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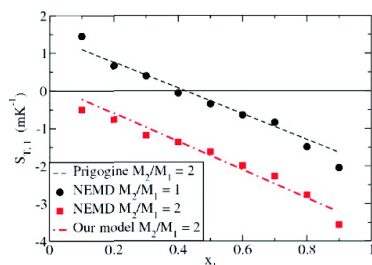
A New Model for Thermal Diffusion: Kinetic Approach

Pierre-Arnaud Artola, Bernard Rousseau, and Guillaume Gallie#ro

$$S_T^A = S_T^{\text{Prigogine}} + \frac{1 - \psi_M}{1 + \psi_M} * \frac{\Delta G_1^{\#} + \Delta G_2^{\#}}{RT^2}$$

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A New Model for Thermal Diffusion: Kinetic Approach

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Abstract: We present a new model for thermal diffusion, and we compare its results for both simple and real systems. This model is derived from a kinetic approach with explicit mass and chemical contributions. It involves self-diffusion activation free energies, following Prigogine's original approach. We performed, furthermore, both equilibrium and nonequilibrium molecular dynamics evaluations in order to compute respectively the self-diffusion activation free enthalpies and the Soret coefficient when no experimental data were available. Our model is in very good agreement with simulation data on Lennard-Jones mixtures, and a good behavior is noted for the water−ethanol mixture, where the composition dependence at which the Soret coefficient changes its sign is predicted very accurately. Finally, we propose a new water−ethanol experiment at higher temperature in order to check the validity of our model.

1. Introduction

The Soret effect, or thermal diffusion, occurs when a mixture is subjected to a thermal gradient. Mole fraction gradients appear along this gradient.[6] At the stationary state, the magnitude of the separation is quantified by the Soret coefficient,[6] defined for each species i as

$$S_{T,i} x_i (1 - x_i) \nabla T = - \nabla x_i \qquad (1)$$

The sign of $S_{T,i}$ gives the direction of separation. According to the above definition, a positive value for $S_{T,i}$ indicates that species i goes preferentially to the "cold" side. Prigogine's work on binary mixtures of organic molecules led to a distinction between two different cases: mixtures where at least one component (in the pure state) is associated (i.e., is a polar molecule with specific and directional interactions like hydrogen bonds) and those of nonassociated compounds.[7,8] In the former case, the Soret coefficient is highly composition dependent and may change in sign as the composition changes. As far as liquid mixtures of organic molecules are concerned, the magnitude of the Soret coefficient is low, of the order of 10^{-2}–10^{-3} K^{-1}, except near a critical point.[9] The situation may be quite different in the area of soft matter. Duhr and Braun[10] measured Soret coefficients as large as 20 K^{-1} for carboxyl-modified polystyrene beads with a diameter of 1 μm.

Because thermal diffusion occurs whenever a mixture is placed under a thermal gradient, it is involved in many natural processes. For example, it affects crude oil along the geothermal gradient in oil fields.[2] It is believed to affect heat and mass transfer in oceans, with some influence on thermohaline convection.[5] The first large application of thermal diffusion was isotopic separation in a gas phase, as predicted by Furry, Jones, and Onsager.[26] More recently, Giddings et al.[4] developed a chromatographic separation technique, also known as thermal field flow fractionation, that utilizes the dependence of the Soret coefficient on molar mass to separate macromolecules.[50] The important thermal gradients that develop during the high activity of radioactive wastes can induce Soret migration of some constituents of nuclear glasses.[3] From a more fundamental point of view, understanding the Soret effect and, more generally, coupled transport phenomena will lead to a better understanding of the relationship between intermolecular interactions and transport coefficients.

In an attempt to rationalize the Soret effect in simple organic mixtures, Debuschewitz and Köhler[11] studied isotopic benzene−cyclohexane mixtures. They showed that the Soret coefficient depends almost additively on three contributions: the mass difference between species, the moments of inertia of the molecules, and finally the "chemical contribution". This additive approach was first proposed by Rutherford,[12–15] based on a theoretical work by Schirdewahn et al.,[16] but was restricted to the mass and moment of inertia terms. An important point of

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(1) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Oxford University Press: Oxford, 1987; pp 192−193.

(2) Costeseque, P.; Fargue, D.; Jamet, P. *Thermal Nonequilibrium Phenomena in Fluid Mixtures*; Köhler, W., Wiegand, S., Eds.; Springer: Berlin, 2000; p 389.

(3) Guy, C.; Schott, J. *Appl. Geochem.* **1992**, *7*, 33–40.

(4) Giddings, J. C.; Hovingh, M. E.; Thompson, G. H. *J. Phys. Chem.* **1970**, *74*, 4291–4294.

(5) Caldwell, D. R. *J. Fluid Mech.* **1974**, *64*, 347–368.

(6) Wiegand, S. *J. Phys.: Condens. Matter* **2004**, *16*, R357–R379.

(7) Prigogine, I.; de Brouckere, L.; Amand, R. *Physica* **1950**, *16*, 577–598.

(8) Prigogine, I.; de Brouckere, L.; Amand, R. *Physica* **1950**, *16*, 851–860.

