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# On the microscopic origin of Soret coefficient minima in liquid mixtures<sup>†</sup>

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Temperature gradients induce mass separation in mixtures in a process called thermodiffusion and quantified by the Soret coefficient. The existence of minima in the Soret coefficient of aqueous solutions at specific salt concentrations was controversial until fairly recently, where a combination of experiments and simulations provided evidence for the existence of this physical phenomenon. However, the physical origin of the minima and more importantly its generality, e.g. in non-aqueous liquid mixtures, is still an outstanding question. Here, we report the existence of a minimum in liquid mixtures of non-polar liquids modelled as Lennard-Jones mixtures, demonstrating the generality of minima in the Soret coefficient. The minimum originates from a coincident minimum in the thermodynamic factor, and hence denotes a maximization of non-ideality mixing conditions. We rationalize the microscopic origin of this effect in terms of the atomic coordination structure of the mixtures.

#### Introduction

Thermal gradients induce the transport of colloids in suspension (thermophoresis) and concentration gradients in liquid mixtures and solutions (thermodiffusion). The Soret coefficient,  $S_{\rm T}$ , measures the mass separation of mixtures in thermal fields and is becoming a central property to characterise the non-equilibrium response of soft matter and fluids.<sup>1–8</sup>

Experimental and computational studies have advanced significantly in recent years, but several outstanding questions remain. One such question is the microscopic origin of the forces driving the phenomenology observed in thermodiffusion measurements. Aqueous solutions feature a particularly rich phenomenology.<sup>9–11</sup> Gaeta *et al.*<sup>10</sup> reported minima in the Soret

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coefficients of NaCl<sub>(aq)</sub> and KCl<sub>(aq)</sub> as a function of concentration. These experiments were performed with thermogravitational columns, and the minima could not be reproduced using state-of-the-art thermal diffusion forced Rayleigh scattering techniques, which circumvent convection effects.<sup>11</sup> Hence the  $S_{\rm T}$  minimum remained controversial for many years. However, this situation changed with recent experiments and computer simulations of LiCl<sub>(aq)</sub>, which support the existence of a minimum in the Soret coefficient.<sup>12,13</sup> Very recently, minima at high concentrations (~2 M) were observed for thiocyanate (NaSCN<sub>(aq)</sub>) and KSCN<sub>(aq)</sub>) and acetate (CH<sub>3</sub>COOK<sub>(aq)</sub>) salt solutions,<sup>14,15</sup> giving further impetus to the investigation of the physical origin of the  $S_{\rm T}$  minima.

In addition to aqueous electrolyte solutions, minima in  $S_{\rm T}$ with composition were observed in mixtures of polar fluids: ethanol/water,<sup>5,16,17</sup> dimethyl-sulfoxide/water<sup>18</sup> and acetone/ water.<sup>18,19</sup> In all these systems (electrolyte solutions and polar fluid mixtures), one of the components is water. This observation might suggest that the  $S_{\rm T}$  minima are interlinked with water as a solvent and, therefore, its specific thermal transport properties. Indeed, molecular simulations of atomistic (non-polar) Lennard-Jones (LJ) binary mixtures at supercritical conditions do not offer evidence for the existence of minima in  $S_{\rm T}$  with composition.<sup>20</sup> However, some experiments of non-polar or weakly polar liquid mixtures reported maxima/minima in  $S_{\rm T}$  (e.g. cyclohexane/cisdecaline) and in some cases, accounting for an extrapolation to infinite dilution, a weak extrema can be inferred (e.g. toluene/1,3dichlorobenzene).<sup>21</sup> That work made no attempt to explain the microscopic origin of the extrema in  $S_{\rm T}$ , but crucially highlights the importance of the thermodynamic factor,  $\Gamma$ , a key quantity determining the heat of transport.13,22

To investigate the existence of Soret coefficient minima in non-polar mixtures, and to probe the microscopic origin of such minima, we have performed computer simulations of the simplest liquid binary mixture, modelled with the Lennard-Jones model, which accounts for dispersion interactions. We show for the first time that a minimum in the Soret coefficient at a specific composition, and constant temperature T and

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pressure *P*, can be observed in simple non-polar liquid mixtures, hence showing that the minimum is a completely general physical phenomenon.

