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Oded Farago[1,2,a]

[1] Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK
[2] Department of Biomedical Engineering, Ben-Gurion University of the Negev, Be'er Sheva 85105, Israel

Abstract. The application of a temperature gradient along a fluid-solid interface generates stresses in the fluid causing "thermo-osmotic" flow. Much of the understanding of this phenomenon is based on Derjaguin's work relating thermo-osmotic flows to the mechano-caloric effect, namely, the interfacial heat flow induced by a pressure gradient. This is done by using Onsager's reciprocity relationship for the equivalence of the thermo-osmotic and mechano-caloric cross-term transport coefficients. Both Derjaguin theory and Onsager framework for out-of-equilibrium systems are formulated in macroscopic thermodynamics terms and lack a clear interpretation at the molecular level. Here, we use statistical-mechanical tools to derive expressions for the transport cross-coefficients and, thereby, to directly demonstrate their equality. This is done for two basic models: i) an incompressible continuum solvent containing non-interacting solute particles, and ii) a single-component fluid without thermal expansivity. The derivation of the mechano-caloric coefficient appears to be remarkably simple, and provides a simple interpretation for the connection between interfacial heat and particle fluxes. We use this interpretation to consider yet another example, which is an electrolyte interacting with a uniformly charged surface in the strong screening (Debye-Hückel) regime.

1 Introduction

Osmotic flows occur when complex fluids are subject of various thermodynamic gradients [1]. Examples include electro-osmosis (flow induced by an gradient of an electric potential) [2], diffusio-osmosis (solute concentration gradient) [3], and thermo-osmosis (temperature gradient) [4]. Osmotic flows are interfacial phenomena arising from stresses induced by the thermodynamics gradients in a microscopic boundary region, where the properties of the fluid are influenced by the interactions with the surface [5]. Osmotic effects are used to manipulate flows in in microfluidic configurations [6], and in water treatment and desalination processes [7]. Osmosis is also one of the fundamental transport mechanisms in biological cells [8].

Here, we focus on the process of thermo-osmosis which was first observed in 1907 by Lippmann who measured the flow of water across a gelatin membrane separating two reservoirs maintained at different temperatures [9]. Contemporary theoretical understanding of this phenomenon is largely based on Derjaguin's work (see Chapt. 11 in ref. [5]) who used Onsager's linear non-equilibrium thermodynamics (LNET) [10,11] to relate the thermo-osmotic

slip to the fluid-surface interaction enthalpy (excess enthalpy). Explicitly, Onsager's phenomenological theory expresses the heat and material fluxes of a complex fluid as linear combinations of the applied temperature and pressure gradients. From general considerations (to be reviewed below), the cross-terms of the transport matrix, namely the thermo-osmotic coefficient describing surface-induced flow under a temperature gradient ∇T and the mechano-caloric coefficient describing heat flux due to a pressure gradient ∇P, must be equal to each other.

Application of the theory requires some dynamical model for the relevant variables. In [5], Derjaguin considered a simple liquid and calculated the slip velocity from the interfacial thermo-osmotic flow using the Navier-Stokes (NS) hydrodynamic equation. A simple analytical expression for the slip velocity can be obtained by assuming no-slip boundary conditions at the surface, and by ignoring the variations in the viscosity of the fluid due to the interactions with the surface. Further assuming that the boundary layer is much smaller than the size of the "flow chamber", then a linear approximation can be used for the flow field, leading to Derjaguin's formula for the slip velocity [5]

$$v_s = -\left[\frac{1}{\eta}\int_0^\infty z\Delta h(z)\mathrm{d}z\right]\frac{\nabla T}{T}, \tag{1}$$

[a] e-mail: ofarago@bgu.ac.il

where z is the perpendicular distance from the surface, $\Delta h(z)$ is the excess enthalpy density, and η is the fluid viscosity. Equation (1) has been recently used to measure the thermo-osmotic slip experimentally [12] and in computer simulations [13].

