

Do thermal diffusion and Dufour coefficients satisfy Onsager's reciprocity relation?*

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Abstract. It is commonly admitted that in liquids the thermal diffusion and Dufour coefficients D_T and D_F satisfy Onsager's reciprocity. From their relation to the cross-coefficients of the phenomenological equations, we are led to the conclusion that this is not the case in general. As illustrative and physically relevant examples, we discuss micellar solutions and colloidal suspensions, where D_T arises from chemical reactions or viscous effects but is not related to the Dufour coefficient D_F . The situation is less clear for binary molecular mixtures; available experimental and simulation data do not settle the question whether D_T and D_F are reciprocal coefficients.

1 Introduction

Onsager's theory for irreversible processes provides a formal framework for non-equilibrium phenomena like diffusion, electrokinetic effects, and heat conduction. The phenomenological equations relate thermodynamic fluxes to forces, for example heat flow to a temperature gradient, or diffusion to a concentration gradient. Intriguing physical properties arise from the cross-terms, such as thermally driven electric currents. Onsager established reciprocal laws between conjugate cross-coefficients [1], thus completing Thomson's derivation for the thermoelectric effects and showing why the Seebeck and Peltier coefficients Π and S differ merely by a temperature factor, $\Pi/S = T$ [2].

As another classical example, the Soret and Dufour effects describe the mass transport in a temperature gradient, and heat flow due to a concentration gradient. There is, however, a long-standing discussion whether, and eventually under which conditions, the corresponding coefficients obey a reciprocity relation. Thus it has been pointed out that the reciprocal laws impose rather strong conditions on the choice of fluxes and forces, which are not always easily verified [3].

The Soret and Dufour effects are often discussed in terms of Onsager's phenomenological equations for the heat and particle currents with cross-coefficients L'_{1Q} and L'_{Q1} . It is then *assumed* that the measured thermal diffusion and Dufour coefficients D_T and D_F correspond to

L'_{1Q} and L'_{Q1} , such that the reciprocity relation for the latter applies equally well to the former. This approach has been taken by various authors, when discussing binary gases [4], organic liquids [5], molecular isotope mixtures [6], premelting solids with colloidal inclusions [7], and far-from-equilibrium systems [8].

Available experiments do not provide clear evidence for or against this assumption. Comparing thermal diffusion and Dufour data for gas mixtures, suggests qualitative agreement [4]. Regarding liquids, D_T and D_F seem to agree well for mixtures of cyclohexane and carbon-tetrachloride [9–11], yet significant discrepancies were reported for benzene-cyclohexane and other systems [9,10]. In recent years the Soret effect of colloidal suspensions has been investigated in great detail [12–15]; unfortunately, there is a lack of corresponding Dufour data. Molecular dynamics simulations show a good agreement of the thermal diffusion and Dufour coefficients, at least for simple model systems [16–19].

Here we discuss the validity of the reciprocity assumption for D_T and D_F on the basis of non-equilibrium thermodynamics. We consider regular systems where Onsager cross-coefficients are identical, *e.g.*, $L'_{1Q} = L'_{Q1}$. Then the title of this paper reduces to the question whether, and eventually under which conditions, thermal diffusion is described by L'_{1Q} . This is formalized in sects. 2 and 3, where we define D_T and D_F , and present Onsager's phenomenological equations. In sect. 4 we discuss the case where the entropy production is given by the vector fluxes, *i.e.*, by the heat flow and particle currents. In sects. 5 and 6 we add chemical reactions and viscous effects; the corresponding contributions to D_T are evaluated for the examples of micellar suspensions, polymers, and colloidal particles. The final sections discuss and summarize our main results.

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2 Thermal diffusion and Dufour coefficients

We consider a binary system with non-uniform temperature and composition. Closely following [2], we present the linear equations for heat and particle flows of a binary system with volume fractions ϕ_1 and $\phi_2 = 1 - \phi_1$.

Then the currents of the two components satisfy $\mathbf{J}_1 + \mathbf{J}_2 = 0$; the first one is defined as

$$\mathbf{J}_1 = -D\nabla\phi_1 - \phi_1\phi_2 D_T \nabla T. \quad (1)$$

Besides gradient diffusion with the coefficient D , it comprises thermal diffusion with coefficient D_T . In the steady state $\mathbf{J}_1 = 0$, a finite temperature gradient imposes a non-uniform concentration $\nabla\phi_1 = -\phi_1\phi_2 S_T \nabla T$, with the Soret coefficient $S_T = D_T/D$.

Similarly, the heat flow is driven by both temperature and concentration gradients,

$$\mathbf{J}'_Q = -\lambda\nabla T - \phi_1 \hat{\mu}'_{11} D_F \nabla\phi_1, \quad (2)$$

where λ is the thermal conductivity, D_F the Dufour coefficient, and $\hat{\mu}'_{11}$ the derivative of the chemical potential [2]. The hat indicates volume specific quantities, such as the molecular chemical potential divided by the molecular volume, $\hat{\mu}_k = \mu_k/v_k$. The choice of volume fraction variables ϕ_k implies that \mathbf{J}_1 has the dimension of a velocity; one readily finds that D_T has the units $\text{m}^2 \text{s}^{-1} \text{K}^{-1}$, whereas D_F has those of a diffusion coefficient, $\text{m}^2 \text{s}^{-1}$.

The heat flow \mathbf{J}'_Q comprises two contributions, ordinary heat diffusion with conductivity λ , and the Dufour effect which is driven by a concentration gradient in an anisotropic medium. Note that \mathbf{J}'_Q does not account for enthalpy transport due to the particle current but is defined at $\mathbf{J}_1 = 0$. In the case of a finite particle current, the total heat flow reads

$$\mathbf{J}_Q = \mathbf{J}'_Q + \hat{h}_1 \mathbf{J}_1 + \hat{h}_2 \mathbf{J}_2 = \mathbf{J}'_Q + (\hat{h}_1 - \hat{h}_2) \mathbf{J}_1, \quad (3)$$

with the specific enthalpies \hat{h}_k of the two components.

In many instances it is assumed that the off-diagonal coefficients D_T and D_F are related through Onsager's reciprocal laws according to

$$D_T \stackrel{?}{=} \frac{D_F}{T}. \quad (4)$$

The temperature factor is due to historical convention, similar to that between the Seebeck and Peltier coefficients, $S = \Pi/T$. Kinetic theory confirms this relation to be satisfied in ideal gas mixtures [20], and there is evidence for its validity in liquid isotope mixtures [6]. Little can be said on ordinary binary liquids [9–11] and complex fluids.

3 Phenomenological equations

The above eqs. (1) and (2) provide the experimental definition of the thermal diffusion and Dufour coefficients. Closely following ref. [2], we summarize the corresponding

theory, that is, Onsager's linear relations for thermodynamic fluxes and forces. We do not discuss the regression hypothesis [21] and suppose that the fluxes are linear functions of the forces; note this assumption is often not justified for chemical reactions.