#### Methods

We consider binary LJ mixtures at constant T and P, and different mole fractions  $x_1$ . Inter-particle interactions were modelled using the LJTS potential, which is the LJ potential  $|\mathscr{V}_{ij}^{\text{LJ}}(r) = 4\varepsilon_{ij}[(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^6]$  truncated and shifted at a cutoff radius of  $r_{\rm c} = 2.5\sigma$ ,  $|\mathscr{V}_{ij}^{\rm LJTS}(r) = (\mathscr{V}_{ij}^{\rm LJ}(r) - \mathscr{V}_{ij}^{\rm LJ}(r_{\rm c}))\theta(r_{\rm c} - r)$  with  $\theta$ being the Heaviside step function. All the particles have the same diameter and mass, but the interactions between of particles of type "1" or "2" are different. The parameters  $\varepsilon = \varepsilon_{22}$  and  $\sigma = \sigma_{11} = \sigma_{22}$  together with the mass of each particle  $m_1 = m_2 = m$  define the usual LJ units. The energy scale was defined in terms of the high-boiling component, with  $\varepsilon_{11}/\varepsilon_{22}$  = 0.6. The Lorentz-Berthelot combining rules were used for  $\varepsilon_{12} = \sqrt{\varepsilon_{11}\varepsilon_{22}} = \sqrt{0.6\varepsilon}$  and  $\sigma_{12} = (\sigma_{11} + \sigma_{22})/2 = \sigma$ . Experiments of liquid-liquid mixtures have reported extrema in  $S_{T}$ , therefore we target subcritical conditions for the LJ mixtures. Mixtures were modelled at  $T = 0.62 \varepsilon k_{\rm B}^{-1}$  ( $k_{\rm B}$  is the Boltzmann constant) and  $P = 0.46 \ \varepsilon \sigma^{-3}$ , below the critical point<sup>23</sup> for both species. The entire  $0 \le x_1 \le 1$  composition domain is therefore expected to be subcritical. We note that along this isobarisotherm, the thermodynamically stable phase for  $x_1 = 0$  is a solid and we estimate the liquids to be at  $x_1 \approx 0.2$  (see the ESI<sup>†</sup>). Simulations below this mole fraction correspond to a metastable liquid-liquid mixture. Nevertheless, as we will show below, the observed  $S_{\rm T}$  minimum is safely within the liquidliquid mixture portion of the phase diagram.

We performed a variety of equilibrium molecular simulations (EMS), molecular dynamics (MD) and Monte Carlo methods, as well as non-equilibrium molecular dynamics (NEMD) simulations to calculate  $S_{\rm T}$  and related quantities. From NEMD,  $S_{\rm T}$  was evaluated at the stationary state characterised by zero net mass flux as  $S_T = -(w_1 w_2)^{-1} (\nabla w_1 / \nabla T) = -(x_1 x_2)^{-1} (\nabla x_1 / \nabla T)$  where  $x_i$ and  $w_i$  are the mole and mass fractions of species *i*. EMS methods calculate  $S_{\rm T} \equiv D_{\rm T}/D_{12}$  from<sup>24</sup> the mutual diffusion coefficient  $D_{12} = L_{11}(\partial \mu_{s,1} / \partial w_1)_{P,T} / (\rho w_2 T)$  and thermal diffusion coefficient  $D_{\rm T} = L'_{1q} / (\rho w_1 w_2 T^2)$ . Onsager's phenomenological coefficients  $L_{\alpha\beta}$  were calculated using the Green–Kubo (GK) integral formulas and taking into account the enthalpy terms for  $L'_{1a}$ . The chemical potential  $\mu_1$ , and subsequently the specific chemical potential  $\mu_{s,1} = \mu_1/m_1$ , was calculated using a free energy perturbation (FEP) method at constant T and P.  $(\partial \mu_1 / \partial x_1)_{P,T}$  was then calculated from the numerical derivative of  $\mu_1$ .  $(\partial \mu_1 / \partial x_1)_{P,T}$  was also obtained from Kirkwood-Buff solution theory via two different methods of evaluating the Kirkwood-Buff integrals (KBIs): (1) from particle number fluctuations in grand canonical Monte Carlo (GCMC) simulations and (2) from the extrapolation to infinite system size of finite-volume KBIs,<sup>25</sup> which were in turn calculated using radial distribution functions (RDFs) from MD simulations in the NVT ensemble. Thus, three EMS methods were used to calculate  $(\partial \mu_1 / \partial x_1)_{P,T}$  and subsequently the thermodynamic

factor: FEP, KBI(RDF) and KBI(GCMC). Combining these with the GK calculations for  $L_{11}$  and  $L'_{1q}$  give three corresponding "equilibrium" routes to  $S_{T}$ : GK + FEP, GK + KBI(RDF) and GK + KBI(GCMC). Other thermophysical properties were also calculated from MD simulations. Details about all these simulations and calculations are given in the ESI.† All simulations were performed using LAMMPS<sup>26</sup> (v. 3 March 2020).