Onsager's reciprocity principle is derived based on the general assumption of microscopic reversibility and does not involve hydrodynamic considerations [14]. The theory is not limited to thermo-osmosis but applies to a large class of transport phenomena, and it does not address examples of specific molecular systems. Here we present a complementary statistical-mechanical approach and consider thermo-osmosis in two fundamental models: i) solvent-solute mixtures, and ii) a single-component fluid. In each model we derive expressions that explicitly relate the thermo-osmotic and mechano-caloric coefficients to equilibrium properties of the model systems. As expected, the derived expressions are identical to each other, which provides a direct demonstration of Onsager's principle. In the former example of a solvent-solute mixture, the solvent is treated as an incompressible stuctureless fluid, which facilitates the calculation of the interfacial stress [15]. It is, however, clear that the excess enthalpy originates from the solute-surface rather than the solvent-surface interactions. Therefore, in the calculation of the transport cross-coefficients, the solute flux must be considered, which is not captured by the NS hydrodynamic equation but rather by a Smoluchowski diffusion equation.

Related to the above last point, we wish to emphasize that the focus on this paper is on the equality of Onsager's transport cross-coefficients, which is the basis for Derjaguin's theory of thermo-osmosis. Accordingly, the paper is organized as follows: in sect. 2 we provide a simple derivation of this fundamental result, which is based on general thermodynamic considerations. Then we use statistical-mechanical tools to derive explicitly expressions for the transport cross-coefficients, thereby demonstrating their equality, in two basic models —the solvent-solute mixtures (sect. 3), and a single-component fluid (sect. 4). We summarize the main results in sect. 5, where we briefly discuss another example of an electrolyte solution. The statistical-mechanical derivations involve some basic assumptions, most importantly, the concept of local thermal equilibrium. At the molecular level, this means that when the particles move across a temperature gradient, their velocity distribution quickly adopts to the local temperature and, therefore, their dynamics must be non-inertial. Following from this assumption is the fact that the temporal evolution of the mass and surface heat energy densities can be described by corresponding diffusion equations, and that in a steady state, the divergences of the relevant currents vanish. The very same basic assumptions have been recently used by Anzini *et al.* to develop a field-theoretical approach for thermo-osmosis [16]. However, the focus on that work was not on the Onsager's cross-coefficients, but on the fluid slip velocity (1), which is a different part of Derjaguin's theory that requires taking into account hydrodynamic considerations (liquids) or kinetic theories (gases). Our approach, in contrast, is purely

statistical mechanics and, therefore, we only briefly discuss the hydrodynamic aspects of Derjaguin's theory in appendix A. A key point in the statistical-mechanical approach presented herein is the assumption that Einstein's relation between the mobility, temperature, and diffusion coefficient, holds at the local level, which is consistent with the local equilibrium picture. In this approach, the hydrodynamic or kinetic behavior of a specific system are implicitly accounted by the local mobility of the transported particles.

2 Onsager-Derjaguin formulation

Consider a thin slab of width dx and cross-sectional area $L_y \times L_z$, which is sufficiently large to be treated as a macroscopic thermodynamic system. Along the x-direction, the system is coupled to two thermodynamic reservoirs with slightly different temperatures (T and $T + \Delta T$) and chemical potentials (μ and $\mu + \Delta \mu$). The temperature and chemical potential gradients cause steady-state heat, J_Q, and particle, J_N, currents to flow throughout the slab. These currents from one reservoir to the other generate entropy, and from the fundamental thermodynamic equation for the differential change in the entropy, $dS = dU/T + dV(P/T) - dN(\mu/T)$, it follows that the rate of net entropy production, $\dot{S}$, is equal to

$$\dot{S} = J_Q \Delta \left(\frac{1}{T}\right) - J_N \Delta \left(\frac{\mu}{T}\right). \tag{2}$$

We note that the three intensive thermodynamic variables (T, P, and μ) are not mutually independent. Thus, $\mu = \mu(T, P)$, and in terms of the temperature and pressure gradient ΔP, eq. (2) reads

$$\dot{S} = J_Q \Delta \left(\frac{1}{T}\right) - J_N \left[\frac{\partial}{\partial T}\left(\frac{\mu}{T}\right)_P \Delta T + \frac{\partial}{\partial P}\left(\frac{\mu}{T}\right)_T \Delta P\right]. \tag{3}$$