3.1 Entropy production

Like any thermodynamic function, the entropy is constant in an equilibrium state. Non-equilibrium phenomena are intimately related to entropy production. For example, gradient diffusion according to Fick's law $\mathbf{J}_1 = -D\nabla\phi_1$ tends to smear out any composition inhomogeneity and produces entropy at a rate $\sigma \propto D(\nabla\phi_1)^2$. By the same token, a non-uniform temperature induces a heat flow $\mathbf{J}_Q = -\lambda\nabla T$ from the hot to the cold and augments the entropy as $\sigma = \lambda(\nabla T/T)^2$. Similar relations arise for chemical reactions and for viscous flow.

In the case of an initial perturbation, the system relaxes toward an equilibrium state ($\nabla\phi_1 = 0$, $\nabla T = 0$, ...) of constant entropy. On the other hand, if the inhomogeneity is maintained through continuous heat or matter supply, the system reaches a stationary non-equilibrium state and produces entropy at a constant rate.

With the mentioned dynamic variables, the rate of entropy production per unit volume reads as

$$\sigma = \mathbf{J}_Q \cdot \nabla \frac{1}{T} - \sum_k \mathbf{J}_k \cdot \nabla \frac{\hat{\mu}_k}{T} - \sum_i \mathcal{J}_i A_i - \frac{\boldsymbol{\Pi} : \mathbf{G}}{T}, \quad (5)$$

where \mathbf{J}_Q is the heat flux, \mathbf{J}_k are the volume currents of the molecular species, \mathcal{J}_i are the composition changes due to chemical reactions, and $\boldsymbol{\Pi}$ is the viscous pressure tensor. The corresponding thermodynamic forces are the gradients of the inverse temperature and the Planck potential $\hat{\mu}_k/T$, the affinities A_i , and the symmetrized rate of change of the fluid velocity field $\mathbf{v}(\mathbf{r})$, with components $G_{mn} = \frac{1}{2}(\partial_m v_n + \partial_n v_m)$.

For sufficiently weak deviations from the equilibrium state, Onsager established linear relations between the fluxes and forces. Because of the Curie symmetry principle, the phenomenological relations do not mix scalar, vector, and tensor quantities. Thus the coefficient matrix of the phenomenological equations is block-diagonal and decays in parts that are characterized by their tensor properties.

3.2 Vector currents

The vector quantities \mathbf{J}_Q and \mathbf{J}_k describe heat and mass diffusion. For a binary system ($n = 2$) they form 3 generalized fluxes which are, however, not linearly independent and can be reduced to 2 independent flows. When describing the composition in terms of volume fractions, the particle currents cancel each other, $\mathbf{J}_2 = -\mathbf{J}_1$; eliminating

that of the second component one obtains

$$\mathbf{J}_1 = L_{1Q} \nabla \frac{1}{T} - L_{11} \nabla \frac{\hat{\mu}_1 - \hat{\mu}_2}{T}, \quad (6a)$$

$$\mathbf{J}_Q = L_{QQ} \nabla \frac{1}{T} - L_{Q1} \nabla \frac{\hat{\mu}_1 - \hat{\mu}_2}{T}. \quad (6b)$$

The last term of each equation gives rise to both thermal and concentration gradients,

$$\nabla \frac{\hat{\mu}_k}{T} = \hat{h}_k \nabla \frac{1}{T} + \frac{\nabla_T \hat{\mu}_k}{T}, \quad (7)$$

where \hat{h}_i is the enthalpy and ∇_T the gradient at constant temperature. Thus the thermodynamic force $\nabla_T \hat{\mu}_k$ involves the derivative of the chemical potential with respect to composition.

In many instances it turns out convenient to regroup all temperature gradients according to

$$\mathbf{J}_1 = L'_{1Q} \nabla \frac{1}{T} - L'_{11} \frac{\nabla_T(\hat{\mu}_1 - \hat{\mu}_2)}{T}, \quad (8a)$$

$$\mathbf{J}'_Q = L'_{QQ} \nabla \frac{1}{T} - L'_{Q1} \frac{\nabla_T(\hat{\mu}_1 - \hat{\mu}_2)}{T}. \quad (8b)$$

Comparison with (5) readily provides relations between unprimed and primed coefficients, *e.g.* $L'_{1Q} = L_{1Q} - L_{11}(\hat{h}_1 - \hat{h}_2)$.

The heat flow \mathbf{J}'_Q is defined such that the entropy production involves products of conjugate forces and currents; for a binary system with $\mathbf{J}_1 + \mathbf{J}_2 = 0$, the contribution of the vector quantities reads

$$\mathbf{J}'_Q \cdot \nabla \frac{1}{T} - \mathbf{J}_1 \cdot \frac{\nabla_T(\hat{\mu}_1 - \hat{\mu}_2)}{T}.$$

According to (3) the primed heat flux accounts for diffusive transport only, whereas \mathbf{J}_Q comprises in addition the enthalpy carried by the particle current \mathbf{J}_1 . In the steady state of a closed system, the latter vanishes and one has $\mathbf{J}_Q = \mathbf{J}'_Q$.

3.3 Scalar and tensor quantities

Now we turn to the remaining terms of the entropy production rate. That involving chemical reactions is described by scalar fields,

$$\mathcal{J}_i = - \sum_j l_{ij} A_j / T, \quad (9)$$

where the coefficients l_{ij} relate the reaction products to the affinities A_i .

Finally, the linear relation between the viscous pressure and the velocity gradient,

$$\mathbf{\Pi} = -\eta \mathbf{G}, \quad (10)$$

involves the fourth-rank viscosity tensor η , which structure is rather simple in isotropic liquids, yet becomes more complex in liquid crystals [22]. For compressible fluids, the contraction $\mathbf{\Pi} : \mathbf{G}$ comprises also a scalar term, which is small for most liquids and thus will be discarded.

3.4 Reciprocal laws

According to Onsager's reciprocal laws, the coefficient matrices \mathbf{L} , \mathbf{L}' , and η are symmetric, and in particular

$$L'_{1Q} = L'_{Q1}. \quad (11)$$

In many works on thermal diffusion, both chemical reactions and viscous flow are discarded from the beginning. Then the different terms in (8) are readily identified with those in (1) and (2),

$$\begin{aligned} \lambda &\stackrel{?}{=} \frac{L'_{QQ}}{T^2}, & D &\stackrel{?}{=} \frac{\hat{\mu}_{11}^\phi L'_{11}}{\phi_2 T}, \\ D_T &\stackrel{?}{=} \frac{L'_{1Q}}{\phi_1 \phi_2 T^2}, & D_F &\stackrel{?}{=} \frac{L'_{Q1}}{\phi_1 \phi_2 T}, \end{aligned} \quad (12)$$

where $\hat{\mu}_{11}^\phi$ is the usual derivative with respect to composition [2]. Since L'_{1Q} and L'_{Q1} are reciprocal coefficients, these relations confirm (4) for the thermal diffusion and Dufour coefficient.

