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## Is Soret equilibrium a non-equilibrium effect?

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## ABSTRACT

Recent thermophoretic experiments on colloidal suspensions revived an old debate, namely whether the Soret effect is properly described by thermostatics, or necessarily requires non-equilibrium thermodynamics. Based on colloidal transport theory and the entropy production of the related viscous flow, our analysis leads to the conclusion that the equilibrium approach may work for small ions, yet fails for colloidal particles and polymers. Regarding binary molecular mixtures, our results shed some doubt on the validity of thermostatic approaches that derive the Soret coefficient from equilibrium potentials.

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## 1. Introduction

Since the early days of thermodynamics there has been a debate whether or not the stationary state of a non-isothermal system can be described in terms of equilibrium properties [1]. Classical examples are the Soret and Seebeck–Peltier effects [2]. The latter accounts for the coupling between heat flow and electric current in a conducting material. Though the Seebeck and Peltier coefficients  $S$  and  $\Pi$  describe dissipative phenomena, Thomson showed that irreversibility drops out in the ratio  $\Pi/S = T$ , which is simply given by temperature. Several attempts at a rigorous derivation failed, until Onsager pointed out the role of microscopic reversibility and established Thomson's relations as special cases of his reciprocal laws [3].

The Soret effect describes the mass flow induced by a temperature gradient in a complex fluid [4–8]. It was first observed for electrolyte solutions, where salt accumulates at the cold side [9–11]; the non-uniform steady-state concentration  $c$  is given by the “Soret equilibrium” [12–14]:

$$\nabla c + c S_T \nabla T = 0 \quad (1)$$

This effect is essential for understanding the compositional grading in the Earth's petroleum reservoirs [15], the isotope fractionation in silicate melts [16], and the energy balance of carbon-nanotube based thermogalvanic cells [17]. In microchannels and thin films, the Soret effect is an efficient means for colloidal confinement and for accumulating molecular solutes at a micron-sized heated spot [18–21]. In spite of various attempts to elucidate its physical mechanisms, there is so far no generally accepted theoretical framework for the Soret coefficient  $S_T$ . The most fundamental question is whether it can be obtained from equilibrium theory, or whether it necessarily reflects the irreversible nature of the underlying dissipative flows. This is not a merely formal issue but affects measurable quantities, e.g., how  $S_T$  depends on the particle size [18,22].

In an early approach, Eastman considered two small but macroscopic cells at temperatures  $T$  and  $T + dT$  [12]. The probability for a particle moving from one cell to the other is related to the corresponding change of entropy, absorbed or released by the surrounding liquid. As an essential step in his argument, Eastman identified this transfer quantity with

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the canonical entropy  $S = -dG/dT$  carried by the solute, where  $G$  is the single-particle free enthalpy or Gibbs energy; his result reads, in modern notation:

$$S_T = \frac{1}{k_B T} \frac{dG}{dT} \quad (2)$$

In this thermostatic approach, the Soret coefficient is related to an equilibrium thermodynamic potential.

A rather different picture emerges from Onsager's non-equilibrium theory, which is based on the entropy balance equation for reversible and irreversible changes; the former correspond to the entropy transfer and the latter to dissipation or entropy production. Heat and mass flows are driven by generalized forces; the current of solute particles:

$$J = -D\nabla c - cD_T\nabla T \quad (3)$$

accounts for Fick diffusion with the Einstein coefficient  $D$  and for thermophoresis with mobility  $D_T$  [1]. Comparing the steady-state condition  $J = 0$  with (1) gives the Soret parameter:

$$S_T = \frac{D_T}{D} \quad (4)$$

Since  $D$  and  $D_T$  do not form a pair of reciprocal coefficients, their ratio is expected to reflect the underlying dissipative motion. In contrast to this view, Eq. (2) relates  $S_T$  to an equilibrium free enthalpy.

This discrepancy was already noted by de Groot in his 1945 thesis [13]. In recent years, a controversial discussion arose from experiments on colloidal suspensions that reported a quadratic [18] or linear [20,22–25] dependence of the Soret coefficient on the particle size. Either of these findings is supported by a number of theoretical works which may be loosely classified as “equilibrium” [26–30] or “dissipative” approaches [31–35].

The present paper intends to resolve this discrepancy by investigating the relation between Eqs. (2) and (4). Starting from a general Gibbs interaction energy and relying on standard colloidal transport theory, we evaluate the viscous factors occurring in (3) and, in particular, determine under which conditions they drop out in the ratio  $D_T/D$ . As an unambiguous signature for dissipation, we calculate the steady-state entropy production of the viscous flow around a solute particle.

## 2. Local thermal equilibrium

We consider a dilute solution in a non-uniform temperature and assume that mechanical and local thermal equilibrium is established. This assumption has several important implications [1]: (i) the macroscopic pressure is constant throughout the system; (ii) the Dufour effect being small in liquids, the temperature profile  $T(\mathbf{r})$  is independent of composition and constant in time; (iii) more generally, the properties of a small but macroscopic subvolume are described by equilibrium thermodynamics.