From the Gibbs-Helmholtz relation we have that $\partial(\mu/T)/\partial T|_P = -H/NT^2$, where H is the enthalpy. Also, $\mu = G/N$, where G is the Gibbs free energy and, therefore, $\partial(\mu/T)/\partial P|_T = (V/NT)$. Using these relations in eq. (3), leads to the following form:

$$\dot{S} = (-J_Q + J_H)\frac{\Delta T}{T^2} + J_V \frac{\Delta P}{T}, \tag{4}$$

where $J_H = J_N H/N$ is the enthalpy current, and $J_V = J_N V/N = J_N/\rho$ is the volume material current. Importantly, while the current J_Q represents the flow of internal energy arising from the intramolecular forces between the constituent particles, the current J_H describes the total enthalpy flow. Thus, the difference between them is the excess enthalpy current associated with the interactions of the particles with the surfaces that bound the system. Denoting the excess enthalpy current by $J_{H_s} = J_H - J_Q$, we arrive at Derjaguin's formula for the rate of entropy production, $\dot{Q} \equiv T\dot{S}$ [5]

$$\dot{Q} = \left[J_{H_s}\frac{T'}{T} + J_V P'\right]dx. \tag{5}$$

For consistency with forthcoming calculations, let us assume that the particles interact only with the surfaces that bound the system in the z-direction, but not in the y-direction. Rather than dealing with extensive thermodynamic quantities, we can divide eq. (5) by $VL_y = \mathrm{d}xL_y^2L_z$ and consider the entropy density (per unit volume) production, per unit length in the y-direction

$$\frac{\dot{\mathcal{Q}}}{\mathrm{d}xL_y^2L_z} \equiv \dot{\mathcal{R}} = j_h\frac{T'}{T} + j_nP', \qquad (6)$$

where j_h and j_n denote, respectively, the excess enthalpy density and particle fluxes, per unit length.

The Onsager reciprocity relation can be now obtained following a simple route [17]. We write the phenomenological linear relation between the fluxes j_h and j_n, and the thermodynamic forces, T'/T and P',

$$\begin{bmatrix} j_h \\ j_n \end{bmatrix} = \begin{bmatrix} L_{hh} & L_{hn} \\ L_{nh} & L_{nn} \end{bmatrix} \begin{bmatrix} \dfrac{T'}{T} \\ P' \end{bmatrix}. \qquad (7)$$

Then, from eqs. (6) and (7) we conclude that

$$L_{hn} = \frac{\partial j_h}{\partial P'} = \frac{\partial^2 \dot{\mathcal{R}}}{\partial P' \partial(T'/T)} = \frac{\partial j_n}{\partial(T'/T)} = L_{nh}, \qquad (8)$$

which is the Onsager relation relevant to thermo-osmosis. Note that in the notation of fluxes per unit length, the cross-coefficient $L_{hn} = L_{nh}$ have units of frequency (inverse time).

3 Solvent-solute systems

Osmotic flows have been frequently studied within the context of liquids containing solute molecules, *e.g.*, polymer suspensions or ionic solutions. In many theoretical studies the solvent is treated as an incompressible medium, while the solute is often assumed to be at low concentration and considered as a gas of particles interacting with the surface but not with each other. Much of this framework has been put forward by Anderson *et al.* in their 1982 paper on diffusophoresis of colloids in non-electrolytes [18]. The largely accepted picture is that the solute interactions with the surface of the colloid lead to an osmotic pressure difference in the solvent due to the preferential (or dispreferential) adsorption of solute particles. Application of a temperature (or a chemical potential) gradient would then generate an asymmetric distribution of solute around the colloid and, thus, a pressure gradient which, in turn, drives a tangential flow of the solvent. Treating the solvent as an incompressible liquid with constant viscosity allows one to calculate the thermo-osmotic force exerted on the surface via the NS equation (see below). In this picture, however, the solvent has no influence on the non-equilibrium thermodynamics of the system and, specifically, on the Onsager transport coefficients. These must be calculated from the fluxes of the solute particles rather than the flow velocity of the solvent. We now derive expressions for the cross-coefficients L_{hn} and L_{nh}, relating them to equilibrium properties of the solute. The derived expressions demonstrate that, indeed, $L_{hn} = L_{nh}$.