(9) Giglio, M.; Vendramini, A. *Phys. Rev. Lett.* **1975**, *34*, 561–564.

(10) Duhr, S.; Braun, D. *Proc. Natl. Acad. Sci., U.S.A.* **2006**, *103*, 19678–19682.

(11) Debuschewitz, C.; Köhler, W. *Phys. Rev. Lett.* **2001**, *87*, 055901.

(12) Rutherford, W. M. *J. Chem. Phys.* **1984**, *81*, 6136–6139.

(13) Rutherford, W. M. *J. Chem. Phys.* **1987**, *86*, 397–399.

(14) Rutherford, W. M. *J. Chem. Phys.* **1989**, *90*, 602–603.

(15) Rutherford, W. M. *J. Chem. Phys.* **1987**, *86*, 5217–5218.

this work is that the mass and inertia effects are almost independent of the composition,[11] although it has been observed from molecular dynamics simulations that, for huge isotopic effects, this is no longer the case.[17] In addition to Debuschewitz and Köhler's description of thermal diffusion, a recent study on simple Lennard-Jones mixtures[18] concluded that the composition dependence of the Soret coefficient is due to interactions between unlike species (called cross-interactions), whereas interactions between same species (called direct interactions) introduces no composition dependence, just like a mass effect.

Although both experimental and molecular simulations (given a good force field) contributions are currently able to give accurate results[6,19,20] and some clues about the molecular mechanism involved, there still lacks a general model to quantitatively predict the Soret coefficient in liquid mixtures. Several attempts have been made using different conceptual approaches. In the 1940s, Haase[21] proposed a model based on pure thermodynamic considerations. Using an analogy with pressure diffusion, he derived an expression for the Soret coefficient in binary mixtures that revealed the role of partial molar enthalpies of species in the process. Haase's results were latter re-derived by Kempers[22] using variational models, but a recent article[23] showed that these approaches are theoretically not sufficient to predict accurately the Soret coefficient. Furthermore, we established[18] that these classical models are not able to predict the Soret coefficient of some Lennard-Jones mixtures. A failure to predict a transport coefficient in such simple systems strongly questions the approach. Another line of investigation originates in the 1950s with the work of Wirtz[24] and Prigogine.[7] There, thermal diffusion was described in the framework of Eyring theory of activated processes.[46] A microscopic mechanism was proposed, involving elementary jumps of species in a thermal gradient (see below for details). Later, Drickamer[25] proposed a similar approach and showed that this "kinetic" point of view is self-consistent with an Onsager phenomenological description[26] for thermal diffusion. A generalized study of this last analogy was made by Sieniutycz.[27] The "kinetic approach" was the initial point of recent derivations by Firoozabadi[28] and Saghir,[29] for instance. In this article, we will show that the original kinetic approach, in the formalism proposed by Prigogine, lacks an important feature: it does not take into account mass effect contributions. This point has already been raised for the "thermodynamic" models.[17] However, it was not expected from the "pure kinetic approach", where, intuitively, any molecular mass effect

should be taken into account. As will be shown, these approaches lead to an expression containing pure thermodynamical quantities that do not include mass effects. To our knowledge, this fundamental limitation of the Prigogine model was not previously known. Therefore, we propose a modification to the original model that gives perfect agreement for Lennard-Jones mixtures.

2. Theory: A New Model

2.1. Prigogine's Original Model. In the original Prigogine model,[7] thermal diffusion proceeds as coupled diffusion-activated processes. The model includes several steps in which fluid holes are involved, but as the hole does not appear at the end, the elementary process can be summarized as a "swap" between two molecules i and j, belonging to different species, along the thermal gradient. The mass flux is then written considering that molecules i and j experience a different local temperature. The mass flux along the z direction (the temperature gradient direction), or "positive flux" is written:

$$J^+ \propto x_1(z - \mathrm{d}z/2)\, x_2(z + \mathrm{d}z/2) \times$$
$$\exp\left(-\frac{\Delta G_1^\#}{R(T - \mathrm{d}T/2)}\right) \exp\left(-\frac{\Delta G_2^\#}{R(T + \mathrm{d}T/2)}\right)$$

where x_i is the local mole fraction of species i, $\Delta G_i^\#$ the activation free enthalpies of species i for the coupled diffusion process, T the local temperature, and R the ideal gas constant. In this expression, particle 1 is located in $z - \mathrm{d}z/2$ at temperature $T - \mathrm{d}T/2$, and particle 2 is located at $z + \mathrm{d}z/2$ at temperature $T + \mathrm{d}T/2$. The total mass flux is obtained from the sum of J^+ and J^-, the mass flux in the other direction. At the stationary state, the total mass flux cancels. A differential derivation gives the expression of Prigogine's Soret coefficient:[7,8]

$$S_{T,1}^{\mathrm{P}} = \frac{\Delta G_2^\# - \Delta G_1^\#}{RT^2} \tag{2}$$

In the original paper, Prigogine related the activation energy $\Delta G_i^\#$ to a fraction of the interaction energy of particle i. However, as was noticed by Tichacek et al.,[25] "the best description of a component motion in a mixture would be obtained from measurements of self-diffusion of that component in the mixture as a function of temperature". At constant pressure and temperature, one would define self-diffusion activation free enthalpies for species i as