Thus we may define a free-enthalpy density  $g(r, T(\mathbf{r}))$  that describes the mutual forces of a particle and of the surrounding fluid. It depends on position both explicitly through the interaction and implicitly through the non-uniform temperature. Relevant mechanisms are the electric double-layer energy, the van der Waals potential, and depletion forces due to an additional molecular solute. The solvation free enthalpy or Gibbs energy of a single particle is given by:

$$G(T(\mathbf{r})) = \int dV g(r, T(\mathbf{r})) \quad (5)$$

The integrand is most significant within the range of interaction  $\lambda$  and rapidly decreases at larger distances [36]. For electric double-layer forces,  $\lambda$  corresponds to the Debye length and  $g$  decays exponentially as  $e^{-(r-R)/\lambda}/r$ . Dispersion forces have no intrinsic length scale, but decrease with a power law; then  $\lambda$  may be taken as the particle size. The main conclusions of this paper are very general and apply to any interactions as long as  $g(r, T(\mathbf{r}))$  decays sufficiently rapidly at large distances.

For low dilution and in the absence of long-range interactions, the chemical potential consists of the single-particle Gibbs energy and a contribution accounting for the translational entropy  $-k_B \ln(c/c_0)$ ,

$$\mu(T, c) = G(T) + k_B T \ln(c/c_0) \quad (6)$$

The spatially varying temperature  $T(\mathbf{r})$  is imposed by the experimental setup, whereas the concentration profile  $c(\mathbf{r})$  remains to be determined.

## 3. Thermostatic approach

We briefly discuss the origin of the relation (2), which was first obtained by Eastman for the Soret effect of electrolyte solutions and since then has been applied to molecular mixtures and colloidal particles. Eastman explicitly discards dissipative processes and retains reversible changes of the thermodynamic potential only. Considering a particle that migrates between “cells” with temperature and concentration differences  $dT$  and  $dc$ , he defines the “entropy of transfer”  $S^*$  through the change of the chemical potential due to the uniform concentration:

$$S^* dT = -(d\mu/dc) dc$$

(At this point, the unknown Soret coefficient  $S_T$  has merely been replaced by the unknown  $S^*$ .) As the essential step of his approach, Eastman then identifies  $S^*$  with the canonical single-particle entropy  $S$  and thus obtains (2).

Subsequent works derived Eastman's formula from the condition that the gradient of the free energy or the chemical potential vanishes. The underlying idea is to interpret  $\nabla\mu$  as the mechanical force acting on a particle and, accordingly, the relation  $\nabla\mu = 0$  as the steady-state condition. To linear order in the gradients one has:

$$0 = \nabla\mu = \frac{dG}{dT}\nabla T + k_B T \frac{\nabla c}{c} \quad (7)$$

Comparing with (1) gives indeed Eastman's expression for the Soret coefficient. (Neglecting the term proportional to  $\ln(c/c_0)\nabla T$ , one circumvents a problem arising from the fact that  $\nabla\mu$  is not invariant under a shift of the zero of entropy. For a discussion of alternative choices, see Ref. [37].)

This thermostatic approach relies on identifying  $\nabla\mu = 0$  with the condition of mechanical equilibrium, which is central to the steady state of dissipative processes [1]. Strictly speaking, the Gibbs energy and the chemical potential are not well defined for a system with non-uniform temperature; thus the steady-state condition Eq. (7) is beyond the domain of equilibrium statistical mechanics. Eastman's approach heavily relies on identifying  $S^*$  with the canonical entropy  $S$ ; so far there is no justification for this essential step in his argument.

#### 4. Transport coefficients and size dependence

Here we evaluate the Soret coefficient from Onsager's theory for non-equilibrium systems. For small particles, we start from the generalized thermodynamic force. For large particles, the thermodiffusion and diffusion currents have to be evaluated separately because of their different viscous properties.

##### 4.1. Diffusion current

Brownian motion of a particle suspended in a liquid was related by Einstein to the thermal agitation of nearby molecules, which acts as a random external force. There are two important consequences, the mean-square displacement increases linearly with time, and a concentration gradient results in a diffusion current  $-D\nabla c$ , where the coefficient is given by the Stokes–Einstein relation:

$$D = \frac{k_B T}{6\pi\eta R} \quad (8)$$

This expression is valid over a large range in solute size, from small molecules of a few Å to large colloidal particles that are visible to the naked eye. The same law holds true for diffusion of polymers, with  $R$  corresponding to the gyration radius [38]. For later use, we give the velocity corresponding to gradient diffusion:

$$u_D = -D \frac{\nabla c}{c} \quad (9)$$

##### 4.2. Thermodiffusion of small particles $R \ll \lambda$ .

In the framework of non-equilibrium thermodynamics, the generalized force exerted on a dispersed particle reads  $\nabla(\mu/T)$  [1]. Inserting (6) and multiplying with  $cT$ , we find:

$$cT\nabla\frac{\mu}{T} = cT\nabla\frac{G}{T} + k_B T\nabla c = -c\frac{H}{T}\nabla T + k_B T\nabla c \quad (10)$$

We have used the implicit spatial variation of the free enthalpy  $G(T(\mathbf{r}))$  and, in the second equality, the Gibbs–Helmholtz equation  $d(G/T)dT = -H/T^2$ , which expresses the relation  $H = G + TS$  between free enthalpy  $G$ , enthalpy  $H$ , and entropy  $S$ .

