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Internal degrees of freedom, molecular symmetry and thermodiffusion

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ABSTRACT

Using the thermodynamic expression for the Soret coefficient for diluted mixtures, expressed through the temperature derivative of the molecule chemical potential at the constant pressure, statistical mechanics is applied to relate this expression to the microscopic molecular parameters. When the contribution of the internal degrees of freedom in molecules is accounted for in the calculations, the results are equivalent to previous approaches, adding new terms to the Soret coefficient. These terms are related to the differences in molecular vibration and rotation between the solute and solvent molecules. These "internal" contributions to molecular thermodiffusion explain the isotopic effect observed in molecular systems. The theory describes most of the experimental data on the thermodiffusion of isolated molecules placed in non-electrolyte liquids. The approach also reveals a strong dependence of molecular thermodiffusion on molecular symmetry.

1. Introduction

The aim of this article is to employ statistical mechanical calculations to incorporate the role of molecular internal degrees of freedom on the Soret coefficient, which characterizes the concentration gradient established in a non-isotherm mixture [1–3]:

$$S_T = -\nabla\phi/\phi(1-\phi)\nabla T \tag{1}$$

Here ϕ is the volume fraction of the selected component in a binary mixture and T is the temperature. The motivation for this work comes from experiments that demonstrate a change in thermodiffusion with isotopic substitutions in molecules [4–7].

Isotopic substitution is a method for changing the mass of a molecule without changing its chemical structure or geometry, while only slightly altering the intermolecular interaction potentials. Using a thermogravitational column, the thermodiffusion of several binary isotopic mixtures were studied in Refs. [4–7], including mixtures of benzene with various degrees of deuteration, isotopically substituted mixtures of halogenated benzenes [8], mixtures of partly and fully deuterated methanol [4], and isotopic mixtures of carbon disulfide [8]. In Refs. [7,9], it was found that the Soret coefficient S_T depends not only on the mass difference between the two isotopic molecules, such as C_6H_6 and C_6D_6, but also on the mass distribution within the molecules, as characterized by the molecular moment of inertia I. The results could be described by a linear function of the relative mass difference and the relative difference in moment of inertia, as had originally been used to describe the behavior of gaseous isotopic mixtures [10] and mixtures of gaseous polyatomic molecules [11].

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Simulations for Lennard-Jones liquids using molecular dynamics showed that the differences in molecular mass, moment of inertia, diameter, and interaction strength contribute additively to S_T in such a way that the molecules with the higher mass, the higher moment of inertia, the smaller diameter, and the stronger interaction show more positive thermodiffusion, that is, movement toward to the cold side [12–17]. In Ref. [18] the isotope effect in a mixture of two different non-isotopic liquids of comparable molecular size and mass, benzene and cyclohexane, was investigated. For these mixtures it was shown that S_T can be separated into additive contributions related to the differences in mass and moment of inertia, plus an additional term related to the molecular structure.

In Ref. [19] it was shown that the Soret coefficient in binary mixtures of isotopically substituted cyclohexanes can be approximated using the following linear function:

$$S_T = S_{iT} + a_m \Delta M + b_i \Delta I \tag{2}$$

Here S_{iT} is the contribution of intermolecular interactions, a_m and b_i are coefficients (further described in Section 4) and ΔM and ΔI are the differences in the mass and the moment of inertia, respectively, for the molecules constituting the binary mixture.

In Ref. [20], a thermodynamic expression for the Soret coefficient was obtained that contains a term related to the difference in thermal velocities, and is expressed through the logarithm of solute to solvent mass ratio. The expression can be transformed into the second term on the right-hand side of Eq. (2) when the mass difference is small. The expression obtained in Ref. [20] also contains a term corresponding to the first term on the right-hand side of Eq. (2), which is related to intermolecular interactions. In that work the molecule was considered to be a uniform sphere having no internal structure. Consequently, the internal degrees of freedom related to molecular rotations and vibrations were not considered. These factors will be investigated here in connection with molecular thermodiffusion.