The above decomposition of the linear relations according to their tensorial properties does not imply, however, that the underlying physical phenomena are decoupled. Whether each of the fluxes (8), (9), and (10) can be treated independently from the others, cannot be determined on formal grounds, but has to be inferred from the physical properties of the system under consideration.

In the following we evaluate D_T for different models and determine in each case whether or not eq. (12) is satisfied.

4 Diffusion

Here we consider the case of a binary system where both chemical reactions and viscous effects are absent. Then the entropy production and phenomenological relations reduce to the vector quantities \mathbf{J}_Q , \mathbf{J}_1 , and \mathbf{J}_2 , implying that D_T and D_F are reciprocal coefficients according to (4). Still, the remaining three independent coefficients have to be determined from physical considerations. The general theory parallels chapt. XI § 8 of ref. [2]; the notation with volume fractions and examples are developed in ref. [23].

4.1 Vector fluxes

It turns out instructive to eliminate the heat current \mathbf{J}_Q , contrary to (8) where we eliminated the current of the second component \mathbf{J}_2 . Then one obtains the particle fluxes as linear functions of the thermodynamic forces $\nabla(\hat{\mu}_k/T)$,

$$\mathbf{J}_1 = -\phi_1 \phi_2 T \left(B_1 \nabla \frac{\hat{\mu}_1}{T} - B_2 \nabla \frac{\hat{\mu}_2}{T} \right), \quad (13)$$

where the coefficients B_i depend on composition and on temperature. (As compared to the notation in [23], a factor $\phi_1 \phi_2 T$ has been introduced for convenience.)

Note that the currents \mathbf{J}_k have the dimension of a velocity. Our choice of volume fraction variables ϕ_i is motivated by the volume conservation in incompressible liquids, which results in the relation $\mathbf{J}_1 + \mathbf{J}_2 = 0$. For gases, where momentum is conserved, one would prefer to take mass fractions.

Equation (13) implies that diffusion and thermal diffusion are given by the gradient of the Planck potentials $\hat{\mu}_k/T$. Spelling out the gradients,

$$\nabla \frac{\hat{\mu}_k}{T} = -\frac{\hat{h}_k}{T^2} \nabla T + \frac{\hat{\mu}_{kk}^\phi}{T} \nabla \phi_k, \quad (14)$$

recollecting the terms in \mathbf{J}_1 and comparing with (1) one obtains the diffusion coefficient

$$D = (\phi_1 B_1 + \phi_2 B_2) \phi_1 \hat{\mu}_{11}^\phi. \quad (15a)$$

Similarly one finds for the thermal diffusion and Dufour coefficients [2]

$$D_T = \frac{\hat{h}_2 B_2 - \hat{h}_1 B_1}{T} = \frac{D_F}{T}. \quad (15b)$$

Equations (8) and (15) provide formally equivalent expressions for the particle current (1): The former depends on two unknowns L'_{11} and L'_{1Q} , and the latter on B_1 and B_2 . These coefficients can not be derived from equilibrium properties; they have to be taken from experiment or molecular dynamics simulations, or inferred from models for the molecular mobility.

On the other hand, the equilibrium quantities appearing in (15), that is, the thermodynamic factor $\phi_1 \hat{\mu}_{11}^\phi$ and the specific enthalpies \hat{h}_i , can be calculated from first principles [24], or can be taken from numerical simulations [18] or experiment [23].

4.2 Comparison to experiment

Thermal diffusion is usually discussed in terms of (8a). When comparing to experiments, however, eqs. (15) turn out to be a more promising starting point. Two mobilities B_k appear in both D and D_T and thus provide a strong relation between thermal diffusion and diffusion data. When taking the parameters B_k as constants, they can be determined from the tracer diffusion coefficients of the two species,

$$\begin{aligned} B_2 &= D(\phi_1)/\phi_1 \hat{\mu}_{11}^\phi & \text{for } \phi_1 \rightarrow 0, \\ B_1 &= D(\phi_1)/\phi_1 \hat{\mu}_{11}^\phi & \text{for } \phi_1 \rightarrow 1. \end{aligned} \quad (16)$$

A slightly different scheme has been used for Soret data of several molecular mixtures such as benzene-cyclohexane [23]. Together with measured values for the partial enthalpies \hat{h}_2 , this allows comparison with the thermal diffusion coefficient D_T .

A particularly interesting situation arises for isotope mixtures. Molecular isotopes show similar thermodynamics, yet differ in dynamical properties such as the attempt frequency of activated jumps. Thus any difference in the mobilities B_k can be related to a specific model. Such approaches have been developed for mass effects. For mixtures such as $\text{CCl}_4\text{-CBr}_4$ the B_k have been expressed through the activation free energy [6, 25]. The isotope effect observed upon deuteration in benzene-cyclohexane mixtures, has been related to the molecular collision rates [26].

4.3 Alkane mixtures

Thermal diffusion behavior according to (15) is expected in mixtures of similar molecules, such as short alkanes. Indeed, small molecules induce weak hydrodynamic flow, which is rapidly superseded by the molecular diffusion. Then the Soret coefficient $S_T = D_T/D$ depends on the partial enthalpies \hat{h}_k , the chemical potentials $\hat{\mu}_k$, and the molecular mobilities B_k .

Assuming that the latter are identical, independently of the molecular weight, we thus have [23]

$$S_T = \frac{1}{T} \frac{\hat{h}_2 - \hat{h}_1}{\phi_1 \hat{\mu}_{11}} \quad (B_1 = B_2). \quad (17)$$

Refining early work by Haase [27], similar relations have been discussed by several authors [28–30]. In fig. 1 we compare this expression with Soret data for equimolar alkane mixtures, which are taken from refs. [31, 32].

The theoretical curve has been calculated from (17), with the thermodynamic factor equal to unity such that $\phi_1 \hat{\mu}_{11} = k_B T / (\phi_1 v_2 + \phi_2 v_1)$, and the specific enthalpy $\hat{h}_n = h_n / v_n$ given by

$$h_n = -(n + 0.65) \times 4.64 \frac{\text{kJ}}{\text{mol}}, \quad (18a)$$

$$v_n = (n + 2.02) \times 16.35 \frac{\text{cm}^3}{\text{mol}}. \quad (18b)$$

These simple laws perfectly fit the measured vaporization enthalpy [33] and molecular volume v_n . The theoretical curve in fig. 1 strongly depends on the off-set parameters 0.65 and 2.02, as discussed in appendix A.

The particularly simple fit arises since the Soret coefficient $S_T = D_T/D$ depends on the ratio B_1/B_2 only (which, moreover, has been put to unity.) A more complex situation occurs when considering thermal diffusion and diffusion data separately. The many data on the composition dependence of D_T and D [34, 35] should unambiguously determine the mobilities B_k and verify whether the assumption $B_1 = B_2$ is justified. On the other hand, if the data for D_T and D turned out not to be compatible with (15), this would suggest that D_T cannot be explained in terms of the vector fluxes (6) but depends on other phenomena such as viscous stress.