$$D_i = D_i^0\, \mathrm{e}^{-\Delta G_i^\#/RT} \tag{3}$$

This expression is based on the same hypothesis as the one written above for fluxes. It can be obtained from a simple calculation based on Brownian diffusion with a jump frequency proportional to $\exp(-\Delta G^\#/RT)$.[46] This approach, initially proposed by Tichacek et al., suffered from a strong lack of data, and so another estimate of the activation energies was done. Today, self-diffusion coefficients can be measured using, e.g., pulsed field gradient NMR or can be computed from equilibrium molecular dynamics (EMD). The Soret coefficient can be predicted by the original Prigogine approach, together with eqs 2 and 3. The result can further be compared with nonequilibrium simulations over the same system to check the validity of the model. Such a comparison is plotted in Figure 1 for a system

(16) Schirdewahn, J.; Klemm, A.; Waldmann, L. *Z. Naturforsch.* **1960**, *16a*, 133–138.
(17) Galliero, G.; Bugel, M.; Duguay, B.; Montel, F. *J. Non-Equilib. Thermodyn.* **2007**, *32*, 251–258.
(18) Artola, P.-A.; Rousseau, B. *Phys. Rev. Lett.* **2007**, *98*, 125901.
(19) Perronace, A.; Leppla, C.; Leroy, F.; Rousseau, B.; Wiegand, S. *J. Chem. Phys.* **2002**, *116*, 3718–3729.
(20) Ning, H.; Wiegand, S. *J. Chem. Phys.* **2006**, *125*, 4.
(21) Haase, R. *Z. Phys.* **1949**, *127*, 1.
(22) Kempers, L. J. T. M. *J. Chem. Phys.* **2001**, *115*, 6330–6341.
(23) Farago, J.; Rousseau, B.; Artola, P.-A. *J. Chem. Phys.* **2006**, *125*, 164508.
(24) Wirtz, K. *Naturwissenschaften* **1939**, *27*, 369.
(25) Tichacek, L. J.; Kmak, W. S.; Drickamer, H. G. *J. Chem. Phys.* **1956**, *60*, 660–665.
(26) Onsager, L. *Phys. Rev.* **1931**, *37*, 405–427.
(27) Sieniutycz, S. *Open Syst. Inf. Dyn.* **2002**, *11*, 185–202.
(28) Shukla, K.; Firoozabadi, A. *Ind. Eng. Chem. Res.* **1998**, *37*, 3331–3342.
(29) Jiang, C. G.; Saghir, M. Z.; Derawi, S.; Kawaji, M. *J. Non-Equilib. Thermodyn.* **2005**, *30*, 337–358.

(30) Chapman, S.; Cowling, T. G. *The Mathematical Theory of Non-Uniform Gases*; Cambridge University Press: Cambridge, 1939.

with same-mass particles. As can be seen, a remarkable agreement is observed between the original model from Prigogine and our nonequilibrium molecular dynamics (NEMD) "numerical experiment". Although the studied system is quite simple, it gives a strong validation of the pertinence of Prigogine's model. However, as can be seen from Figure 4 (below), the model fails to predict the Soret coefficient for a mass ratio different from 1. Indeed, the main problem of this model is that it is unable to reproduce any mass effect since activation free enthalpies are pure thermodynamic quantities.

Firoozabadi[28] and Saghir[29] coupled this approach to thermodynamic approximations in order to estimate the diffusion activation enthalpies easily from equations of state. It was shown that these approaches predict accurately the chemical part of the Soret coefficient with high accuracy at low numerical cost.[18] However, because Prigogine's model does not include the mass effect, Firoozabadi and Saghir models will not either.

2.2. Our New Model. As Truhlar noted,[31] in transition state theory, it is essential to define correctly the reaction coordinate and to rescale it in terms of the ideal part of the partition function. In thermal diffusion, it is not so simple, as we are in a non-constant-temperature situation. This difficulty can be overcame by taking the temperature as the reaction coordinate. Rescaling the reaction coordinate in terms of the ideal part of the partition function means to displace the position of the diffusion transition state as a barycenter of the relative masses. We propose the following expression for the positive mass flux:

$$J^+ \propto x_1(z - dz/2)\, x_2(z + dz/2)\times$$

$$\exp\left(-\frac{\Delta G_1^{\#}}{R(T - \xi_1\, dT)}\right) \exp\left(-\frac{\Delta G_2^{\#}}{R(T + \xi_2\, dT)}\right)$$

where ξ_i, which defines the transition state position, is given by

$$\xi_1 = \frac{M_2}{M_1 + M_2}$$

$$\xi_2 = \frac{M_1}{M_1 + M_2}$$

M_i being the molar mass of species i. The same kind of flux can be expressed in the other direction. Again, a differential derivation gives

$$S_{T,1}^{A} = 2\frac{\Delta G_2^{\#} - \psi_M \Delta G_1^{\#}}{(1 + \psi_M)RT^2} \tag{4}$$

where $\psi_M = M_2/M_1$ is the mass ratio. This equation can be expressed in the form of different contributions, as introduced by Köhler:

$$S_{T,1}^{A} = \frac{\Delta G_2^{\#} - \Delta G_1^{\#}}{RT^2} + \frac{M_2 - M_1}{M_2 + M_1}\frac{\Delta G_2^{\#} + \Delta G_1^{\#}}{RT^2} \tag{5}$$

The first term is the usual Prigogine model for thermal diffusion.