The general thermodynamic expression for the Soret coefficient in a dilute binary mixture is [21,22]

$$S_T = \frac{1}{2kT}\frac{\partial \mu_P^*}{\partial T} \tag{3}$$

where μ_P^* is the combined chemical potential, which is defined as

$$\mu_P^* = \mu_P^2 - \frac{N_2 v_2}{v_1}\mu_P^1 \tag{4}$$

Parameters μ_P^1, μ_P^2 are the chemical potentials of the respective components at constant pressure, v_1 and v_2 are the specific molecular volumes of the solvent molecule and the molecule or atom constituting the molecule, respectively, and N_2 is the number of internal molecules or atoms in the molecule. We note here that the chemical potential at constant pressure should be used, a fact that was not accounted for in previous theories. The expression for the Soret coefficient using the parameter μ^* at the constant volume was also obtained in Ref. [23].

In our calculations we will use the fact that there is certain symmetry between the chemical potentials contained in Eq. (4). Thus, the term $\frac{N_2 v_2}{v_1}\mu_P^1$ can be written as $N_1\mu_1$, where N_1 is the number of the solvent molecules that displaced from the volume $N_2 v_2$. Using the known determination of free energy as the sum of chemical potentials, we can say that $N_1\mu_P^1$ is the chemical potential of a virtual particle consisting of the molecules of solvent displaced by the suspended molecule. For this reason, we can extend the results obtained in calculations of the chemical potential of the suspended molecule μ_P^2 to the calculation of parameter $N_1\mu_P^1$ by a simple change in the respective designations 2 → 1. We will consider a suspended molecule containing N_2 internal atoms interacting with molecules of the surrounding liquid. This approach was successfully used in Ref. [20].

2. Statistical mechanics of mass transport

For an isolated molecule in a liquid solvent, the chemical potential at constant volume can be calculated using a modification of the expression [24,25]

$$\mu_2 = \mu_{02} + 4\pi \int_0^1 \mathrm{d}\lambda \int_R^\infty \frac{g_{21}(r,\lambda)}{v_1}\Phi_{21}^*(r) r^2 \,\mathrm{d}r \tag{5}$$

where R is the molecular radius and r is the distance between the center of the molecule and a molecule of the solvent. Parameter $g_{21}(r,\lambda)$ is the pair correlative function, which expresses the probability of finding a solvent molecule at $\vec{r}_1$ ($r = |\vec{r}_1|$) if the internal molecule or atom is placed at $\vec{r}_2$. The Hamaker potential, which is defined as

$$\Phi_{21}^*(r) = \int_{V_{in}} \frac{\mathrm{d}V_{in}}{v_2}\Phi_{21}\big(|\vec{r}_2 - \vec{r}_1|\big) \tag{6}$$

is commonly used in colloid science [16,17] to study the interactions of colloid particles. In Eq. (6) $\Phi_{21}(|\vec{r}_2 - \vec{r}_1|)$ is the respective intermolecular potential. The Hamaker potential is applicable at distances of about one molecular size. Since we are considering a molecule rather than a colloid particle, the integral in Eq. (6) should, in the strictest sense, be replaced by the sum of the respective atomic interaction potentials, but we will ignore this difference in our calculations and use the commonly accepted model potentials. We will also consider the molecule as a spherical particle, within which the mass distribution may be non-uniform. This allows us to consider the spherical molecules distinct in their moment of inertia, which reduces redundancies in the mathematics.

Parameter

$$\mu_{02} = -\frac{3}{2}kT \ln\left[\frac{2\pi N_2 m_2 kT}{h^2}\right] - kT \ln N_2 v_2 - kT \ln Z_{rot} - kT \ln Z_{vib} \tag{7}$$

is the chemical potential, or the free energy of the non-interacting internal atoms that constitute the molecule (in that sense, the interaction potential $\Phi_{21}(|\vec{r}_2 - \vec{r}_1|) = 0$), and h is Planck's constant. Parameter λ describes the gradual "switching on" of the intermolecular interaction. A detailed description of this representation can be found in Refs. [24,25]. Z_{rot} and Z_{vib} are rotational and vibrational statistical sums, respectively. The molecular vibrations make no significant contribution to the thermodynamic parameters except in special situations, which will not be discussed here. The rotational statistical sum for polyatomic molecules is written as (Ref. [26])

$$Z_{rot} = \frac{\sqrt{\pi}}{\gamma h^3}\sqrt{\left(8\pi^2 kT\right)^3 I_1 I_2 I_3} \tag{8}$$

where γ is the symmetry value, which is the number of possible rotations about the symmetry axes when the molecule is carried into itself. For H_2O, $\gamma = 2$; for NH_3, $\gamma = 3$; for CH_4 and C_6H_6, $\gamma = 12$. I_1, I_2, and I_3 are the main values of the tensor of the moment of inertia. Linear molecules have only one moment of inertia.