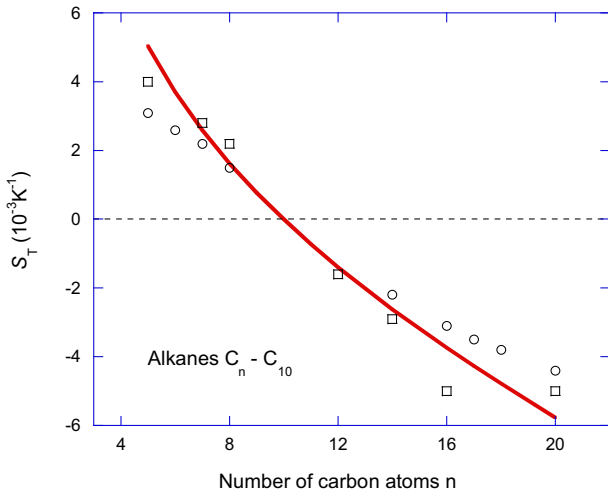


Fig. 1. Soret data for mixtures of normal alkanes C_{10} - C_n , where the number n of carbon atoms of the second component varies from 5 to 20. The experimental data are from Leahy-Dios and Firoozabaadi [31] (squares) and Blanco *et al.* [32] (circles). The theoretical curve is calculated from (17) as discussed in the main text.

4.4 Comparison with heat conductivity

So far we discussed the relation between diffusion and thermal diffusion coefficients in terms of the quantities B_k . As shown by de Groot and Mazur, a more general formulation of the heat and particle flows relates the coefficients D and D_T to the heat conductivity λ . To this purpose, we note that the thermodynamic forces on component k can be written as $\sum_l a_{kl} \nabla(\hat{\mu}_l/T)$, with a mobility matrix that is symmetric ($a_{12} = a_{21}$) and positive definite ($a_{11}a_{22} \geq a_{21}^2$).

The B_k appearing in (13) depend on these mobilities through

$$B_1 = \frac{\phi_2 a_{11} - \phi_1 a_{12}}{\phi_1 \phi_2 T}, \quad B_2 = \frac{\phi_1 a_{22} - \phi_2 a_{21}}{\phi_1 \phi_2 T}. \quad (19)$$

Insertion in (15) provides the diffusion and thermal diffusion coefficients in terms of the a_{kl} . Similarly, the heat conductivity is given by the mobilities according to [2]

$$\lambda = \frac{a_{11} \hat{h}_1^2 + 2a_{12} \hat{h}_1 \hat{h}_2 + a_{22} \hat{h}_2^2}{T^2}. \quad (20)$$

Thus the three transport coefficients D , D_T , and λ are expressed through three parameters a_{11} , a_{22} , and a_{12} . These quantities vary with composition, such that a set of experimental data for $D(\phi_1)$, $D_T(\phi_1)$, and $\lambda(\phi_1)$ determines the mobility matrix $a_{kl}(\phi_1)$.

Here one should remind that (15) and (20) rely on the assumption that vector fluxes and forces entirely determined the heat and particle currents. Thus in the first place, these relations provide a criterion for the validity of this assumption. As a crude estimate, we replace the mobilities by $a_{kl} \sim a$, neglect composition factors $\phi_i \sim 1$, and thus obtain $D \sim ak_B/v$ and $\lambda \sim a(H/v)^2/T^2$, where

H and v are the molar enthalpy and volume. Eliminating a leads to $\lambda \sim H^2 D/vk_B T^2$; inserting typical values of H , D , v , as measured *e.g.* for benzene, one finds a thermal conductivity $\lambda \sim 0.03 \text{ W m}^{-1} \text{ K}^{-1}$ which is about five times smaller than the experimental value.

This estimate suggests that it could be instructive to fit experimental or simulation data for D , D_T , and λ with eqs. (15) and (20). The elements of the mobility matrix a_{kl} do, however, not necessarily provide a good starting point; thus according to (19) and (16), constant diagonal elements a_{kk} would result in a diverging diffusion coefficient D . In view of (16) one would rather prefer to replace the a_{kl} with well-behaved quantities; as a possible choice we note B_1 , B_2 , and

$$B_3 = \frac{a_{12}}{\phi_1 \phi_2 T}.$$

Then the expressions in (15) are completed by the thermal conductivity

$$\lambda = \frac{\phi_1 \hat{h}_1^2 B_1 + \phi_2 \hat{h}_2^2 B_2 + (\phi_1 \hat{h}_1 + \phi_2 \hat{h}_2)^2 B_3}{T}. \quad (21)$$

The positivity condition for the mobility matrix imposes

$$B_1 B_2 + (\phi_2 B_1 + \phi_1 B_2) B_3 \geq 0.$$

We recall that the B_k depend on composition. The relations (15) and (21) suggest that, in a simple model, these quantities could be taken as constants.

5 Chemical reactions

Here we discuss how chemical reactions modify heat and mass flow. In physical terms, it is clear that they affect the local composition and thus induce diffusion currents; inversely, thermal diffusion creates a non-uniform composition which in turn perturbs the chemical equilibrium and thus provokes reactions.

Because of the Curie principle, the phenomenological equations (8) and (9) do not contain cross-terms between the scalar and vector quantities, and thus do not mix the reaction kinetics and diffusion. This does not imply, however, that scalar and vector fluxes are independent of each other, nor that diffusion is simply determined by the matrix \mathbf{L} .

5.1 Reaction-diffusion coupling

Consider the case of a single chemical reaction between two components. Then the entropy production (5) comprises the scalar fluxes $\mathcal{J}_i = \dot{\phi}_i$. The reaction kinetics obey the rate equations

$$\dot{\phi}_1 = \gamma \phi_2 - \Gamma \phi_1 = -\dot{\phi}_2, \quad (22)$$

where the point indicates time derivatives and the transitions $1 \leftrightarrow 2$ occur with rates γ and Γ . According to the

principle of detailed balanced, their ratio $\gamma/\Gamma = e^{-G/k_B T}$ is determined by the free enthalpy difference G of the two states.

In addition to the reaction velocity $\dot{\phi}_k$, the total change of the volume fraction with time comprises the divergence of the diffusion current \mathbf{J}_k ,

$$\frac{d}{dt}\phi_k = \dot{\phi}_k + \nabla \cdot \mathbf{J}_k, \quad (23)$$

where the last term corresponds to a source or sink for the considered species. Equation (23) provides a coupling between the scalar and vector fluxes $\dot{\phi}_k$ and \mathbf{J}_k , and thus induces a relation between the a priori independent phenomenological equations (8) and (9).