3. Molecular Dynamics Simulations

Molecular dynamics make it possible to check the validity of our new model. We computed the self-diffusion free
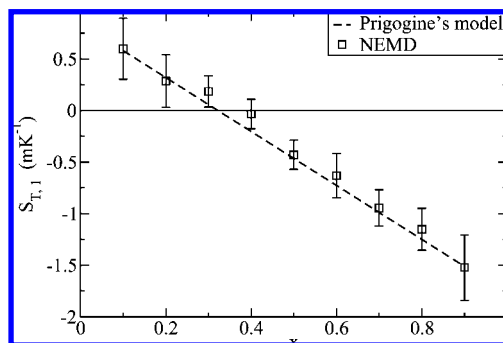
Figure 1. Soret coefficient for a Lennard-Jones mixture versus composition (see text for details and definitions of the different parameters). Comparison between Soret coefficient computed using NEMD simulations and using the original Prigogine equation (eq 2) plus activation free enthalpies obtained from EMD for a Lennard-Jones system with same-mass particles. Parameters are $k_{12} = 1.5$, $\psi_\varepsilon = 1.4$, and $\psi_M = 1.0$. Error bars correspond to statistical errors as determined from an average over 10 independent blocks of data.[1]
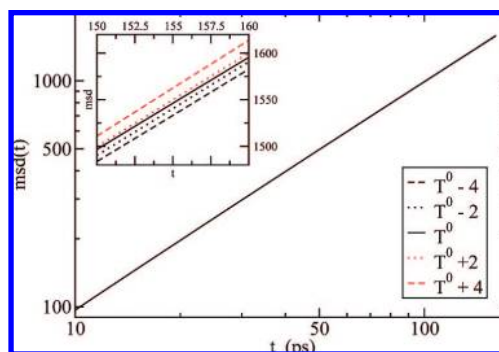
Figure 2. Mean square displacements msd(t) (given in Å^2) of species 1 for a Lennard-Jones mixture ($k_{12} = 1.75$, $\psi_\varepsilon = 1.4$, and $x = 0.5$, $T^0 = 386.73$ K) at different temperatures in the diffusive regime. As temperatures are very close, the different curves almost superimpose. The main graph presents the msd(t) at a given temperature, and the inset presents all msd(t)'s for all temperatures.

activation enthalpies $\Delta G_i^{\#}$ from EMD simulations. We did simulations in the NVT ensemble, using the Nosé−Hoover algorithm with a time-reversible integrator,[32] to compute the mean square displacement of each of our species at five different temperatures: T_0, $T_0 \pm 2$ K, and $T_0 \pm 4$ K. Self-diffusion coefficients were deduced from the slope of the mean square displacement versus time in the diffusive regime, as can be seen, for instance, in Figure 2. The problem of the finite-size box for measurement of the self-diffusion coefficient has been taken into account using a hydrodynamic correction.[33] The self-diffusion activation free enthalpies were obtained from a plot of the logarithm of the self-diffusion versus inverse temperature (see an example in Figure 3). Soret coefficients based on the Prigogine model and our model were computed using eqs 2 and 4. This method was applied to both Lennard-Jones systems and water−ethanol mixtures.

On the other hand, boundary-driven nonequilibrium molecular dynamics can be used to obtain the "true" Soret coefficient without assumption or knowledge of some thermodynamic
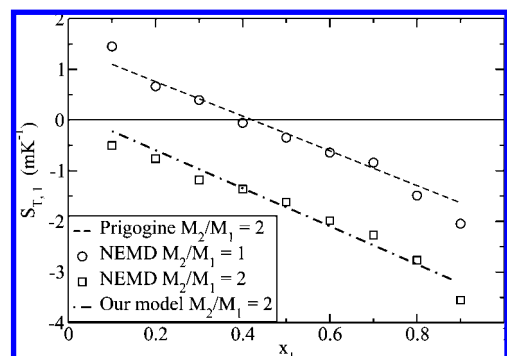
(31) Fernandez-Ramoz, A.; Miller, J. A.; Klippenstein, S. J.; Truhlar, D. G. *Chem. Rev.* **2006**, *106*, 4518–4584.
(32) Martyna, G. J.; Tuckerman, M. E.; Tobias, D. J.; Klein, M. L. *Mol. Phys.* **1996**, *87*, 1117–1157.
(33) Yeh, I.-C.; Hummer, G. *J. Phys. Chem. B* **2004**, *108*, 15873–15879.
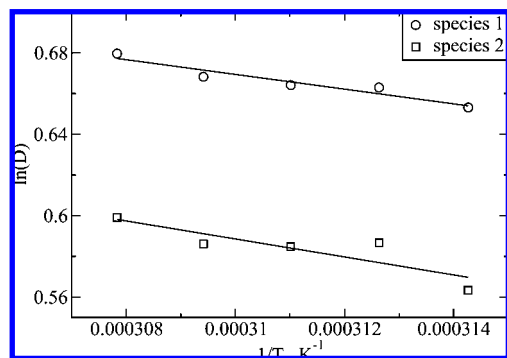
Figure 3. Logarithm of the diffusion coefficient versus inverse temperature for a Lennard-Jones system ($k_{12} = 1.75$, $\psi_\varepsilon = 1.4$, and $x = 0.5$).