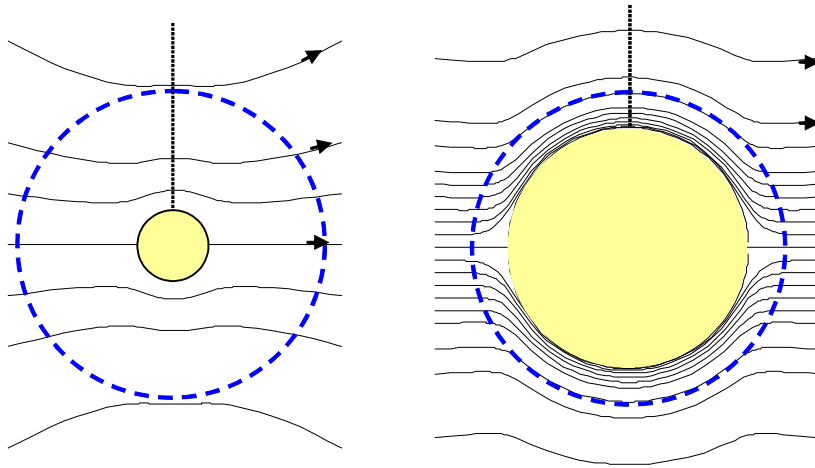
The Soret coefficient is obtained from two conditions. First, we identify the stationary state with zero thermodynamic force,  $\nabla(\mu/T) = 0$ . Second, we assume that the mobility parameter of both force terms in (10) is given by Stokes friction  $1/(6\pi\eta R)$ . This is obvious for the diffusion term (8) and provides a good approximation of the thermodiffusion current in the limit  $R \ll \lambda$ , in analogy to Hückel's treatment of electrophoresis [39,40]. Comparison with (3) then gives:

$$D_T = -\frac{1}{6\pi\eta R} \frac{H}{T} \quad (11)$$

Corrections to this approximate result are of the order  $R/\lambda$ .

The Soret coefficient is given by the ratio:

$$\frac{D_T}{D} = \frac{d}{dT} \left( \frac{G}{k_B T} \right) = -\frac{H}{k_B T^2} \quad (12)$$



**Fig. 1.** Flow pattern  $\mathbf{v}(\mathbf{r})$  in the vicinity of an immobile solute particle. The velocity is zero at the particle surface, increases exponentially within the interaction length  $\lambda$  indicated by a dashed circle, and decays as  $1/r$  at larger distances. The left and right panels show the cases of small and large particles, respectively. The velocity profile along the vertical dotted lines is shown in Fig. 2.

Irreversibility drops out since  $D$  and  $D_T$  carry the same friction coefficient. Eq. (12) states that for particles much smaller than the range of the solute–solvent interaction, the Soret coefficient is given by the solvation enthalpy  $H$ . A particle that strongly interacts with the solvent ( $H < 0$ ) moves to the cold, whereas a solute with a positive solvation enthalpy is driven to the warm.

The above result significantly differs from Eastman’s formula. The latter provides a good approximation only if  $G/T$  is small as compared to the derivative  $dG/dT$ . This seems to be the case for small ions in an electrolyte solution: the Soret coefficient obtained by Dhont [26] from (2) corresponds to the result from the non-equilibrium thermodynamics approach [40]. The thermodynamic force (10) agrees with the Boltzmann-type distribution function  $c = c_0 e^{-G/k_B T_0}$  that was used by Duhr and Braun [18] and confirmed by Astumian [27]. The general 1D steady-state distribution was given by van Kampen in a study on diffusion in non-uniform media [41]. As a common feature, these works assume, more or less explicitly, that the dissipative factor of the drift velocity  $u_0$  is given by Stokes–Einstein form  $6\pi\eta R$ ; this is justified for small particles of radius  $R \ll \lambda$ .

#### 4.3. Thermophoresis of large particles $R \gg \lambda$

Now we turn to the opposite case, illustrated in the right panel of Fig. 1.

Then the viscous stress on the fluid is concentrated in a boundary layer of thickness  $\lambda$  at the particle surface, where Stokes’ equation takes a rather simple form [36]. From a general argument relying on the symmetry of Onsager’s coefficients, Derjaguin calculated the quasi-slip velocity [42] which gives the thermophoretic mobility in the form:

$$D_T = -\frac{2}{3\eta} \frac{\hat{h}}{T} \tag{13}$$

where  $\hat{h}$  is an integral over the solvation enthalpy density  $h(z, T)$ :

$$\hat{h} = \int_0^\infty dz zh(z, T) \tag{14}$$

In the latter integral, the quantity  $z = r - R$  is the distance from the particle surface.

For large particles both the enthalpy density  $h$  and the quantity  $\hat{h} \sim \lambda^2 g(0)$  are independent of the radius  $R$ , whereas the volume integral  $H = 4\pi R^2 \int dz h$  is proportional to the surface area. As a most important feature, the velocity  $u_0 = D_T \nabla T$  and the mobility  $D_T$  are independent of the solute size; this is a particular case of a general rule for motion driven by interfacial forces [36]. The above form for the diffusion coefficient implies that the ratio:

$$\frac{D_T}{D} = \frac{4\pi R}{k_B T} \frac{\hat{h}}{T} \propto R \tag{15}$$

increases linearly with the particle radius. This result generalizes previous work on electrostatic and dispersion forces [31–35]; for charged particles, the double-layer enthalpy  $h$  comprises the energy density of the electric field and the excess ion osmotic pressure [34]. The underlying hydrodynamic treatment of interfacial forces parallels Smoluchowski’s treatment

of electrophoresis and is widely used in colloidal transport theory [36]. We have discarded the possibility of hydrodynamic slippage [43].