#### **Results & discussion**

Fig. 1(a) contains the main result of this communication:  $S_{\rm T}$  features a minimum as a function of composition at  $x_1^{\min(S_{\rm T})} \sim 0.5$ . Fitting cubic functions to the data give  $x_1^{\min(S_{\rm T})} = 0.5 \pm 0.1$  for all four methods: NEMD, GK + FEP, GK + KBI(RDF) and GK + KBI(GCMC). The thermodiffusion response at the minimum is significantly enhanced with respect to diluted mixtures, by  $\sim 30$ –40% relative to  $x_1 = 0.1$ , 0.9, and by  $\sim 60$ –80% when compared to the extrapolated value of  $S_{\rm T}$  at  $x_1 = 1$ . For all compositions,  $S_{\rm T} < 0$  which indicates that species 1 (the low-boiling component) is thermophilic and preferentially collects in the hot region. The  $S_{\rm T}$  values calculated from NEMD and all three EMS methods are in excellent agreement.

 $S_{\rm T} \equiv D_{\rm T}/D_{12}$  is determined by  $D_{12}$  and  $D_{\rm T}$ , which monotonically increase and decrease with  $x_1$ , respectively (Fig. 1(b)). Thus, the  $S_{\rm T}$  minimum arises from a balance of  $D_{\rm T}$  and  $D_{12}$ , as opposed to being carried through only by one of the transport coefficients.

The Soret coefficient  $S_{\rm T}$  can be written in terms of the phenomenological coefficients and the thermodynamic factor  $\Gamma$ , as<sup>24</sup>

$$S_{\rm T} = \frac{L_{1q}'}{L_{11}Tw_1} \left(\frac{\partial\mu_{\rm s,1}}{\partial w_1}\right)_{P,T}^{-1} = \frac{1}{k_{\rm B}T^2L_{11}} \frac{L_{1q}'m_1}{\Gamma}$$
(1)

$$\Gamma = \frac{x_1}{k_{\rm B}T} \left( \frac{\partial \mu_1}{\partial x_1} \right)_{P,T} \tag{2}$$

where  $m_1 = m_2 \Leftrightarrow x_1 = w_1$ . The analysis of the different contributions to the RHS of eqn (1) offers microscopic insight into the mechanisms determining the minimum in  $S_T$ . We find that the ratio  $L'_{1q}/L_{11}$  is essentially constant for all compositions (Fig. 1(d)). This suggests that the minimum arises from the  $w_1(\partial \mu_1/\partial w_1)_{P,T}$  term. As shown in Fig. 1(c),  $\Gamma$  features a distinctive minimum at  $x_1^{\min(\Gamma)} \sim 0.5$ , with all three EMS methods predicting values in good agreement with each other. *The minimum in*  $S_T$  *is connected to the minimum in the thermodynamic factor, and therefore the minimum signals the composition at which the mixture features the largest non-ideality*, max $|1 - \Gamma|$ .

We note that in our work, the minimum in  $\Gamma$  leads to a minimum in  $S_{\rm T}$  since  $L'_{1q} < 0 \Leftrightarrow D_{\rm T} < 0$  ( $L_{11} \ge 0$ ,<sup>24</sup> and a stable single-phase binary mixture requires  $\Gamma > 0$ ). For  $L'_{1q} > 0 \Leftrightarrow D_{\rm T} > 0$ , the minimum in  $\Gamma$  leads to a maximum in  $S_{\rm T}$ . Indeed, since  $S_{\rm T}$  and  $D_{\rm T}$  change sign under the permutation of components in a binary mixture ( $S_{{\rm T},1} = -S_{{\rm T},2}$  and  $D_{{\rm T},1} = -D_{{\rm T},2}$ ), the  $\Gamma$  minimum leads to a maximum in the Soret coefficient of species 2.