Figure 4. Soret coefficients computed from NEMD simulations compared to our new kinetic model including the mass effect. Parameters are $k_{12} = 1.75$, $\psi_\varepsilon = 1.4$, and $\psi_M = 1.0$ and 2.0.

quantities.[19] More specifically, we used the HeX algorithm,[34] where, at each time step, a fixed amount of kinetic energy is exchanged between cold and hot regions in the simulation box. A thermal gradient is rapidly established, followed by a composition gradient.

At the stationary state, the Soret coefficient is computed using eq 1 from local composition and temperature in the molecular simulation box. This method has proven to be a powerful tool to compute the Soret coefficient[19,35] in some organic mixtures.

In the work described in this paper, we used this approach to compute the Soret coefficient in Lennard-Jones mixtures, and we made use of reference experimental data for the Soret coefficient in water−ethanol mixtures.[6,36−38]

We note that, to our knowledge, there is no hydrodynamic correction available to cancel the finite size effect, like the one we used for the self-diffusion coefficient.[33]

Our Lennard-Jones particles were interacting through a truncated Lennard-Jones potential:

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

$$= 0 \qquad \text{else} \qquad (7)$$

where r_{ij} is the distance between particles i and j, ε_{ij} the depth of the intermolecular potential, and σ_{ij} the characteristic distance of the potential. We chose a truncated potential with a cutoff value $r_c = 2.5\sigma$ and added long-range corrections to energy and pressure, assuming a radial distribution function equal to 1 for $r > r_c$. It has been shown[39] that this cutoff value is completely acceptable for dense fluids. The self-diffusion coefficients were computed in a box containing 300 molecules. The Soret coefficients were computed with a parallelepipedic box with dimensions $(L,L,2L)$, containing 1000 molecules. The box is elongated in the direction of the thermal gradient in order to allow periodic boundary conditions[34] and to reach local equilibrium in regions where local composition and temperature are computed. To our knowledge, there are no hydrodynamic corrections for thermal diffusion, and the large box size used prevents such a problem.

In a recent work,[18] it was shown that cross-energetic interactions are responsible for the composition dependence of the Soret coefficient, whereas direct interactions act as a mass effect for same-size particles. In order to account for such effects, we introduced two energetic parameters: a cross-interaction parameter k_{12} and a direct interaction parameter ψ_ε, defined as

$$\varepsilon_{12} = k_{12}\sqrt{\varepsilon_{11}\varepsilon_{22}}$$

$$\psi_\varepsilon = \varepsilon_{22}/\varepsilon_{11}$$

In these studies, component 1 corresponds to argon, with $\varepsilon = 0.99607$ kJ/mol and $\sigma = 0.3405$ nm. We considered here only particles with identical size as a simplification in order to quantify the influence of the energetic parameters.

To allow comparison with experimental methodologies, simulations for a given system (fixed k_{12} and ψ_ε) were done at the same pressure and temperature. For each system, the thermodynamics state of the equimolar mixture was a super-critical dense state, to avoid demixion:

$$T/T_c = 1.5$$

$$\rho/\rho_c = 2.0$$

where the subscript "c" indicates the critical point coordinates. We performed an NVT simulation of the equimolar mixture to compute the pressure for this system. Next, we performed 200 ns simulation runs at different compositions using this computed pressure with a time step of 2 fs. The equimolar critical point was obtained from a Van der Waals one-fluid approximation.[40]

In order to test our model on more "realistic" systems, we considered a very well studied system:[41−43] the water−ethanol mixture. The Soret coefficient of the water−ethanol mixture presents a complex behavior: it varies over a relatively large range, its sign changes with mole fraction, and it varies nonlinearly with composition. All of these features are typical of a strongly interacting system, here due to the presence of hydrogen bonding. We chose a very classical semiempirical potential for these molecules. At room temperature, the optimized potentials for liquid simulations (OPLS) force field for