#### 4.4. Polymers

Regarding the ratio (4), we first note that the diffusion coefficient of polymers is proportional to the inverse gyration radius  $D = k_B T / \kappa \eta R_g$ , due to long-range hydrodynamic interactions between the flexible units of the polymer [38]. The thermophoretic mobility  $D_T$  is independent of the molecular weight, as first derived by Brochard and de Gennes from general arguments; for more details, see [8,44]. In physical terms, the Gibbs energy  $g$  does not cause hydrodynamic interactions beyond the interaction range  $\lambda$ . Thus Eq. (15) remains valid for polymers. Since the gyration radius scales with the number  $N$  of monomers according to the power law  $R_g = \ell N^\nu$ , the Soret coefficient:

$$\frac{D_T}{D} \propto R_g \quad (16)$$

shows a characteristic molecular-weight dependence. As a side remark, this scaling ceases to be valid for chains of less than hundred monomers, where an additional thermodiffusion mechanism sets in [35,45,46].

#### 4.5. Comparison with experiment

*Polymers.* As first shown by Giddings and co-workers [47], the Soret coefficient of high polymers is proportional to the gyration radius  $R_g$ :

$$S_T \propto R_g \sim \ell N^\nu \quad (\text{exp}) \quad (17)$$

For ideal flexible polymers,  $\ell$  is the diameter of a monomer and  $\nu = \frac{1}{2}$ . For most real polymers,  $\ell$  rather corresponds to the persistence length and is larger than that of a monomer; accordingly,  $N$  gives the number of such units. The exponent depends on intrachain interactions and on the solvation energy; in a “good solvent”, one has  $\nu \approx 0.6$ . The experimental law is in perfect agreement with the expression obtained from the ratio of transport coefficients (16).

For sufficiently long chains, the Gibbs energy is proportional to the molecular weight,  $G = N g_1$ , and so is Eastman’s expression:

$$S_T = N s_1 \quad (18)$$

with the monomer Soret coefficient  $s_1 = -(k_B T)^{-1} h_1 / T$ . This linear dependence does not match the experimental finding. Since the scaling law  $H = N h_1$  is a fundamental thermodynamic property of high polymers, the failure of Eastman’s expression cannot be mended. The same argument holds true for similar approaches based on the chemical potential, which for a long chain is an extensive quantity,  $\mu = N \mu_1$ .

*Colloidal particles.* We discuss the size dependence of the Soret coefficient of large colloidal particles. For charged polystyrene beads confined in a 10-micron chamber, a quadratic variation  $S_T \propto R^2$  was found for radii ranging from 20 nm to 1  $\mu\text{m}$  [18], whereas subsequent experiments reported a linear dependence  $S_T \propto R$  for both solid particles [20,22–24] and microemulsion droplets [25].

The Gibbs energy of large particles is proportional to the surface area,  $G \propto R^2$ , resulting in the quadratic law  $S_T \propto R^2$  for Eastman’s expression (2), which has been used for fitting the data of Ref. [18]. On the other hand, since the Einstein coefficient is inversely proportional to the radius and  $D_T$  independent of the particle size [8,32,36], the ratio (15) results in  $S_T \propto R$ , in agreement with the data of Refs. [20,22–25].

A more complex situation occurs for strongly hydrophobic particles with a finite slip length, where a quadratic dependence is obtained for intermediate particle size [40]; yet this effect can be discarded for micron-sized beads.

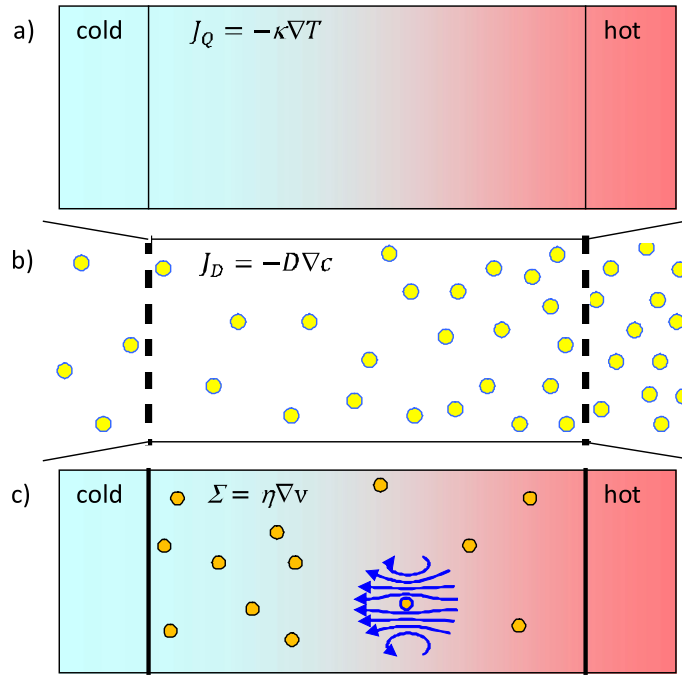
## 5. Entropy production

Here we relate the title of this paper to the question whether or not the Soret equilibrium (1) produces entropy. The thermostatic approach (2) relies on the assumption that the non-uniform solute distribution does not contribute to dissipation. This is obvious from Eastman’s argument: the “entropy of transfer”  $S = -dG/dT$  accounts only for the reversible change that occurs while a particle migrates between regions of different temperatures. In this picture, the non-uniform steady state described by (1) is not related to dissipation and, as a consequence, does not produce entropy.