*α*<sup>2</sup>

P

**Fig. 1** The Soret coefficient  $S_T$  and related properties as a function mole fraction  $x_1$ . (a)  $S_T$ ; the solid lines show cubic functions fit to the  $S_T(x_1)$  data. (b) The mutual diffusion coefficient  $D_{12}$  (left axis) and thermal diffusion coefficient  $D_T$  (right axis). (c) The thermodynamic factor  $\Gamma$ ; the solid lines show polynomial functions fit to  $\Gamma(x_1)$  with the infinite-dilution constraint  $\Gamma(1) = 1$ . (d) The ratio of phenomenological coefficients  $L'_{1q}/L_{11}$ ; the solid line shows the weighted arithmetic mean.

The results presented above indicate that the non-ideal contribution dominates at conditions near the minimum. This can be visualised by splitting  $\Gamma$  into its ideal (id) and excess (ex) parts (see ESI,† Section S1.2), showing as expected that  $\Gamma^{ex}$ , is responsible for the minimum in  $\Gamma$ . To gain insight into the microscopic origins of the minimum in  $\Gamma$  and  $S_T$ , we turn to

Kirkwood–Buff theory, which connects  $\Gamma$  to the structural properties of the binary mixture,

$$\Gamma = 1 - \frac{x_1 x_2 \rho_N (G_{11} + G_{22} - 2G_{12})}{1 + x_1 x_2 \rho_N (G_{11} + G_{22} - 2G_{12})}$$
(3)

where  $\rho_N$  is the total number density of the mixture. The Kirkwood–Buff integral (KBI)  $G_{ij}$  is defined as the spatial integral over  $g_{ij}^{\mu VT}(r) - 1$ , and quantifies the excess (or deficiency) of species *j* around *i*.  $g_{ij}^{\mu VT}(r)$  is the pair correlation function in the grand canonical ensemble. The KBIs can be expressed in terms of the excess coordination numbers  $n_{ij}^{\text{ex}}(r') = n_{ij}(r') - n_{ij}^{\text{id}}(r')$  where  $n_{ij}$  is the total coordination number, obtained from an integral over the pair correlation function, and  $n_{ij}^{\text{id}} = (4\pi/3)\rho_{N,j}r_c^{\prime 3}$  is the ideal coordination number.  $\rho_{N,j}$  is the number density of species *j*. Hence, the KBIs are given by  $\rho_{N,j}G_{ij} = \lim_{r' \to \infty} n_{ij}^{\text{ex}}(r') = n_{ij}^{\text{ex},\infty}$ , and the thermodynamic factor by  $\Gamma = (1 + f)^{-1}$  where  $f = (1 - x_1)n_{11}^{\text{ex},\infty} + x_1n_{22}^{\text{ex},\infty} - 2x_1n_{12}^{\text{ex},\infty} = f_{11} + f_{22} + f_{12}$ .

In order to disentangle the contributions from  $n_{11}^{ex,\infty}$ ,  $n_{22}^{ex,\infty}$ and  $n_{12}^{\text{ex},\infty}$  we take the first-order approximation to the thermodynamic factor,  $\Gamma^{(1)} = 1 - f$ . As shown in Fig. 2(c),  $\Gamma^{(1)}$  results in underestimations of 1-35% across the range of compositions, with larger errors for more non-ideal mixtures, but nevertheless provides insight into the relative importance of the  $f_{ii}$  terms.  $f_{12}$ features a maximum at  $x_1 \sim 0.5$  (Fig. 2(b)), indicating that the cross-species contribution is responsible for the minimum in  $\Gamma^{(1)}$  and  $\Gamma$ .  $|(f_{11} + f_{22})/f_{12}| = 0-0.41$  making the cross-species contribution much more significant, and  $\sim$  3-4 times larger in the region of the  $\Gamma^{(1)}$  and  $\Gamma$  minima. Consequently, the phenomenology of  $\Gamma^{(1)}$  and  $\Gamma$  are primarily determined by  $f_{12}$ . Thus, the composition dependence of  $n_{12}^{ex,\infty}$  (Fig. 2(a)), which represents a net depletion of species 2 around 1 relative to the ideal state, and increases monotonically with  $x_1$ , is the primary microscopic origin of the minimum in  $\Gamma$  and therefore  $S_T$ .