(34) Hafskjold, B.; Ikeshoji, T.; Ratkje, S. K. *Mol. Phys.* **1993**, *80*, 1389–1412.
(35) Nieto-Draghi, C.; Bonet Ávalos, J.; Rousseau, B. *J. Chem. Phys.* **2005**, *122*, 114503.
(36) Dutrieux, J. F.; Platten, J. K.; Chavepeyer, G.; Bou-Ali, M. M. *J. Phys. Chem. B* **2002**, *106*, 6104.
(37) Kölodner, P.; Williams, H.; Moe, C. *J. Chem. Phys.* **1988**, *88*, 6512.
(38) Zhang, K. J.; Briggs, M. E.; Gammon, R. W.; Sengers, J. V. *J. Chem. Phys.* **1996**, *104*, 6881.
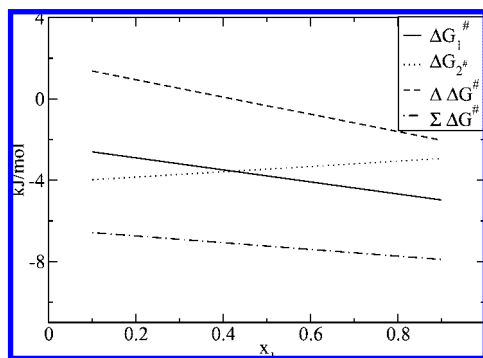
(39) Bordat, P.; Reith, D.; Müller-Plathe, F. *J. Chem. Phys.* **2001**, *115*, 8978–8982.
(40) Johnson, J. K.; Zollweg, J. A.; Gubbins, K. E. *Mol. Phys.* **1993**, *78*, 591–618.
(41) Nagamachi, M. Y.; Francesconi, A. Z. *J. Chem. Thermodyn.* **2006**, *38*, 461–466.
(42) Larkin, J. A. *J. Chem. Thermodyn.* **1975**, *7*, 137–148.
(43) Boyne, J. A.; Williamson, A. G. *J. Chem. Thermodyn.* **1967**, *12*, 318.

Figure 5. Activation free enthalpies, their difference, and their sum from EMD simulation. Parameters are $k_{12} = 1.75$, $\psi_\varepsilon = 1.4$, and $\psi_M = 1.0$.

Figure 6. Excess enthalpy of the water−ethanol mixture from experimental data (300 and 331 K) and EMD simulations (260 and 300 K).

ethanol[44] describes quite well both thermodynamic and dynamic properties. For the water molecule, we chose the TIP4P 2005 potential, which gives very good perfomance for a large set of thermodynamic properties over a wide range of temperatures and pressures.[45] In this study, all simulations were done at atmospheric pressure and room temperature, using 300 molecules, with a production run of 50 ns and a time step of 2 fs. For these systems, the common Lorentz−Berthelot mixing rules for the Lennard-Jones part of the potentials was used:

$$\varepsilon_{12} = \sqrt{\varepsilon_{11}\varepsilon_{22}}$$

$$\sigma_{12} = \frac{\sigma_{11} + \sigma_{22}}{2}$$

We employed a cutoff value of 2.5 times the greater σ of the system for Lennard-Jones interactions, whereas electrostatic interactions were computed using the Ewald summation method.

4. Results and Discussion

4.1. Lennard-Jones Mixtures. We present in Figure 4 the results of both Prigogine's and Artola's models for a Lennard-Jones mixture with two mass ratios: $\psi_M = 1$ and $\psi_M = 2$. It can be seen that the Prigogine prediction for a $\psi_M = 2$ gives Soret coefficients at a mass ratio equal to 1. As was mentioned before, Prigogine's model accurately predicts the slope of $S_{T,i}(x_i)$ but does not take into account any mass effect. Indeed, activation free enthalpies are mass independent: the mass dependence of the self-diffusion coefficient appears only in the pre-exponential term.[46] On the other hand, our new model quantitatively predicts the Soret coefficient for a mass ratio $\psi_M = 2$.

From eq 5, because activation free enthalpies depend on composition, we may expect a change in the slope of $S_{T,i}(x_i)$ with mass ratio. We plotted in Figure 5 the activation free enthalpies versus composition for both species. Also plotted is the sum, $\Sigma\Delta G^{\#}$, and difference, $\Delta\Delta G^{\#}$, between these quantities, as they appear directly in eq 5. Because the slopes of $\Delta G_i^{\#}$ versus composition are of opposite sign, the term $\Sigma\Delta G^{\#}$ varies less with composition than $\Delta\Delta G^{\#}$. Therefore, the mass effect has a smaller influence on the slope of the Soret coefficient, as observed in literature, at least for small mass ratios.[11,17] Although this system is far from being quite general, some understanding of the behavior of $\Delta G_i^{\#}$ may be obtained from a
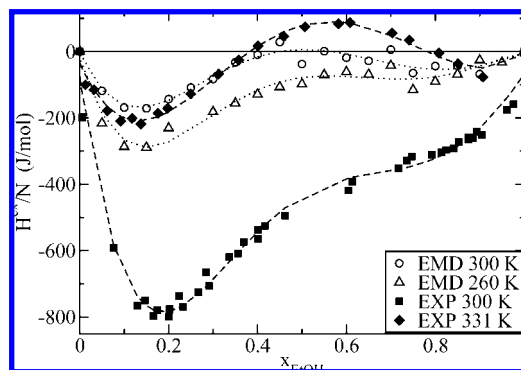
picture at infinite dilution. If we consider particle 1 at infinite dilution, i.e., $x_1 \rightarrow 0$, its activation energy $\Delta G_1^{\#}$ is controlled by the cage rigidity formed by particles 2, hence by ε_{22}. When $x_1 \rightarrow 1$, particle 1 has to escape from a cage formed by itself, i.e., $\Delta G_1^{\#}$ depends on ε_{11}. Because $\varepsilon_{22} > \varepsilon_{11}$ ($\psi_\varepsilon = 1.4$ in this case), we expect a negative slope for $\Delta G_1^{\#}$. Following the same reasoning for particle 2, we can show that the slope of $\Delta G_2^{\#}$ versus x_1 must be positive. Consequently, the difference between activation free enthalpies varies more rapidly than their sum. Therefore, the composition dependence of the mass effect (second term of eq 4) is slower than the pure chemical effect (first term of the same equation). Indeed, in Figure 4, the two slopes are identical, even with a mass ratio $\psi_M = 2$.