3. Microscopic calculations

There is no satisfactory method for calculating the pair correlation functions in liquids, so we will use the reasonable approximation

$$g_{21}(r, \lambda) = 1 \tag{9}$$

This approximation means that the local distribution of solvent molecules is not disturbed by the considered molecule. This approximation is widely used in the theory of liquids and its effectiveness has been shown. In Refs. [27–29] the approximation was used in a kinetic approach to the thermodiffusion of colloid molecules; in Refs. [30–32] it was used in the hydrodynamic approach to thermodiffusion in polymer solutions.

The approximation of constant local density is used in the theory of regular solutions for the study of liquids [33]. Using this approximation, we have

$$\mu_2 = \mu_{02} + 4\pi \int_R^\infty \frac{\Phi_{21}^*(r)}{v_1} r^2 \, \mathrm{d}r \tag{10}$$

where the last term on the right-hand side is exactly the expression obtained in Refs. [27–29].

Using the symmetry between parameters μ_2 and $N_1\mu_1$ discussed above, we can write the combined chemical potential at constant volume $\mu_2 - N_1\mu_1$ as

$$\mu_2 - N_1\mu_1 = \frac{3}{2}kT \ln\left(\frac{N_1 m_1}{N_2 m_2}\right) + \frac{kT}{2}\ln\left(\frac{\gamma_2}{\gamma_1}\right)^2 \frac{(I_1 I_2 I_3)_1}{(I_1 I_2 I_3)_2} + 4\pi \int_R^\infty \frac{\Phi_{21}^*(r) - \Phi_{11}^*(r)}{v_1} r^2 \, \mathrm{d}r \tag{11}$$

In Eq. (11), the parameters with subscripts 2 and 1 are related to the considered molecule and the virtual particle consisting of solvent molecules replaced by the molecule under consideration, respectively. Note, that in general this virtual particle can have a higher symmetry because it contains identical molecules of the solvent, while the molecule under consideration can contain different atoms.

The chemical potentials at constant pressure and volume for a suspended molecule or colloid particle are related by the forces acting on the molecule or particle at uniform and non-uniform pressure, respectively:

$$\nabla\mu_P^2 = \nabla\mu_2 + \int_{V_{out}} \nabla\Pi \, \mathrm{d}v \tag{12}$$

Here Π is the local distribution of excess pressure around the dissolved or suspended molecule or particle. The local pressure distribution is widely used in hydrodynamic theories of the kinetic effects in liquids [30–32,34–36], and is usually obtained from the condition of local mechanical equilibrium in the liquid. This local equilibrium condition is written as $\nabla[\Phi_{21}^*(r)/v_1 + \Pi] = 0$. In Refs. [20,21], the local pressure distribution was also used in a thermodynamic approach in formulating the condition for establishment of local equilibrium in a thin layer of thickness l and area S around the molecule that has shifted from position r to $r + \mathrm{d}r$. The condition expresses the local conservation of specific free energy $F(r) = \Phi^*_{21}(r)/v_1 + \Pi(r)$ for the isothermal system in such a shift. The change in the free energy is written as:

$$\mathrm{d}F(r) = \nabla\left[\frac{\Phi^*_{21}(r)}{v_1} + \nabla\Pi\right] lS\,\mathrm{d}r = 0 \tag{13}$$

Thus, the expression used for the local pressure distribution around the molecule in hydrodynamic and thermodynamic approaches is obtained from the condition of zero change in the free energy after a shift in the thin layer of liquid surrounding the molecule. However, this layer creates a closed surface around the molecule.