Here we consider the steady state where $d\phi_k/dt = 0$. The resulting equation

$$\dot{\phi}_k + \nabla \cdot \mathbf{J}_k = 0 \quad (24)$$

does not imply the arrest of the reaction nor that the currents \mathbf{J}_k vanish. It simply requires that a local creation of molecules ($\dot{\phi}_1 > 0$) is balanced by a net outgoing particle flow, and annihilation ($\dot{\phi}_1 < 0$) by an incoming flow. In general the solution of (24) cannot be given in closed form, especially if the rate ratio $\gamma/\Gamma = e^{-G/k_B T}$ depends on temperature.

Thermal conductivity of a binary system with constant rates has been studied in detail by de Groot and Mazur in chapt. XI § 8 of ref. [2]. As a main result these authors find that the diffusivities are not simply given by the matrix \mathbf{L} , but depend on the reaction parameters; moreover, the explicit result for the thermal conductivity shows an intricate spatical variation. This leads to the conclusion that eq. (12) is not valid in the presence of chemical reactions.

5.2 Micelle kinetics

As an instructive example, we consider a solution of tensioactive molecules that partly aggregate to micelles. The micellar and molecular states occupy volume fractions ϕ_1 and ϕ_2 , with $\phi_1 + \phi_2 \ll 1$. For the sake of simplicity we suppose that the cross-coefficients in the vector fluxes are small and thus put

$$L'_{kQ} = 0 = L'_{Qk}. \quad (25a)$$

Then the particle currents take the form $\mathbf{J}_k = -D_k \nabla \phi_k$, where

$$D_k = \frac{L'_{kk} \phi_k \hat{\mu}_{kk}^\phi}{\phi_1 \phi_2 T}, \quad D_T = 0 \quad (25b)$$

implies the absence of thermal diffusion.

Now we take the kinetics of micelle formation into account [36]. Micellar aggregation of N molecules and dissolution through the inverse process, as described by the rate equation (22). This ‘‘chemical reaction’’ occurs on a time scale of nanoseconds, and thus is much faster than diffusion over macroscopic lengths L , which occurs on a

time scale L^2/D that by far exceeds seconds. This means that the second term in (24) is small.

The steady state of a homogeneous system is determined by the equilibrium of the chemical reaction ($\dot{\phi}_1 = 0$) which reads as $\phi_1/\phi_2 = \gamma/\Gamma = e^{-G/k_B T}$. Yet here this ratio is not constant in space but varies because of the non-uniform temperature $T(\mathbf{r})$. Expanding the rate equation (22) to linear order in the coordinates \mathbf{r} , we have

$$\gamma\phi_2 - \Gamma\phi_1 + \mathbf{r} \cdot \nabla (\gamma\phi_2 - \Gamma\phi_1) + \nabla \cdot \mathbf{J}_1 = 0. \quad (26)$$

The first term describes the equilibrium state at $\mathbf{r} = 0$. Since diffusion is much slower than the chemical reaction, $D/L^2 \ll \gamma$, the last term is negligible. Evaluating the gradient of the remainder we find

$$0 = \Gamma\phi_1 \frac{H}{k_B T^2} \nabla T + \gamma \nabla \phi_2 - \Gamma \nabla \phi_1, \quad (27)$$

where we have inserted the Gibbs-Helmholtz relation

$$\frac{d}{dT} \frac{G}{k_B T} = -\frac{H}{k_B T^2},$$

with the enthalpy H .

Thus chemical equilibrium in the presence of a non-uniform temperature gradient imposes gradients of the micellar and molecular volume fractions, which in turn drive the diffusion currents $\mathbf{J}_k = -D_k \nabla \phi_k$. Inserting $\mathbf{J}_1 + \mathbf{J}_2 = 0$ in (27) we find the steady-state composition gradients

$$\nabla \phi_1^{\text{st}} = \phi_1 \frac{D_2 \Gamma}{D_1 \gamma + D_2 \Gamma} \frac{H}{k_B T^2} \nabla T \quad (28)$$

and $\nabla \phi_2^{\text{st}} = -(D_1/D_2) \nabla \phi_1^{\text{st}}$. This implies a finite stationary current of micelles

$$\mathbf{J}_1^{\text{st}} = -\phi_1 \frac{D_1 D_2 \Gamma}{D_1 \gamma + D_2 \Gamma} \frac{H}{k_B T^2} \nabla T = -\phi_1 D_T \nabla T, \quad (29)$$

and the opposite flow of the molecular state. The second equality defines a thermal diffusion coefficient D_T for the first component. Its dependence on the rates γ and Γ , and on the micellar enthalpy H , indicates that this current is driven by the chemical reaction. The micelle and molecular currents \mathbf{J}_1^{st} and \mathbf{J}_2^{st} are shown in fig. 2 and related to the gradient of the chemical equilibrium condition (27).

Finally we define the Soret coefficient of the solution through the gradient of the total surfactant content $\phi^{\text{st}} = \phi_1^{\text{st}} + \phi_2^{\text{st}}$,

$$\nabla \phi^{\text{st}} + \phi^{\text{st}} S_T \nabla T = 0.$$

Rearranging the above expressions one finds

$$S_T = \frac{D_1 - D_2}{D_1 \gamma + D_2 \Gamma} \frac{\gamma \Gamma}{\gamma + \Gamma} \frac{H}{k_B T^2}. \quad (30)$$

This contribution could be relevant for thermophoresis experiments on SDS solutions [37].

As a summary of this section, the non-uniform equilibrium condition (27) imposes the steady-state composition gradient $\nabla \phi_1^{\text{st}}$, which in turn, induces the thermally driven micellar current \mathbf{J}_1^{st} . Thus we have $D_T \neq 0$ in spite of $L'_{kQ} = 0$, which clearly invalidates eq. (12).

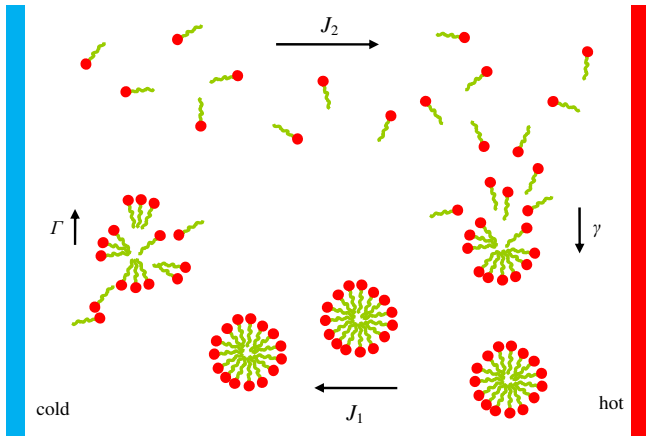


Fig. 2. Steady-state currents resulting from the equilibrium between micellar and molecular states in a surfactant solution. For $H > 0$, micelle formation is favored at high temperatures, and the dissolved molecular state at lower temperatures. This temperature-dependent equilibrium feeds stationary micelle and molecular currents J_1 and J_2 . For $H < 0$ all arrows point in the opposite direction.