Now we examine the accuracy of theoretical approaches to predict the  $S_{\rm T}$  minimum reported above. We note that existing theoretical models do not accurately predict  $S_{\rm T}$  in general.<sup>27–33</sup> In some cases, even the sign of  $S_{\rm T}$  is not predicted correctly.<sup>28–33</sup> Especially in earlier works, the discrepancies can, at least in part, be attributed to inaccuracies in experimentally determined properties. For example the Haase<sup>30,34</sup> and Kempers<sup>30</sup> models are very sensitive to partial molar properties, and therefore the equation of state used.<sup>30,31</sup> In computer simulations all the required quantities can be accurately calculated, and as shown here using an exact model, all the theories examined herein feature noticeable deviations from the  $S_{\rm T}$  values obtained by direct simulation. Previous simulations have shown that the theories are accurate only in a very limited number of cases, even for simple LJ mixtures and hard-sphere mixtures.<sup>20,32,33</sup> We have tested the standard theoretical models against our simulation data. We calculate the Soret coefficient according to the models of Haase<sup>30,34</sup> ( $S_{T}^{H}$ ), Kempers<sup>30</sup> ( $S_{T}^{K}$ ), Shukla and Firoozabadi<sup>29</sup> (S<sub>T</sub><sup>SF</sup>), and Artola, Rousseau and Galliéro<sup>32</sup>/Prigogine<sup>35,36</sup> ( $S_{\rm T}^{\rm ARG/P}$ ). Further details are given in the ESI.†

We show in Fig. 3 the Soret coefficients predicted by these models, alongside the NEMD values for reference. Out of the



**Fig. 2** Analysis of the thermodynamic factor  $\Gamma$  as a function of mole fraction  $x_1$  using Kirkwood–Buff theory. (a) Excess coordination numbers  $n_{ij}^{e,\infty}$  and (b) related functions f and  $f_{ij}$ . (c)  $\Gamma$  and its first-order approximation  $\Gamma^{(1)}$ . Symbols: sideways triangles and dotted lines ( $\cdots \lhd \cdots$ ) denote the KBI(RDF) data; downwards triangles ( $-\nabla -$ ) and dashed lines denote the KBI(GCMC) data. In (c), dotted and dashed lines show polynomial functions fit to the KBI(RDF) and KBI(GCMC) data respectively. Fits to  $\Gamma(x_1)$  were performed with the infinite-dilution constraint  $\Gamma(1) = 1$ .



**Fig. 3** Soret coefficient  $S_T$  as a function of  $x_1$  as predicted by various models, as defined in the main text. The NEMD values  $S_T^{\text{NEMD}}$  are shown for reference. The solid lines show cubic functions fit to the  $S_T(x_1)$  data.

four models,  $S_{\rm T}^{\rm SF}$  is the most accurate: it overestimates  $|S_{\rm T}|$  by ~20–50%.  $S_{\rm T}^{\rm K}$  and  $S_{\rm T}^{\rm H}$  overestimate  $|S_{\rm T}|$  by ~400–500% and ~300–400%, respectively.  $S_{\rm T}^{\rm ARG/P}$  underestimates  $|S_{\rm T}|$  by ~100–110%, predicting values ~10<sup>-1</sup>  $k_{\rm B}\varepsilon^{-1}$ . Furthermore, the model predicts the wrong sign:  $S_{\rm T}^{\rm ARG/P} > 0$  or straddles 0 when accounting for the associated uncertainties.

 $S_{\rm T}^{\rm H}, S_{\rm T}^{\rm K}$  and  $S_{\rm T}^{\rm SF}$  all possess a minimum because they contain  $x_1(\partial \mu_1/\partial x_1)_{P,T} = k_{\rm B}T\Gamma$  in the denominator (see the ESI†). The  $x_1(\partial \mu_1/\partial x_1)_{P,T}$  term in  $S_{\rm T}^{\rm SF}$  originates directly from the phenomenological equations for thermodiffusion from linear non-equilibrium thermodynamics, which the model uses as a

starting point for its derivation. For  $S_T^K$ , the  $x_1(\partial \mu_1/\partial x_1)_{P,T}$  term arises naturally from the statistical thermodynamics approach employed by Kempers. Originally an educated guess,  $S_T^H$  can be derived more rigorously within the framework of Kempers.<sup>30</sup> In contrast,  $S_T^{ARG/P}$  does not predict a minimum: it features a weak concentration dependence, and generally decreases with increasing  $x_1$ .  $S_T^{ARG/P}$  contains  $k_BT$  (as opposed to  $k_BT\Gamma$ ) in the denominator, which is only valid for ideal mixtures. Indeed the ARG/P model does not explicitly consider a concentration gradient along the reaction coordinate; doing so would result in a similar "non-ideality" term in the denominator.<sup>37</sup>