### 5.1. Relevant dissipation mechanisms

As a fundamental aspect of Onsager’s non-equilibrium thermodynamics, dissipation is related to flows of heat and matter. Here we consider three contributions to the rate of entropy production [1],

$$\sigma = -\frac{J_Q \cdot \nabla T}{T^2} - \frac{J \cdot k_B \nabla c}{c} - \frac{\Sigma : \nabla \mathbf{v}}{T} \quad (19)$$



**Fig. 2.** Non-equilibrium systems with stationary heat and matter flow. (a) A constant temperature gradient drives a heat flow  $J_Q = -\kappa \nabla T$  from the hot to the cold side. (b) An open system is in contact with two reservoirs at different solute concentration  $c$ . Gradient diffusion results in a steady particle current  $J = -D \nabla c$  from high to low concentration, with Einstein coefficient  $D$ . (c) In the steady state of a closed system, the particle current vanishes. Yet the viscous flow  $\mathbf{v}(\mathbf{r})$  in the vicinity of each solute particle dissipates energy. These situations correspond to the three terms of the rate of entropy production (19).

The first one accounts for heat flow  $J_Q$  from the hot to the cold side of the sample, as illustrated in Fig. 2(a). The steady-state heat current  $J_Q = -\kappa \nabla T$  is proportional to the temperature gradient and the thermal conductivity  $\kappa$ .

The second term in (19) describes dissipation due to a particle flow  $J$  in a concentration gradient  $\nabla c$ . The steady state of a closed system corresponds to  $J = 0$ . As an example for a finite stationary particle current, Fig. 2(b) shows an open system at constant temperature that is in contact with two reservoirs at different concentrations. This concentration gradient results in a stationary current  $J = -D \nabla c$ , which is constant throughout the sample. Since the entropy per particle is higher in the low-concentration reservoir, the entropy per unit time leaving at the left boundary exceeds that entering at the right. This net outward flow is supplemented by the entropy production within the system. For later use we give the entropy production per particle,

$$\dot{S}_D = k_B \frac{u_D^2}{D} = \frac{6\pi\eta u_D^2}{T} R \tag{20}$$

The last term in  $\sigma$  is given by the contraction of the tensor of velocity derivatives  $\nabla \mathbf{v}$  and the symmetric part of the viscous stress  $\Sigma$ . In the stationary state the latter reads  $\Sigma = -\frac{1}{2}\eta(\nabla \mathbf{v} + \nabla \mathbf{v}^T)$ , with the solvent viscosity  $\eta$  [1]. The total entropy production  $\dot{S}$  due to the viscous flow in the vicinity of a single particle is obtained by spelling out the components of the stress tensor  $\Sigma$  and taking the volume integral [1]:

$$\dot{S} = \frac{\eta}{2T} \sum_{ij} \int dV \left( \frac{dv_j}{dx_i} + \frac{dv_i}{dx_j} \right)^2 \tag{21}$$

In the following we show that the solute particles dissipate energy, even in the steady state  $J = 0$ . Though the entropy production is much smaller than the heat current-driven term  $\kappa(\nabla T)^2/T^2$  and thus difficult to measure, it is an important signature for the dissipative nature of the Soret equilibrium state.

In the following we consider the entropy production due to the solute particles. The steady state  $J = 0$  is attained if diffusion and drift velocities cancel each other,  $u_D + u_T = 0$ . Each of the contributions to (3) engenders characteristic flow patterns in the vicinity of each particle, which are denoted  $\mathbf{v}_D(\mathbf{r})$  and  $\mathbf{v}_T(\mathbf{r})$ , respectively. As a most important aspect, we discuss the implications of the steady-state condition on the total velocity field

$$\mathbf{v} = \mathbf{v}_D + \mathbf{v}_T \tag{22}$$

Zero mean velocity of the solute particle ( $J = 0$ ) requires that the fluid velocity field vanishes at its surface,  $\mathbf{v}|_R = 0$ . Yet this does not imply that  $\mathbf{v}$  is zero everywhere. Quite to the contrary, the well-known long-range behavior  $\mathbf{v}_D \sim 1/r$  and

$\mathbf{v}_T \sim 1/r^3$  implies that  $\mathbf{v}$  is finite at distances beyond the particle radius ( $r > R$ ) [36,48]. Thus each solute acts as a pump that stirs the surrounding fluid, as shown schematically in Fig. 2(c).

The mean velocity field related to gradient diffusion reads:

$$\mathbf{v}_D(\mathbf{r}) = \frac{R}{2r}(1 + \hat{\mathbf{r}}\hat{\mathbf{r}}) \cdot \mathbf{u}_D$$

where  $\hat{\mathbf{r}} = \mathbf{r}/r$  is the radial unit vector and  $\mathbf{u}_0$  the velocity at the particle surface. The term arising from the thermophoretic drift cannot be given in closed form; in the following, we discuss two limiting cases with respect to the particle size.