We consider a semi-infinite system which is bound at $z = 0$ by a surface, with which the solute particles interact via a short-range interaction potential $u(z)$. We further assume that the concentration of solute particles, c, is low and, thus, ignore their interactions with each other. Denoting by c_0 the bulk concentration at $z \to \infty$, the equilibrium concentration at constant temperature T_0 is given by

$$c(z) = c_0 e^{-u(z)/k_BT_0}, \qquad (9)$$

where k_B is Boltzmann's constant. We now wish to calculate the mechano-caloric and thermo-osmotic Onsager coefficients, and demonstrate their equivalence. In the following derivations, we will use two commonly made approximations: The first one, which has also been used in Anderson's framework ref. [18], is that the Péclet number is small. This means that the term associated with the solvent velocity field relative to the solute particles can be ignored in the expression for the solute current. The second one is the local thermal equilibrium (LTE) approximation that underlies the classical thermodynamic approach to the problem. In this approximation, the concentration at (x, z) is given by eq. (9) with $T = T(x)$: $c(x, z) = c_0(T(x)) \exp[-u(z)/k_BT(x)]$. This local equilibrium distribution is not affected by the application of a pressure gradient that causes the particles to flow, but at a rate which is assumed to be sufficiently low such that they quickly adopt to the local temperature.

We begin with the calculation of the mechano-caloric coefficient by assuming constant temperature $T(x) = T_0$ and a small uniform pressure gradient along the x-direction: $P(x) = P_0 + P'x$. The application of a small external pressure gradient, $P(x) = P_0 + P'x$ generates a constant flux of solute particles which is equal to $\boldsymbol{j}_n = -\mu_0P'\hat{x}$, where μ_0 is the mobility of the solute particles. The excess heat flow is associated with the interfacial interaction energy that the moving particles carry. Thus, the excess heat (enthalpy) density flux at distance z from the surface is then given by $\boldsymbol{j}_h(z) = u(z)c(z)\boldsymbol{j}_n = -u(z)c(z)\mu_0P'\hat{x}$. The total heat flux per unit length is obtained by integration $\boldsymbol{j}_h = \int_0^\infty \boldsymbol{j}_h(z)\mathrm{d}z$, and by comparison with eq. (7), we conclude that

$$L_{hn} = -\mu_0c_0\int_0^\infty u(z)e^{-u(z)/k_BT_0}\mathrm{d}z. \qquad (10)$$

The calculation of the thermo-osmotic coefficient L_{nh} is more complicated. It begins with the assumptions that the system is driven out of equilibrium by the application of a small temperature gradient, $T(x) = T_0 + T'x$, while the pressure is maintained uniform. The solute flux per unit volume is now given by

$$\boldsymbol{j}_n = -\mu_0\{\boldsymbol{\nabla}[k_BT(x)c(x, z)] + c(x, z)\boldsymbol{\nabla}u\}, \qquad (11)$$

where the first term takes into account the fact that the diffusion coefficient $D(x) = \mu_0k_BT(x)$ depends on the co-

ordinate x. The steady-state flux can be found by solving the equation

$$\boldsymbol{\nabla} \cdot \boldsymbol{j}_n = 0, \qquad (12)$$

subject to the boundary condition at $z \to \infty$ that $c(x)T(x) = c_0 T_0$. This condition expresses the fact that the bulk osmotic pressure of the solute, which is treated as an ideal gas of non-interacting particles, must be uniform [19,20]. Thus, far away from the surface, $c(x, z \to \infty) = c_0 T_0 / T(x)$ which, to linear order in T', can be also written as

$$c(x, z \to \infty) \simeq c_0 \left[1 - \frac{T'x}{T_0} \right]. \qquad (13)$$

The non-uniform bulk concentration is a manifestation of the Soret effect (see extensive review in [21]). Typically, the dominant contribution to this effect arises from the inter-molecular forces. These generate effective mechanical thermophoretic forces on the molecules that distort their distribution either in the direction or opposite to the temperature gradient. In this section we consider an ideal gas of solute particles and, therefore, the only contribution to the Soret effect is the, so called, ideal gas term arising from the random thermal collisions whose strength grows with the local temperature (see discussion in [19,20]). This is the reason for the absence of a thermophoretic force term in eq. (11).

