: as $\Delta h = \partial(H/N)/\partial x_1$ (H being the total enthalpy of the mixture), a change of sign of $S_{T,1}$ versus x_1 is expected at compositions for which H/N versus x_1 presents an extremum.

At the present stage, it is of some interest to introduce here a comparison between the NEMD results and the theoretical models given by Kempers [18], Haase [19] and Firoozabadi [20]. Because these models rely on thermodynamical data which are not always available, the required data are often derived from an equation of state. This introduces another source of error which makes difficult the correct evaluation of the model. In our case, thanks to the EMD simulations, we possess all the necessary input data to compute the Soret coefficient given by these models:

$$S_{T,1}^H = -\frac{h_1/v_1 - h_2/v_2}{x_1 \frac{\partial \mu_1}{\partial x_1} T},$$

$$S_{T,1}^K = -\frac{h_1/M_1 - h_2/M_2}{x_1 \frac{\partial \mu_1}{\partial x_1} T},$$

$$S_{T,1}^F = -\frac{u_1/\tau_1 - u_2/\tau_2}{x_1 \frac{\partial \mu_1}{\partial x_1} T} - \frac{(v_2 - v_1)(\sum_i x_i u_i/\tau_i)}{(\sum_i x_i v_i)x_1 \frac{\partial \mu_1}{\partial x_1} T},$$

where the superscripts H , K , and F refer to Haase,

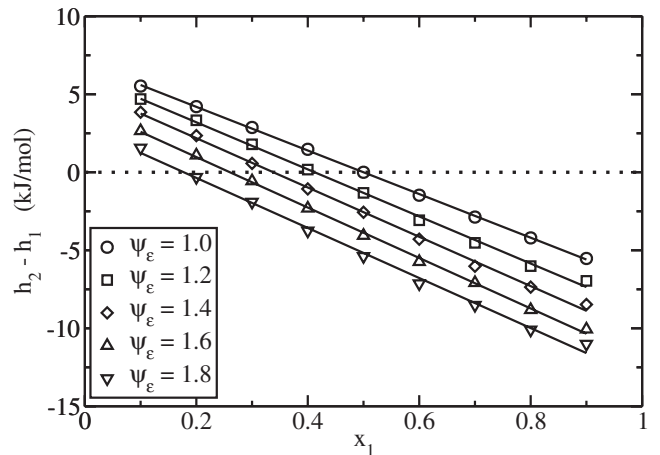


FIG. 4. Difference between partial molar enthalpies $h_2 - h_1 = -\Delta h$, versus the molar fraction for all ψ_ε values tested at $k_{12} = 1.5$. Symbols are EMD results.

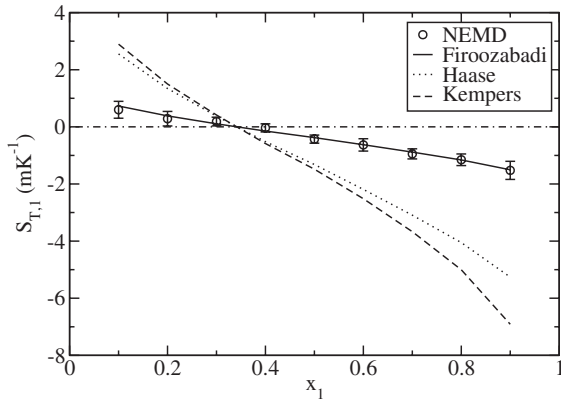


FIG. 5. NEMD determination of the Soret coefficient and different model predictions for a system with $k_{12} = 1.5$ and a $\psi_\varepsilon = 1.4$.

Kempers, and Firoozabadi. In Firoozabadi's model (derived from a kinetic approach with thermodynamic contributions), τ_i is an adjustable parameter with value between 3.0 and 4.0 for usual simple mixtures [20]. We considered a value of 3.5 for the τ_i and checked that the final result is almost independent of τ_i in the proposed range as it only slightly affects the slope of $S_{T,1}$. The u_i represent the partial molar internal energies, very close to partial molar enthalpies for fluids, μ_i are the chemical potentials, and v_i the partial molar volumes. In Fig. 5, we compare the predictions of the models with the NEMD data for a typical system ($k_{12} = 1.5$, $\psi_\varepsilon = 1.4$). Although all models predict a change of sign of $S_{T,1}$ for these systems at the correct molar fraction, only Firoozabadi's model agrees quantitatively with our NEMD results. Surely the physical dependence is achieved, but only such a kinetic approach seems to give accurate predictions. This fact should be taken into account for the construction of new predictive models for the Soret coefficient in liquids.

In summary, our work is able to elucidate the dependence of the Soret coefficient on chemical effect. We clearly show that the slope of $S_{T,1}$ versus x_1 depends on the cross interaction parameter k_{12} , whereas the direct energy ratio parameter ψ_ε has an influence similar to mass or inertia effects. Linking the microscopic and macroscopic approaches, we have seen that k_{12} is responsible for the nonideality of the mixtures and as evidenced by the similar behavior of Δh and $S_{T,1}$ versus x_1 . A clear correlation between mixture nonideality and a strong composition dependence of $S_{T,1}$ has been established making our results more general. From the study at infinite dilution, we show that the direction of separation is given by the sign of $k_{12} - \sqrt{\psi_\varepsilon}$ when $x_1 \rightarrow 0$ (or $k_{12} - \sqrt{1/\psi_\varepsilon}$ when $x_2 \rightarrow 0$). Thus, in order to observe a change of sign of $S_{T,1}$, it is

necessary that, if cross interactions are favorable to species 1 when $x_1 \rightarrow 0$, they become favorable to species 2 when $x_2 \rightarrow 0$. Finally, we have been able to assess the most common predictive models for the Soret coefficient. We obtained a remarkably good agreement between our NEMD data and Firoozabadi predictions based on equilibrium properties computed by EMD. A major issue is now to find accurate numerical methods to predict cross thermodynamic excess properties for realistic systems, such as alkane mixtures, and extend our approach to more complex systems like associated mixtures or colloid and polymer solutions.

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