In such a closed layer, the change in free energy $\frac{\Phi^*_{21}(r)}{v_1} l\,\mathrm{d}S$ due to the change in layer area $\mathrm{d}S$ should be taken into account. For a spherical layer, the changes in volume and surface area are related by $\mathrm{d}V = 2r\,\mathrm{d}S$, and we obtain the following modified version of Eq. (13) for a closed spherical surface:

$$\nabla\left[\frac{\Phi^*_{21}(r)}{v_1} + \Pi\right] + \frac{2\Phi^*_{21}(r)}{v_1 r}\vec{r}_0 = 0 \tag{14}$$

where $\vec{r}_0$ is the unit radial vector. The pressure gradient related to the change in surface area has the same nature as the Laplace pressure gradient obtained in Ref. [37]. Solving Eq. (14), we obtain

$$\Pi = -\frac{\Phi^*_{21}(r)}{v_1} - \int_{\infty}^{r} \frac{2\Phi^*_{21}(r')}{v_1 r'}\,\mathrm{d}r' \tag{15}$$

Substituting the pressure distribution from Eq. (15) into Eq. (12), using Eq. (11), and calculating the temperature-induced gradients related to the temperature dependence of the solvent specific molecular volume v_1, we obtain the following potential term related to intermolecular interactions:

$$\frac{\partial \mu_P^2}{\partial T} = \frac{2\alpha_T \nabla T}{v_1} \int_{V_{out}} \mathrm{d}v \int_{\infty}^{r} \frac{\Phi^*_{21}(r')}{r'}\,\mathrm{d}r' \tag{16}$$

Here ∇T is the temperature gradient in the bulk liquid and α_T is the thermal expansion coefficient of the solvent. The same procedure can be applied to the virtual particle consisting of the liquid displaced by the real molecule, in order to obtain

$$S_T = \frac{3}{4T}\ln\left(\frac{N_2 m_2}{N_1 m_1}\right) + \frac{1}{4T}\ln\left(\frac{\gamma_2}{\gamma_1}\right)^2 \frac{(I_1 I_2 I_3)_2}{(I_1 I_2 I_3)_1} - \frac{\pi^2 \alpha_T}{v_1 kT} \int_{\sigma_{12}}^{\infty} r^2\,\mathrm{d}r \int_{\infty}^{r} \frac{\Phi^*_{21}(r') - \Phi^*_{11}(r')}{r'}\,\mathrm{d}r' \tag{17}$$

The molecular interaction potential is the London potential (see Ref. [38]):

$$\Phi_{12} = -\varepsilon_{12}(\sigma_{12}/r)^6 \tag{18}$$

where ε_{12} is the energy of interaction and σ_{12} is the minimal molecular approach distance. In the integration, the lower limit is $r = \sigma_{12}$. The potential Φ_{11} is determined in a similar way.

4. Results and discussion

The molecular Soret coefficient can be written as

$$S_T = \frac{3}{4T}\ln\left(\frac{N_2 m_2}{N_1 m_1}\right) + \frac{1}{4T}\ln\left(\frac{\gamma_2}{\gamma_1}\right)^2 \frac{(I_1 I_2 I_3)_2}{(I_1 I_2 I_3)_1} + \frac{\pi^2 \alpha_T \sigma_{12}^3 \varepsilon_{12}}{18 v_1 kT}\left(1 - \frac{v_2 \sigma_{11}^6 \varepsilon_{11}}{v_1 \sigma_{21}^6 \varepsilon_{12}}\right) \tag{19}$$

Eq. (19) yields the main features for the thermodiffusion of molecules in a dilute system. These features include the kinetic term $\frac{3}{4T}\ln(N_2 m_2/N_1 m_1)$, expressed through the mass difference between the suspended molecule and the virtual particle of displaced liquid. This term is related to thermal translational motion of non-interacting atoms and molecules, whose intensity is altered by the temperature gradient. A similar kinetic term related to translational thermal motion was obtained in Refs. [27–29], but that term did not contain a mass dependence, and it is non-zero, even in the case when the molecule and liquid have the same density. Any volume of liquid may play the role of such a molecule and should move in the temperature gradient, which means that the motion of pure unbound liquid in a temperature gradient is occurred, what impossible, by definition.