6 Viscous effects — thermophoresis

Now we turn to the case where the entropy production (5) comprises a viscous term. We repeat that the phenomenological equations are block-diagonal, and thus do not mix viscous and particle fluxes Π and \mathbf{J}_k . Yet there is ample experimental evidence that thermally driven motion in colloidal dispersions is essentially determined by viscous effects. In physical terms the moving particle engenders in the surrounding fluid a velocity field $\mathbf{v}(\mathbf{r})$, which produces entropy according to the last term in (5). Accordingly, most theoretical works on colloidal thermophoresis rely on a hydrodynamic approach which deals with the coupling of the mass flux \mathbf{J}_1 in (8) and the viscous pressure tensor (10).

We consider colloidal particles dispersed in continuous solvent without molecular structure. The chemical potential per particle $\mu = h - Ts$, or partial free enthalpy, is given by the interaction enthalpy h and the translational entropy $s = -k_B \ln \phi_1$; the former is proportional to the particle surface and the latter decreases with the particle content ϕ_1 . From the thermodynamic force (7) one expects that D and D_T arise from the volume fraction and temperature derivatives, respectively.

In this section we sketch the derivation of D and D_T in terms of Stokes' equation $\eta \nabla^2 \mathbf{v} = \nabla P$, with the solvent viscosity η , velocity field \mathbf{v} , and pressure P . A rather simple physical picture emerges for the diffusion coefficient, where the hydrodynamic flow corresponds to the Stokes drag of a particle subject to an entropic force $-k_B T \nabla \phi_1$. Regarding the thermophoretic mobility D_T , the relation between the thermodynamic force and the particle velocity is less straightforward, but relies on an argument developed by Derjaguin and on the concept of an effective slip velocity close to a solid surface [38]. The latter provides a

hydrodynamic boundary condition with links viscous flux with the particle motion.

6.1 Stokes-Einstein diffusion coefficient

Gradient diffusion in a colloidal dispersion is determined by the interplay between thermal noise and Stokes drag; in the present notation the coefficient reads

$$D = \frac{\phi_1 \mu_{11}^\phi}{6\pi\eta R} = \frac{k_B T}{6\pi\eta R}. \quad (31)$$

The numerator results from the thermodynamic force $\nabla \mu$ exerted by a concentration gradient, whereas the denominator accounts for Stokes friction for a sphere of radius R . In the second equality we have used that in a dilute suspension the thermodynamic factor simplifies according to $\phi_1 \mu_{11}^\phi = k_B T$ [2].

In the absence of viscous effects and for $\phi_1 \rightarrow 0$, eq. (15a) gives

$$D = B_2 \phi_1 \hat{\mu}_{11}^\phi = k_B T B_2 / v_1,$$

with the solvent molecular mobility B_2 and the particle volume v_1 [23]. In the present macroscopic hydrodynamics approach (31), the mobility B_2 has disappeared, or rather is subsumed in the viscosity parameter η . The dependence on the particle size R is characteristic for the solvent velocity field associated with the diffusing particle.

6.2 Surface forces and slip velocity

Now we turn to the thermophoretic mobility D_T , which describes colloidal motion driven by a temperature gradient. For the case of thermal diffusion, the coefficient (15b) was obtained as the product of the thermodynamic forces with the molecular mobilities. Thermophoresis is more complex since the motion is related to a velocity field $\mathbf{v}(\mathbf{r})$ in the surrounding fluid; the resulting viscous pressure Π contributes significantly to the entropy production.

As pointed out by Anderson [38], the fundamental principle of thermophoresis is similar to electrophoresis and to motion in concentration gradients. As shown in fig. 3, the temperature gradient induces a shear stress within a boundary layer of thickness λ . At distances beyond λ , the resulting flow profile saturates at the effective slip velocity v_S . Matching the far-field $\mathbf{v}(\mathbf{r})$ to the boundary condition v_S , one finds that the particle moves at a velocity

$$u = -D_T \nabla T = -\frac{2}{3} v_S. \quad (32)$$

Thus calculating D_T is reduced to the hydrodynamic problem of evaluating the flow around the particle.

In the phenomenological equations, there are no cross-terms between the particle current \mathbf{J}_k and the viscous flux

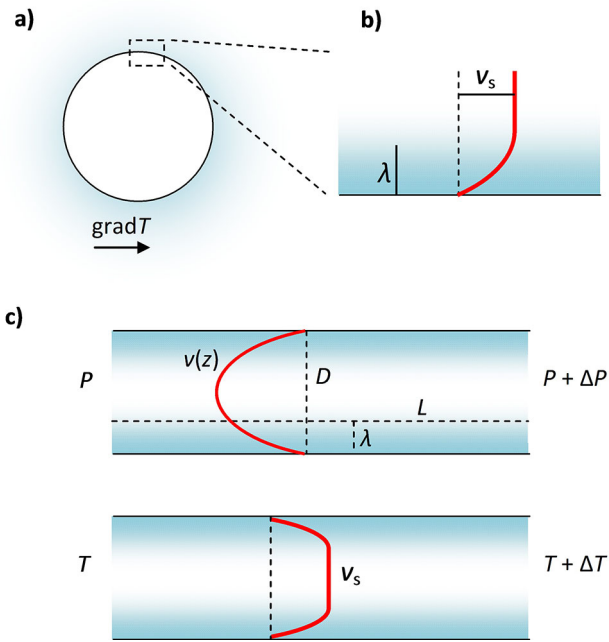


Fig. 3. a) Colloidal particle in a temperature gradient. The boundary layer is characterized by the excess specific enthalpy \hat{h} (grey-blue). b) The case of a thin boundary layer ($\lambda \ll R$) is equivalent to a flat surface where, at distances beyond λ , thermoosmosis leads to an effective slip velocity v_s . c) Heat and volume flows in a capillary. The pressure gradient $\Delta P/L$ results in Poiseuille flow with parabolic velocity profile $v(z)$. Since $\hat{h} = 0$ in the core of the capillary, the excess heat flow (36) occurs in the boundary layers of thickness λ . A temperature gradient $\Delta T/L$ results in thermal creep flow along the solid boundary; the velocity profile in the boundary layer depends on the detail of $h(z)$. The constant velocity in the core of the capillary can be determined from Onsager's reciprocal law for the coefficients in (33). Then the resulting slip velocity (38) applies equally well at the surface of a colloidal particle and, finally, determines the thermophoretic mobility according to (32).

II. Yet the hydrodynamic boundary conditions couple the particle motion to the fluid velocity field. In the following we give Derjaguin's evaluation for this coupling.

6.3 Onsager relation for enthalpy and volume flows

In their 1941 paper on the thermoosmotic effect, Derjaguin and Sidorenkov consider the conjugate heat flow instead of the thermally driven velocity [39, 40]. In a second step, the latter is obtained from a reciprocity relation. This is achieved in the geometry shown in fig. 3c, where the height D of the capillary is much smaller than its length L and its width w . The thermophoretic coefficient D_T is obtained by mapping the boundary problem on the surface of a colloidal particle to the capillary flow velocity, according to (32).