#### **Closing remarks**

We close this communication with a discussion of our results in the context of recent literature. LJ mixtures are representative of mixtures of approximately spherical non-polar molecules, in which intermolecular interactions are dominated by van der Waals forces. Comparing to mixtures of non-polar organic solvents, at 25 °C cyclohexane/*cis*-decalin possesses a  $S_{\rm T}$  maximum at  $x_1 \approx 0.2$  but  $\Gamma \approx 1.0$  for the entire  $0 \le x_1 \le 1$  range (there is a very shallow  $\Gamma$  minimum at  $x_1 \approx 0.8$ ), indicative of a different origin compared to the LJ mixture. Also in contrast with the LJ mixture, cyclohexane/benzene features a monotonic increase of  $S_{\rm T}$  with  $x_1$  at 25 °C, but does have a strong minimum in  $\Gamma$  at  $x_1 \approx 0.5$ .<sup>21</sup>

 $S_{\rm T}$  minima have been observed in mixtures of polar organic solvents with water. Ethanol/water and acetone/water mixtures have minima at  $x_1 \sim 0.6$  and  $x_1 \sim 0.5$ , respectively, roughly coincident with minima in  $D_{12}$  and  $\Gamma$  for both mixtures.<sup>5,16–19,38,39</sup> Comparing to aqueous solutions, while the  $S_{\rm T}$  minimum examined in this work originates from a coincident minimum in  $\Gamma$ , for LiCl<sub>(aq)</sub>,  $\Gamma$ increases monotonically in the concentration range of the  $S_{\rm T}$ minimum.<sup>13</sup> Furthermore, simulations have highlighted the importance of ion solvation structure on the existence of the minimum in LiCl<sub>(aq)</sub>.<sup>40</sup> In contrast, local structural changes in the LJ mixture are minor (see ESI,† Section S1.4). We note that This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

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many simple salts are thought to have a  $D_{12}$  minimum at low concentrations (~10<sup>-1</sup> mol dm<sup>-3</sup>) often attributed to ion-pair formation and solute–solvent association.<sup>14,41–43</sup> Recent experiments observed  $S_{\rm T}$  minima in NaSCN<sub>(aq)</sub>, KSCN<sub>(aq)</sub>, K<sub>2</sub>CO<sub>3(aq)</sub> and CH<sub>3</sub>COOK<sub>(aq)</sub> that are carried through  $D_{\rm T}$ .<sup>14,15</sup> Hence, the physical origin of the minima in aqueous solutions and mixtures might be quite different to the one reported here for nonpolar liquids, since the LJ mixtures do not feature extrema in  $D_{12}$  or  $D_{\rm T}$ .

It is evident that the physical origins of  $S_{\rm T}$  minima/maxima must be considered on a case-by-case basis for different mixtures, even those belonging to the same class (aqueous solution, non-polar organic solvent mixtures, etc.). We provide here a proof of principle and demonstrate that  $S_{\rm T}$  minima can exist in even the simplest of mixtures, as exemplified by a binary LJ mixture in which the components differ by only the interaction parameter  $\varepsilon$ . The concentration dependence of the  $S_{\rm T}$  is, at least for simple mixtures, typically attributed to the cross-interactions between unlike particles<sup>20</sup> - a notion sustained in recent reviews.7,44,45 For dense supercritical LJ mixtures with cross-interactions given by  $\varepsilon_{12} = k_{12}\sqrt{\varepsilon_{11}\varepsilon_{22}}$  it was found that  $S_{\rm T}(x_1) \approx bx_1 + c$ , with the slope *b* controlled by  $k_{12}$ .<sup>20</sup> Greater  $|1 - k_{12}|$  values resulted in greater |b| values. In this work, we identify a mixture with  $k_{12} = 1$  that nevertheless features a strong composition dependence and more complex phenomenology (the  $S_{\rm T}$  minimum). Extrapolating our results, we expect that the observation of Soret coefficient minima/ maxima in LJ mixtures is strongly correlated with their degree of non-ideality; sufficiently non-ideal mixtures might be more difficult to achieve at e.g. supercritical conditions. Clearly, further work is required to explain the composition dependence of  $S_{\rm T}$  in liquid mixtures and different thermodynamic conditions.

#### Conflicts of interest

There are no conflicts to declare.

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