The term $\frac{1}{4T}\ln(\frac{\gamma_2}{\gamma_1})^2 \frac{(I_1 I_2 I_3)_2}{(I_1 I_2 I_3)_1}$ describes rotational effects related to the difference in the symmetry, size, and mass. The difference in symmetry is expressed through the ratio $\frac{\gamma_1}{\gamma_2}$, which is always equal to or greater than unity for the reasons discussed above; its contribution to the Soret coefficient is always positive. The ratio $\frac{(I_1 I_2 I_3)_2}{(I_1 I_2 I_3)_1}$ may be responsible for both positive and negative contributions to the Soret coefficient, depending on molecular parameters. It is also dependent on the symmetry of the molecules, but to a much less extent.

The terms in Eq. (19) may describe the isotopic effects in thermodiffusion reported in Refs. [4–19]. When the difference in the internal molecular parameters is small, Eq. (19) can be written in the form

$$S_T = \frac{3(M_2 - M_1)}{4TM_1} + \frac{(\gamma_1)^2(I)_2 - (\gamma_2)^2(I)_1}{4T(\gamma_2)^2(I)_1} + \frac{\pi^2\alpha_T\sigma_{12}^3\varepsilon_{12}}{18v_1kT}\left(1 - \frac{v_2\sigma_{11}^6\varepsilon_{11}}{v_1\sigma_{21}^6\varepsilon_{12}}\right) \tag{20}$$

where $(I)_{1,2} = (I_1I_2I_3)_{1,2}$ and $M_{1,2} = N_{1,2}m_{1,2}$. Eq. (20) has the same structure as the empirical equation (2) obtained in Ref. [19]. In the case of isotopic substitution, the indices 1 and 2 should be related to molecules with different degrees of substitution. Formally, we consider mixture of the same molecules with a distinct degree of isotopic substitution. Theoretical expressions for the constants included in this equation can be written as

$$a_m = \frac{3}{4TM_1} \tag{21}$$

$$b_i = \frac{(\gamma_1)^2}{4T(\gamma_2)^2(I)_1} \tag{22}$$

Ref. [19] yields $a_m = 0.99 \cdot 10^{-3}\ \mathrm{K}^{-1}$, while Eq. (21) yields $a_m = 0.03 \cdot 10^{-3}\ \mathrm{K}^{-1}$ for cyclohexane ($M_1 = 84$) at room temperature ($T = 300$ K). As for the parameter b_i, there is no information in the literature. There are several possible reasons for the discrepancy between theoretical and empirical values. First, the theory used an oversimplified molecular geometry. The cyclohexane molecule has a shape distinct from a sphere or spheroid, which could change the structure of the basic equations [Eqs. (14), (15)]. Second, isotopic substitution can change the interaction potential. Third, the first right-hand term in Eq. (20) is not the only term containing a mass dependence; the second right-hand term also contains such a dependence. An implicit mass dependence is also present in the empirical parameter a_m but not in the theoretical expression given by Eq. (21). The latter mass dependence is potentially much stronger when the change of mass occurs near the periphery of the molecule.

The discrepancy between theory and experiment may also be related to the sharp change in molecular symmetry upon isotopic substitution. For example, cyclohexane studied in [19] has a high symmetry value. It can be carried into itself by six rotations about the axis perpendicular to the plane of the carbon ring and by two rotations around the axes placed in the plane of the ring and perpendicular to each other. Thus, cyclohexane has $\gamma_1 = 24$. However, partial isotopic substitution violates this symmetry. We can start with the assumption that for substituted molecules $\gamma_2 = 1$. When the molecular geometry is unchanged by substitution, so that only the moment of inertia related to the axis perpendicular to the ring plane is changed, we obtain

$$\frac{(\gamma_1)^2(I)_2 - (\gamma_2)^2(I)_1}{4T(\gamma_2)^2(I)_1} = \frac{(\gamma_1)^2(M_2 - M_1)}{4T(\gamma_2)^2M_1} + \frac{(\gamma_1)^2 - (\gamma_2)^2}{4T(\gamma_2)^2} \tag{23}$$