The thermodynamic forcers, that is the temperature gradient $\nabla T = \Delta T/L$ and pressure gradient $\nabla P = \Delta P/L$, are constant and oriented along the capillary axis. The

corresponding fluxes, that is the flows of heat and volume, are linear functions of the forces,

$$J_V = \frac{\dot{V}}{wD} = -L_{VQ} \frac{\nabla T}{T} - L_{VV} \nabla P, \quad (33a)$$

$$J_Q = \frac{\dot{Q}}{wD} = -L_{QV} \frac{\nabla T}{T} - L_{QQ} \nabla P. \quad (33b)$$

Here \dot{V} and \dot{Q} are the integrated volume and heat flows through the capillary, whereas J_V and J_Q are the average current densities, like \mathbf{J}_Q in previous sections. The dimension of \dot{Q} is energy/time, and that of \dot{V} is volume/time.

The diagonal coefficients L_{VV} and L_{QQ} are described by the Hagen-Poiseuille law for laminar flow and the thermal conduction of the liquid, respectively. The off-diagonal coefficients account for the cross-currents; L_{QV} gives the pressure-driven heat flow, and L_{VQ} the temperature-driven volume flow. According to Onsager's reciprocal relations, these coefficients are identical,

$$L_{QV} = L_{VQ}. \quad (34)$$

The transport coefficients are calculated from Stokes' equation $\eta \nabla^2 v = \nabla P$ for the velocity field $v(z)$, completed with the boundary conditions $v(0) = 0 = v(D)$.

First consider the flows driven by a pressure difference. In a narrow capillary, the velocity depends on the vertical coordinate z only. Then Stokes' equation reduces to $\eta \partial_z^2 v = \nabla P$; it is solved by

$$v(z) = \frac{z(z-D)}{2\eta} \nabla P \quad (0 \leq z \leq D) \quad (35)$$

and results in the volume flow $\dot{V} = -(wD^3/12\eta) \nabla P$ and $L_{VV} = D^2/12\eta$. The heat flow consists of the excess enthalpy of the liquid close to the upper and lower boundaries of the capillary

$$\dot{Q} = w \int_0^D dz \hat{h}(z) v(z). \quad (36)$$

The specific enthalpy \hat{h} is measured with respect to that of the bulk liquid, \hat{h}_∞ , such that $\hat{h} \rightarrow 0$ outside the interaction layers. Dividing the integral by wD and identifying with $J_Q = -L_{QV} \nabla P$, we find the transport coefficient

$$L_{QV} = -\frac{1}{\eta} \int_0^{D/2} dz z \hat{h}(z). \quad (37)$$

Here we have used that the lower and upper boundaries of the capillary carry identical amounts of heat, and have inserted the velocity profile close to the lower boundary, $v(z) = -zD \nabla P / 2\eta$ for $z \ll D$.

Now we turn to the temperature-driven volume flow at constant pressure. Except for the boundary layer, the velocity profile is constant across the capillary; to leading order in λ/D , the volume current reads $J_V = v_s$. Identifying this with $J_V = -L_{VQ} \nabla T / T$ and using the reciprocal relation (34), we find

$$v_s = -\frac{\nabla T}{\eta T} \int_0^\infty dz z \hat{h}(z). \quad (38)$$

We have used that \hat{h} is finite in the boundary layer of thickness $\lambda \ll D$ only and vanishes in the core of the capillary; thus we have replaced the upper bound $D/2$ with infinity. (In passing we note that the additional factor 2 occurring in previous work [40,41] is related to the missing $\frac{1}{2}$ in the Poiseuille velocity profile used there.)

6.4 Thermophoretic and Dufour coefficients

The above cross-coefficient L_{QV} applies to any surface with an excess enthalpy \hat{h} within a thin boundary layer. In particular, v_S describes the quasislip velocity v_S occurring close to the surface of a colloidal particle, as illustrated in fig. 3b. From the hydrodynamic boundary condition (32) one readily obtains the thermophoretic mobility of the particle

$$D_T = -\frac{2}{3\eta T} \int_0^\infty dz z \hat{h}(z) = \frac{2}{3} \frac{L_{QV}}{T}. \quad (39)$$

In the second equality we have used (37) with $\lambda/D \rightarrow 0$. Note that D_T does not depend on the particle radius R . (This is valid as long as the particle radius is larger than the interaction length, $R \gg \lambda$. In the opposite case, the numerical prefactor $\frac{2}{3}$ has to be replaced with unity [15].)

Thus thermophoresis stems from the volume flow \dot{V} driven by thermo-osmosis along a solid-liquid interface. The coefficient $L_{VQ} = L_{QV}$ has been evaluated through the conjugate phenomenon, that is, the heat flow \dot{Q} due to a Poiseuille flow. The second equality in eq. (39) relies explicitly on the Onsager reciprocity law (34). It is clear that D_T as defined above, has no relation with the Dufour effect D_F . In physical terms, the above argument does not lead to heat flow induced by a non-uniform colloidal volume fraction, and the actual conjugate flux \dot{Q} has nothing to do with a non-uniform composition.

Still, in a colloidal suspension with non-uniform volume fraction ϕ , there may be an additional heat flux $\dot{Q}_F \propto L'_{Q1} \nabla \phi$, and the reciprocal coefficient L'_{1Q} is expected to contribute an additional term to (39). The many data collected for colloidal thermophoresis suggest, however, that this extra term is small. In particular, experiments show that D_T is independent of the particle size; it would be rather surprising if the heat flow \dot{Q}_F , and thus the thermal diffusion and Dufour coefficient $L'_{Q1} = L'_{1Q}$, did not vary with the particle size.

7 Discussion

7.1 Are D_T and D_F reciprocal coefficients?

Reciprocity is an undoubted property of the cross-coefficients in Onsager's equations, such as L'_{1Q} and L'_{Q1} in (8), or L_{QV} and L_{VQ} in (34). This paper addressed the question to what extent these reciprocal relations imply $D_T = D_F/T$ for the thermal diffusion and Dufour coefficients in liquids, and under which conditions the identification of eq. (12) is valid. In the absence of scalar and vector

fluxes, we find that the model equations (1) are identical to Onsager's linear relation (8), implying $D_T = D_F/T$.

Adding a chemical reaction and coupling to the vector fluxes through (24), we obtain a finite D_T even for $L'_{1Q} = 0$. The corresponding micelle current (29) is driven by the equilibrium composition of the chemical reaction. Thus we find that eq. (12) is not satisfied in the presence of chemical reactions, in agreement with the more formal study by de Groot and Mazur [2].

A similar result is obtained for viscous effects. Thermophoresis in colloidal suspensions is governed by hydrodynamic flow in the vicinity of the particle, as shown in general by Anderson [38] and worked out in detail for electric-double layer interactions [15,42]. The mobility D_T is given by the interaction enthalpy in the boundary layer. The corresponding Onsager coefficient L_{QV} is not related to Dufour effect and its coefficient L'_{Q1} .