### 5.2. Small particles $R \ll \lambda$

For the entropy production  $\dot{S}$  we need the net velocity field  $\mathbf{v} = \mathbf{v}_D + \mathbf{v}_T$ . For an exponentially screened interaction-free enthalpy, one finds to lowest order in  $R$  [40,48]:

$$\mathbf{v} = (e^{-(r-R)/\lambda} - 1)\mathbf{v}_D$$

This means that  $\mathbf{v}_D$  and  $\mathbf{v}_T$  cancel each other at the particle surface. This expression constitutes a poor approximation for  $r \gg \lambda$ ; yet this range is of little interest here. Calculating the viscous stress tensor in spherical coordinates and inserting in (21), one obtains:

$$\dot{S} = \frac{14\pi\eta u_D^2}{T} \frac{R^2}{\lambda} \ln \frac{\lambda}{R} \quad (23)$$

Thus in the limit of a point particle  $R/\lambda \rightarrow 0$ , the entropy production vanishes, and the Soret equilibrium is indeed an equilibrium effect. It turns out instructive to express  $\dot{S}$  through the entropy production of a diffusion current given in (20),

$$\dot{S} = \frac{7}{3} \frac{R}{\lambda} \ln \frac{\lambda}{R} \dot{S}_D \quad (R \ll \lambda) \quad (24)$$

The small prefactor implies  $\dot{S} \ll \dot{S}_D$ ; in other words, the dissipation related to the Soret equilibrium of small particles is much smaller than that of a corresponding diffusion current.

### 5.3. Large particles

Now we turn to the entropy production  $\dot{S}$ . In the boundary layer the fluid velocity changes by  $u_T$ , resulting in a shear rate of the order  $u_T/\lambda$ . Integrating  $\sigma = (\eta/2T)(u_T/\lambda)^2$  over the interaction volume  $4\pi R^2\lambda$  and noting  $u_T = -u_D$ , we find:

$$\dot{S} = \xi \frac{6\pi\eta u_D^2}{T} \frac{R^2}{\lambda} \quad (25)$$

where  $\xi$  is a numerical factor of the order of unity that depends on the precise form of the velocity field. At distances well beyond the interaction length, the velocity  $v \sim u_T(R/r)$  results in a shear rate  $u_T R/r^2$ . Its contribution to  $\dot{S}$  is of the form  $\sim (\eta/T)u_T^2 R$ , which is by a factor  $\lambda/R$  smaller than (25) and thus may be neglected. Like in the small particle case, the entropy source strength varies with the square of the solute size. Inserting that of the diffusion current, we have:

$$\dot{S} = \xi \frac{R}{\lambda} \dot{S}_D \quad (\lambda \ll R) \quad (26)$$

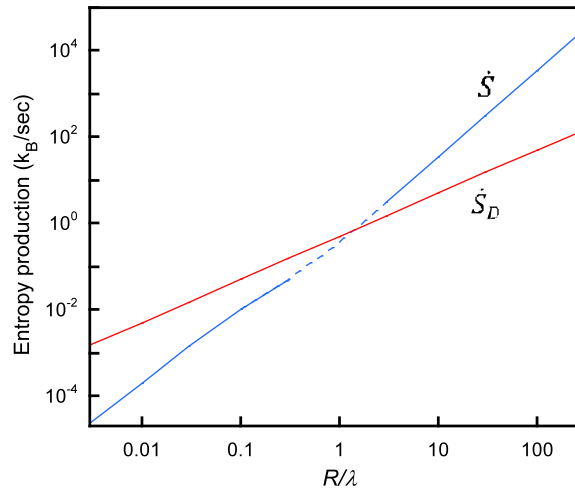
Thus the single-particle entropy production of the Soret equilibrium is much larger than that of the corresponding diffusion current.

### 5.4. Conclusion

From the argument given below (22) it is clear that the Soret effect of any solute engenders a finite velocity field  $\mathbf{v}$  and thus dissipates energy at a finite rate  $T\dot{S}$  per particle. Strictly speaking, this implies that the Soret equilibrium is not a true equilibrium property, yet does not exclude that Eastman's approach describes experimental findings.

We found it instructive to compare the entropy production per particle of the Soret equilibrium,  $\dot{S}$ , to that of diffusion with the same concentration gradient,  $\dot{S}_D$ . In the limit  $R \ll \lambda$ , where the particle radius is much smaller than the interaction range, the Soret effect dissipates little energy and, according to (24), produces less entropy than the corresponding diffusion current. In physical terms, this is related to the weak fluid flow in the vicinity of the particle and to the partial cancellation of  $\mathbf{v} = \mathbf{v}_D + \mathbf{v}_T$ . As a consequence, the Soret coefficient is well described by Eastman's thermostat approach (2), in spite of its non-equilibrium nature.

On the contrary, in the large-particle limit  $\lambda \ll R$ , the non-uniform colloidal concentration is a source of significant dissipation. The rate of entropy production (26) by far exceeds that of the corresponding diffusion current  $\dot{S}_D$ . This excess dissipation occurs in the boundary layer within one interaction length from the particle surface, and arises from the large shear rate that is characteristic for surface forces. In this range, the Soret effect cannot be viewed as an equilibrium phenomenon.