4.2. Water−Ethanol Mixtures. The water−ethanol mixture has been studied by different authors, both for its equilibrium properties[41-43] and its nonequilibrium properties, in particular the Soret coefficient.[6,36-38] From simulations on simple Lennard-Jones systems,[18] we know that the change of the Soret coefficient with composition is controlled by cross interactions. From a thermodynamic point of view, excess properties reveal the nature of cross interactions. We present in Figure 6 experimental and EMD excess molar enthalpy, H^{ex}/N, for the water−ethanol mixture:

$$H^{ex}/N = H/N - \sum_{i=1}^{2} x_i H_i^{*}/N \tag{8}$$

In this equation, H is the total enthalpy, x_i the molar fraction of species i, N the total number of particles, and H_i^{*} is the enthalpy for the pure component i taken at identical pressure and temperature. The complex behavior of this mixture can be seen from the experimental data at 300 and 331 K. At 300 K, the molar excess enthalpy is negative, and the mixture is enthalpically favored over the entire concentration range. At 331 K, three different extrema are observed for H^{ex}/N, with both endothermic and exothermic regions. This behavior is attributed to the creation and destruction of the hydrogen bond network with temperature and composition. The simulation results at 300 K reproduce qualitatively the experimental behavior, but the magnitude is not correct. Indeed, our simulation data at 300 K rather correspond to experimental data at 331 K. Although the TIP4P 2005 model gives the best agreement among many classical water semiempirical force fields,[45] its freezing point is more than 20 K lower than the experimental one. Consequently, a simulation done with this potential at 300 K may correspond to an experimental situation at higher temperature. More importantly, due to the arbitrary Lorentz−Berthelot mixing rules, cross interactions must also not be very well described.

(44) Jorgensen, W. L.; Maxwell, D. S.; TiradoRives, J. *J. Am. Chem. Soc.* **1996**, *118*, 11225–11236.

(45) Abascal, J. L. F.; Vega, C. *J. Chem. Phys.* **2005**, *123*, 234505.

(46) Glasstone, G.; Laider, K. J.; Eyring, H. *Theory of Rate Processes*; McGraw-Hill Book Co., Inc.: New York, 1941.
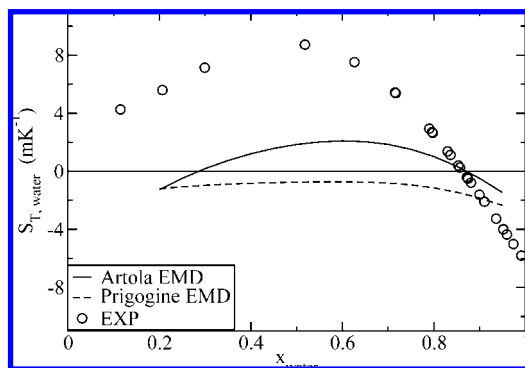
Figure 7. Prigogine's and Artola's models for Soret coefficient of water−ethanol mixtures obtained from EMD simulations (300 K) compared to experimental data compiled in ref 6 (293−298 K).

Figure 8. Temperature dependence of the water−ethanol Soret coefficient from experiments and our model.

As was shown in ref 18, because the slope of the Soret coefficient with composition strongly depends on cross interactions, we expect some discrepancies between the slope observed for the Soret coefficient from experiments and from molecular simulations.

We now turn to the predictions of the Soret coefficient using our model and EMD data. We present, in Figure 7, Prigogine's and Artola's predictions and compare them with experimental data compiled by Wiegand in ref 6. Prigogine's predictions differ from experimental data on two points: there is no change of sign of the Soret coefficient and a small dependence on composition is observed, although the general trend is very close to the experimental behavior. Our model predicts quantitatively the molar fraction at which the Soret coefficient changes sign but underestimates the modulus of the Soret coefficient. Clearly, the mass effect included in our model enhances the prediction of the Soret coefficient by adding a mole-fraction-dependent term for the water−ethanol mixture. This is consistent with simulation at high mass ratio, where a mole fraction dependence has been noted.[47]

Nieto-Draghi et al.[35] performed NEMD simulations with a different model of water, with a different algorithm for electrostatic interactions (reaction field instead of Ewald summation), a smaller system (800 molecules), and relatively short production runs (20 ns, compared to the 200 ns done for the Lennard-Jones mixtures in this work). The results reproduced the change of sign of the Soret coefficient and are qualitatively in agreement with both experiments and our new model due to large statistical errors bars.