Our analysis suggests that the mobility D_T defined in (1) and measured in many experiments, comprises different contributions: thermal diffusion, thermophoresis, spatially varying chemical reaction rates, etc. In each case, there is a conjugate effect with a reciprocal coefficient. Above we have discussed the relation between thermal diffusion and the Dufour effect ($L'_{1Q} = L'_{Q1}$), and thermophoresis and the pressure-driven heat flow ($L_{VQ} = L_{QV}$). Similarly, the equilibrium between the molecular and micellar states in a surfactant solution, feeds a steady micelle current (29) that is proportional to the temperature gradient; the coefficient D_T is determined by the reaction rates of micelle formation.

7.2 Thermal diffusion or thermophoresis?

Most authors use "thermal diffusion" for molecular mixtures and "thermophoresis" for colloidal suspensions, though in both cases the coefficient D_T is defined by (1). The above discussion gives a more precise meaning to this distinction. In the case of thermal diffusion, viscous effects are absent, and D_T and the Dufour coefficient are related by reciprocity. In the stationary state the particle currents vanish, $\mathbf{J}_1 = 0$, and so does the corresponding entropy production.

Thermophoresis, on the other hand, is determined by viscous flow. Then the mobility D_T is given by the Onsager cross-coefficient L_{VQ} which describes volume flow due to a temperature gradient. As worked out in a previous paper [43], the entropy production related to the particle fluxes vanishes in the steady state $\mathbf{J}_1 = 0$, the viscous flux continues to dissipate energy. The hydrodynamic flow around each particle maintains a finite rate of entropy production $\mathbf{II} : \mathbf{G} > 0$.

7.3 Comparison with experiment and simulations

According to the preceding discussion, the reciprocity relation between D_T and D_F is valid for thermal diffusion only. In other words, reciprocity requires that diffusion and thermal diffusion coefficients can be expressed

through the mobilities B_k as in (15). In view of the fit of $S_T = D_T/D$ in fig. 1, the alkane data are not in contradiction with the thermal diffusion picture. In order to obtain conclusive evidence, one would have to consider the coefficients D_T and D separately, and this at different composition. On the contrary, data on polymer solutions and particle suspensions rather agree with thermophoresis mechanism, indicating that viscous effects prevail if the solute is much larger than the solvent molecules [44, 45]. Yet the break-down of the thermal diffusion picture may occur well before viscous behavior in the sense of macroscopic hydrodynamics sets in.

In technical terms, (15) ceases to be valid if the molecules respond differently to the thermal and concentration gradients in the thermodynamic force (14). Yet nothing is known about the underlying mechanisms and the relevant parameters. At present it is not even clear whether the thermal diffusion picture applies to mixtures of organic molecules of similar size and weight, such as benzene, cyclohexane, and alkanes. Whereas thermal diffusion data are available for many systems [5, 46–49], there are only few studies on the Dufour effect [9–11]. Comparison of measured D_T and D with (15) could provide valuable information.

In recent years, molecular dynamics simulations have become a powerful tool for studying the thermal diffusion and transport properties. Besides the dependencies on molecular enthalpy, mass, and size [50–52], both diagonal and off-diagonal Onsager coefficients have been evaluated [16–19]. For the investigated Lennard-Jones systems, the simulations confirm reciprocity of the thermal diffusion and Dufour coefficients. So far there is no systematic numerical study of the validity of (2) and (15). The above discussion suggests a break-down of the thermal diffusion picture upon differentiating the two components in molecular size or shape.

8 Summary

In this paper we discussed the coefficient D_T of thermally driven transport in three situations, where the entropy production is dominated by diffusion, chemical reactions, or viscous flow. In the first case, D_T is determined by the molecular enthalpy and diffusion constants B_i according to (15). The conjugate effect is the Dufour effect, and D_T and D_F are reciprocal coefficients.

As an example of chemical reactions, the temperature-dependent equilibrium between micellar and molecular states in a surfactant solution, imposes a steady-state diffusion current. The resulting coefficient D_T in (29) is given by reaction rates and the micelle enthalpy H . As the reciprocal effect, an externally imposed micelle current feeds a stationary reaction flux $\mathcal{J} = \dot{\phi}_1$.

If dissipation is dominated by viscous stress, as for colloidal suspensions in (39), D_T depends on the interaction enthalpy and the solute viscosity. The reciprocal cross-coefficient L_{QV} accounts for advective heat flow in a pressure gradient.

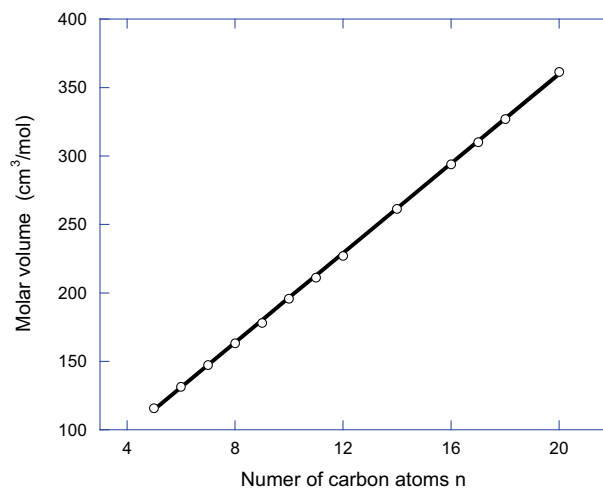


Fig. 4. Molar volume of normal alkanes. The circles give the measured values at room temperature, the solid line has been calculated from eq. (18b).

Thus in the presence of chemical reactions or viscous effects, D_T is not related to the Dufour effect. In future work, it would be interesting to study whether and to which extent, the thermal diffusion picture (15) is valid in binary molecular mixtures.

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Appendix A. Alkane enthalpy and volume

The fit of alkane Soret data in fig. 1 relies heavily on the variation of the molecular enthalpy and volume (18) with the number n of carbon atoms. In particular, the relative off-set values of 0.65 and 2.02 determine to a large extent the theoretical curve. If these numbers were identical, the specific enthalpy $\hat{h} = h/v$ would be independent of n , and S_T would vanish for all mixtures; exchanging the off-set values would result in a positive Soret effect for the lighter component.

An at least qualitative explanation for the off-set of $0.65 \times 4.64 \approx 2.9$ kJ/mol is given by a simple geometrical argument for polymers on a 3D cubic lattice. A monomer has 6 couplings with next nearest-neighbor molecules and a dimer has $\frac{10}{2} = 5$ such couplings per unit. For a rigid high polymer there are $4(n+2)$ couplings, that is, about 4 per monomer, and a slightly smaller value occurs for flexible polymers. These numbers are very close to the factor in (18a).

The volume off-set accounts for the fact that the density of shorter alkanes is smaller; it is related to the larger entropy of short chains. Figure 4 shows measured values of the molecular volume v_n . The solid curve, calculated from (18b), provides a very good fit to these data.

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