**Fig. 3.** Entropy production  $\dot{S}$  as a function of the reduced particle radius  $R/\lambda$ . The two branches of the curve  $\dot{S}$  indicate the limiting laws (23) and (25) for the entropy produced by the viscous flow around a single particle; the dashed line is an interpolation. The curve  $\dot{S}_D$  shows the entropy production (20) due to a diffusion current. We have used the parameters  $u_0 = 1 \mu\text{m/s}$ ,  $\lambda = 100 \text{ nm}$ , the viscosity of water, and the numerical factor  $\xi = 1$ . The relative magnitude of these two dissipation mechanisms is obvious from Eqs. (24) and (26). At  $R = \lambda$ , a cross-over occurs in the relative dissipation strength of the steady states illustrated in Figs. 2(b) and 2(c). For small particles, maintaining a given concentration gradient through the Soret effect dissipates less energy than maintaining a diffusion gradient in an open system,  $\dot{S} < \dot{S}_D$ , whereas for big particles the Soret equilibrium produces more entropy,  $\dot{S} > \dot{S}_D$ .

## 6. Binary molecular mixtures

The above laws for polymers and solid particles heavily rely on Stokes hydrodynamics. Simple results are obtained in the dilute limit for particles that are much smaller or much larger than their range of interaction. A more intricate situation is encountered for binary mixtures of non-ionic molecules. Since the range of dispersion forces is given by the molecular size, there is no clear separation of length scales; as a consequence, hydrodynamic and interaction effects occurring at similar distances are not easily distinguished. In general none of the components is dilute. Thus the surrounding of a given molecule consists of all species; the low-dilution limit does not apply, and thermodiffusion of a given species has to be evaluated self-consistently.

### 6.1. Thermostatic approach

In order to avoid these difficulties, thermodiffusion of non-ionic molecular liquids has been described in a thermostatic approach, where the Soret coefficient:

$$S_T = -\frac{Q_1 - Q_2}{k_B T^2} \tag{27}$$

is given by the heat  $Q_i$  carried by each of the components. Their difference  $Q_1 - Q_2 = TS$  is related to Eastman's entropy of transfer  $S$  introduced above (2). Dissipative aspects have been discussed by identifying  $Q$  with Eyring's viscous activation energy  $E$ , which is defined through the temperature dependence of the viscosity  $\eta = \eta_0 e^{E/k_B T}$  [49–52]; a similar picture arises when relating  $Q$  to partial enthalpies [53], partial volumes [54] or the self-diffusion activation energy [55]. A refined description for the mutual interactions of the molecular species is achieved by introducing thermodynamic or “activity” factors in the chemical potential or the partial pressure [56,57].

### 6.2. Hydrodynamic approach

Thermostatic approaches assume, more or less explicitly, that the viscous or mobility factors of  $D$  and  $D_T$  cancel each other. The above results suggest that this is not necessarily a good approximation. Since the interaction range of dispersion forces is comparable to the molecular size,  $\lambda \sim R$ , the small-particle limit is not well justified, and one rather expects that  $D$  and  $D_T$  carry different kinetic or hydrodynamic factors.

Though it may seem questionable at first sight, macroscopic hydrodynamics works surprisingly well at the molecular scale: the Stokes–Einstein coefficient (8) provides a good description for the diffusion of small molecules and even of ions. Even an additional coarse-graining in mesoscale simulations does not affect colloidal transport [58,59]. Thus one would expect that the characteristic flow pattern due to the drift velocity persists for small molecules. In a recent work, we have evaluated thermodiffusion in binary mixtures in a mean-field model and found the Soret coefficient [60]:



$$S_T = \frac{\xi_1 - \xi_2}{\phi_1 D_2 + \phi_2 D_1} \quad (28)$$

where  $\xi_i$  are thermodiffusion coefficients,  $D_i = k_B T / 6\pi\eta R_i$  the tracer diffusion coefficients, and  $\phi_i$  the volume fractions.

The denominator corresponds to the Hartley–Crank model for the mutual diffusion coefficient [61]. Its dependence on the molecular radii  $R_i$  constitutes a well-known hydrodynamic effect, which provides a good description for quasi-ideal binary systems such as normal alkanes [62]. The numerator of  $S_T$  depends on the composition as

$$\xi_1 = \frac{2\beta}{9\pi\eta d_0} F_1(\phi_1 H_{11} + \phi_2 H_{12}), \quad \xi_2 = \frac{2\beta}{9\pi\eta d_0} F_2(\phi_1 H_{21} + \phi_2 H_{22})$$

where  $\beta$  is the thermal expansion coefficient,  $d_0$  a molecular length,  $H_{ij}$  usual Hamaker constants, and  $F_i$  a correction factor that depends on the molecular size. In the dilute limit  $\phi_1 \rightarrow 0$ , one recovers an expression that describes experiments on polymer and particle solutions [60].