We believe that the discrepancy between experimental results and our new model has the same origin as the one observed for excess properties, i.e., the choice of the potential used for these simulations. Indeed, the mole fraction dependence of the Soret coefficient is due to cross interactions which, as seen from excess enthalpy predictions, are clearly underestimated with these force fields. Therefore, we expect the Soret coefficient to be underestimated due to this "potential temperature shift". This is further reinforced by the trends observed for the Soret coefficient in this system with temperature. As shown by Kölodner,[37] the change of sign of the Soret coefficient for the water−ethanol mixture is temperature independent and can be observed at x_{water} ≈ 0.84. However, its magnitude decreases with increasing temperature, as can be seen in Figure 8. As temperature is
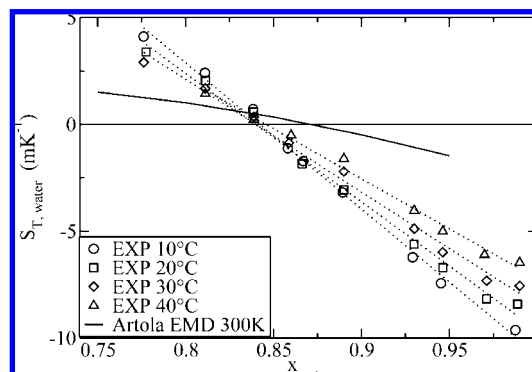
increased, our predictions are in better agreement with experimental data. We believe that a good agreement would be observed at temperature close to 331 K, in line with the temperature shift observed for excess properties.

We are particularly interested in the second change of sign of the Soret coefficient that we predict using our new model. This peculiar feature would be observed only at high temperature, and therefore we suggest new experiments! Furthermore, at a lower temperature, we reproduce the general trend, but we do not fit to experimental data. For these two reasons, it seems to us that a new experiment at higher temperature would be the most reasonable.

5. Conclusion

In this paper, we have shown that the original Prigogine model, in which thermal diffusion is described as an activated process, does not include mass effects. In this kinetic model, the predicted Soret coefficient is independent of the mass ratio of the species in the mixture. Starting from the same picture and rescaling the reaction coordinate so as to displace barycentrically the diffusion transition state, we propose a new model that accounts for mass effects. The new formula relies on activation self-diffusion free enthalpies that can be obtained quite easily using EMD. We have demonstrated the validity of our new formula by comparing nonequilibrium molecular dynamics simulations on Lennard-Jones mixtures (used as a reference set of data) and model predictions. However, there remain some theoretical difficulties:

- In our new formula, no moment of inertia term appears. A similar approach should introduce this term, but for flexible molecules the meaning of a single moment of inertia is physically not relevant. We are not able, at this stage, to propose a formula. Some work has already been done on this problem and suggests a not-so-simple picture of the independence of the mass and the moment of inertia terms.[47]
- In the low-density limit, we are no longer in an activated regime, and this approach is not relevant. Therefore, Chapman−Enskog theory may be more relevant.[30]
- In the case of isotopic mixtures (where activation free enthalpies are equal), our formula seems to predict a Soret coefficient independent of the composition. However, it has been observed by molecular dynamics[17] that a mole fraction dependence appears at very high mass ratio. This feature is not taken into account in this model yet.

When our model is applied to a more realistic system, the water−ethanol mixture, we obtain a good prediction of the

(47) Galliero, G.; Duguay, B.; Caltagirone, J.-P.; Montel, F. *Fluid Phase Equilib.* **2003**, *208*, 171–188.

composition at which the Soret coefficient changes sign. However, the predicted Soret coefficient is underestimated. By studying equilibrium properties for this mixture, we have shown that the force fields employed underestimate excess properties or, equivalently, cross interactions. As a consequence, the Soret coefficient we can compute from our model is underestimated due to the "potential temperature shift". In real systems, when temperature is increased, the excess properties decrease, along with the magnitude of the Soret coefficient. From the Soret measurements in the range 283−313 K, we believe that our simulated systems behaves like a real system at 331 K. New experiments in this temperature range could provide an important validation of this work on realistic mixtures.

Further work will be to include a Firoozabadi-like extension of this model, in order to propose a very efficient way to estimate accurately the Soret coefficient of a mixture. This extension must include a very precise study of the adjustable parameters of this model[28] that are not yet understood, as several means of estimation have already been proposed.[28,46,48] One way could be the algorithm proposed in ref 49.

(48) Pan, S.; Saghir, M. Z.; Kawaji, M.; Guobing, C.; Yan, Y. *J. Chem. Phys.* **2007**, *126*, 014502.
(49) Galliero, G.; Volz, S. *J. Chem. Phys.* **2008**, *128*, 064505.
(50) Schimpf, M. E.; Semenov, S. N. *Physical Review E* **2004**, *70*, 031202.