Eq. (23) yields

$$a_m = \frac{3}{4TM_1} = \frac{1}{4TM_1}\left[3 + \left(\frac{\gamma_1}{\gamma_2}\right)^2\right] \tag{24}$$

Using the above parameters and Eq. (24), we obtain $a_m \approx 5.7 \cdot 10^{-3}\ \mathrm{K}^{-1}$, which is about six times more that the empirical value from Ref. [19]. This discrepancy means that we have overestimated the degree of symmetry violation by isotopic substitution. The true value of this parameter is obtained when $\gamma_2 \approx 2$–3. One should understand that the value of parameter γ_2 is to some extent conditional, since isotopic substitutions in the experiment occur at random positions. In the temperature gradients, the molecules with the equal degree of the isotopic substitution but with different symmetry are the multicomponent mixture. Thus, Eq. (24) can be used in the evaluation of a characteristic degree of symmetry from the experimental parameter a_m rather than specific theoretic values of this parameter can be used in calculations.

According to Eq. (23), the Soret coefficient also contains the term $\frac{(\gamma_1)^2-(\gamma_2)^2}{4T(\gamma_2)^2}$, which is related to the change in molecular symmetry for structural isotopes of the same mass. For example, this term contributes to the Soret coefficient of short olefin chains or benzene rings that contain side residuals in symmetric versus asymmetric positions.

The expressions for the Soret coefficient contain also the potential term related to Hamaker interactions. In respect to this potential term, the thermodynamic and hydrodynamic approaches predict practically the same thermodiffusion behavior for an isolated molecule (or polymer chain), and the differences are due to approximations used in calculations. In both theories, the direction of molecular thermophoretic motions is determined by the parameters $1 - v_2\sigma_{11}^6\varepsilon_{11}/v_1\sigma_{21}^6\varepsilon_{12}$ [20]. The molecular Soret coefficient is proportional to the ratio σ_{12}^3/v_1, which is practically independent of molecular size. It is fully consistent with scaling estimates obtained using the hydrodynamic approach in Ref. [39]. The present theory may also explain why the contribution of the kinetic term and the isotope effect has only been seen in molecular systems. In colloid systems the Soret coefficient is dominated by the intermolecular interaction term due to the magnitude of $R\sigma_{21}^2/v_1$. In fact, the colloidal Soret coefficient is about R/σ_{21} times that measured on its molecular analog (see Ref. [20]), which is consistent with numerous experimental data, as well as with the hydrodynamic theory.

5. Conclusion

Theory shows that the isotopic effect in cyclohexane thermodiffusion is in large part related to the change in molecular symmetry upon isotopic substitution. The theory also shows that there is a contribution to thermodiffusion related to the difference in molecular symmetry between components even when there is no difference in molecular mass or in the interaction characteristics between components.

The consistence between thermodynamic and hydrodynamic theories regarding the size dependence of the thermodiffusion parameters is made possible by the concept expressed in Eqs. (14), (15). Thus, the Laplace-like pressure established in the force field of the considered molecule yields the correct size dependence for the Soret coefficient.

Eqs. (19), (20) yield potential terms related to the intermolecular interactions, which are equivalent to the respective hydrodynamic expressions and yield kinetic terms related to the translational and rotational thermal motion expressed through the relative mass, moment of inertia, and difference in the symmetry values between the molecule and displaced liquid. These terms also include the proportionality between thermodiffusion and the thermal expansion coefficient of the solvent. Such dependence was observed in experiments [40] on a number of solvent–particle combinations. Presently, our theories are the only reasonable explanation for this experimental result. The thermodynamic theory also yields terms related to the translation and rotation of the molecules.

Thus, a thermodynamic approach supplemented by statistical mechanical calculations is consistent with the hydrodynamic approach and can provide additional information on the kinetic contribution to thermodiffusion. The approach provides the range of molecular sizes where the kinetic contribution should be seen. This range is limited to the molecular solutes, and potentially to polymers with very high degrees of isotopic substitution, while the effect should be negligible for colloidal systems. Finally, we note that the theory is applicable only to dilute molecular solutions in non-electrolyte liquids but can be extended easily to concentrated systems.

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