### 6.3. Isotope effect

Different isotopes of a given molecule differ in their thermodiffusion coefficients, as shown by experiments [63,64] and confirmed by molecular dynamics simulations [65–67]. Comparison with kinetic theory for gas mixtures [68] suggests that this mass effect arises from the kinetic energy of the molecules, with the mean value  $\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_B T$ . Since the mean momentum  $p \sim \sqrt{mk_B T}$  varies with the square root of mass and temperature, lighter molecules and those coming from the hot side transfer more momentum during a collision. By equilibrating this thermodynamic force with the Stokes drag and imposing that there is no net force on a given volume element, it was shown that lighter molecules are driven toward the warm because of their stronger velocity fluctuations  $\overline{v^2}$  [69]; the rotational motion turns out to contribute significantly to the Soret coefficient, in agreement with experiment [64].

This kinetic approach can be reformulated in terms of thermostatic quantities, by noting that the molecular energy corresponds to the translational entropy  $S = k_B \ln V$  where  $V$  is the available free volume per molecule. Explicit formulae are given by Waldmann for ideal gases, in terms of the first virial coefficients [68]. The volume  $V$  is related to the molecular size and the mean distance  $\ell_0$  of Ref. [69]. Though these hard-sphere models simplify the rather complex collisions of interacting molecules, they agree well with molecular dynamics simulations of Lennard–Jones liquids [65–67].

Artola et al. pointed out that the isotope effect is not accounted for by thermostatic approaches such as Prigogine's model [67]. This is illustrated by a recent work claiming that the mass dependence of thermodiffusion is a purely quantum phenomenon that vanishes when taking the classical limit  $\hbar \rightarrow 0$  [70]. On the other hand, experiments in gases and liquids [64,68], numerical simulations [67], and theory [69] concur to the conclusion that the mass dependence of thermodiffusion is essentially a classical effect.

## 7. Discussion and summary

### 7.1. Range of validity of Eastman's approach

Eq. (12) shows that for small particles the approach based on Onsager's non-equilibrium thermodynamics reduces to a thermostatic expression for the Soret coefficient. This has been traced back to the fact that drift and diffusion of small particles lead to rather similar velocity fields  $\mathbf{v}_T$  and  $\mathbf{v}_D$  [40,48] and thus carry the same friction factor. The latter drops out in the steady state, and  $S_T$  is determined by the solvation enthalpy  $H$ . For large particles, on the contrary,  $\mathbf{v}_T$  and  $\mathbf{v}_D$  have little in common. Thus it does not come as a surprise that the transport coefficients differ in their viscous factors and, as a consequence, in their dependence on the particle radius,  $D \propto 1/R$  and constant  $D_T$ . From a general transport theory point of view, this analysis parallels what is known for electrophoresis, where our Eqs. (11) and (13) correspond to the Hückel and Smoluchowski limits [39].

These considerations are supported by experimental findings. Most data on colloidal particles [20,22–24] confirm the linear dependence  $S_T \propto R$  of (15), whereas Eastman's expression (2) predicts a variation with the surface area  $S_T \propto R^2$ . By the same token, Eastman's equilibrium approach fails when applied to polymers.

The free enthalpy of a polymer chain increases with the number  $N$  of monomers and would result in  $S_T \propto N$  according to (2). Soret data on dilute polystyrene solutions, however, vary with the gyration radius  $R \propto N^\nu$  where  $\nu \approx 0.6$  in a good solvent [47], in agreement with Brochard and de Gennes' general argument [71], which is defined in our Eq. (15). The law  $S_T \propto R$  provides an unambiguous signature for dissipative motion: The thermophoretic mobility  $D_T$  of polymers is constant because of the associated short-range viscous flow, whereas the dependence  $D \propto 1/R$  arises from long-range hydrodynamic interactions.

### 7.2. Binary mixtures

The cases where the range of interaction  $\lambda$  is much smaller or much larger than the solute size  $R$ , can be treated in controlled approximations.

A more difficult situation arises for molecular mixtures with dispersion forces, where both length scales are comparable. Though none of the approximation schemes apply in this case, the relation  $\lambda \sim R$  suggests that the thermostatic approach does not in general provide a reliable expression for the Soret coefficient. One may expect that Eq. (28) describes, at least qualitatively, the variation with the composition and the molecular size ratio. Regarding the isotope effect, purely thermostatic theories do not account for the mass dependence [67].

### 7.3. Is Soret equilibrium an equilibrium effect?

We have seen that for small solute particles, the Einstein and thermodiffusion coefficients  $D$  and  $D_T$  carry the same mobility factor, such that the ratio  $D_T/D$  reduces to an equilibrium quantity. The physical origin of this cancellation of viscous factors, however, is less fundamental than the microscopic reversibility that operates in Thomson's relation  $\Pi/S = T$  for the Peltier and Seebeck coefficients, or in the reciprocal law relating  $D_T$  and the Dufour coefficient [1].

As a main result of this paper we have shown that a non-uniform solute concentration in a temperature gradient implies necessarily dissipation due to viscous flow  $\mathbf{v}(\mathbf{r})$  in the vicinity of each solute particle, as illustrated in Fig. 2(c). Diffusion and thermophoretic particle currents in (3) cancel each other, whereas the corresponding velocity fields  $\mathbf{v}_T + \mathbf{v}_D$  do not, thus resulting in a steady entropy increase  $\dot{S} > 0$ . Since any equilibrium state is characterized by constant entropy, this means that the Soret coefficient in Eq. (1) is not an equilibrium quantity.

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