Obviously, in the absence of a temperature gradient $(T(x) = T_0)$ the solution of eq. (12) is the equilibrium distribution (9). Under the influence of a small temperature gradient, the solution assumes the form: $c(x, z) = c_0 e^{-u(z)/k_B T_0} + c_1(x, z)$, where the perturbation, c_1, is, to leading order, linear in the temperature gradient: $c_1 \sim T'$. Substituting this form of the solution in the steady-state eq. (12) and keeping only linear terms in T', leads to the following equation for $c_1(x, z)$:

$$k_B T_0 \nabla^2 c_1 + \frac{\partial c_1}{\partial z} u'(z) + c_1 u''(z) =$$
$$-k_B T' x c_0 \left[-\frac{u''(z)}{k_B T_0} + \left(\frac{u'(z)}{k_B T_0} \right)^2 \right] e^{-u(z)/k_B T_0}. \qquad (14)$$

Attempting a solution of the form

$$c_1 = c_0 (T'x/T_0) f(z) e^{-u(x)/k_B T_0}$$

in (14), yields the following equation for the unknown function $f(z)$:

$$f'' - f' \frac{u'}{k_B T_0} = \frac{u''}{k_B T_0} - \left(\frac{u'}{k_B T_0} \right)^2. \qquad (15)$$

The solution of this equation is $f = u/k_B T_0 + A$, and from the boundary condition (13) we find that $A = -1$, such that (to linear order in T')

$$c \simeq c_0 \left[1 - \frac{T'x}{T_0} \left(1 - \frac{u(z)}{k_B T_0} \right) \right] e^{-u(z)/k_B T_0}. \qquad (16)$$

Substituting this expression for the solute concentration in (11) yields the solute flux. We find that the z-component is quadratically small in the temperature gradient: $\boldsymbol{j}_n \cdot \hat{z} \sim (T')^2$. For the x component, we have

$$j_n(z) = -\left(\frac{T'}{T_0} \right) \mu_0 c_0 u(z) e^{-u(z)/k_B T_0} \hat{x} + \mathcal{O}\left[(T')^2 \right]. \qquad (17)$$

The total solute flux (per unit length) is obtained by integration, $j_n = \int_0^\infty j_n(z) \mathrm{d}z$, and by comparing with eq. (7), we arrive at

$$L_{nh} = -\mu_0 c_0 \int_0^\infty u(z) e^{-u(z)/k_B T_0} \mathrm{d}z, \qquad (18)$$

which is equal to L_{hn} in eq. (10).

4 One-component simple fluids

The identical expressions (10) and (18), derived in the previous section for the transport cross-coefficients, vanish when the concentration of solute $c_0 = 0$. This, however, does not mean that thermo-osmosis does not exist in pure liquids. We recall that within the model considered above, the solvent was treated as a structureless medium in which the solute particles are suspended. There is no wonder, therefore, that the limit $c_0 \to 0$ yields no thermo-osmotic effect. In order to study thermo-osmosis in a pure fluid we must take its molecular structure into account, as done in the following section.

Let us consider a setup similar to the one in sect. 3, namely a semi-infinite system with a surface at $z = 0$, but this time containing a simple fluid consisting of a single type of spherical particle. As in the previous section, we denote the (short-range) interaction between the particles and the surface by $u(z)$. Let us denote the bulk density of the particles (at $z \to \infty$) by ρ_0, and in what follows we will neglect the thermal expansivity of the fluid, *i.e.*, assume that ρ_0 is independent of T within the relevant temperature range. The latter assumption is an approximation which is essential for allowing a simple derivation of analytical expressions for the Onsager cross-coefficients. At a given thermodynamic state ($T(x)$ and $P(x)$, within a thin slab), the excess surface enthalpy is the change in the system energy arising from the presence of the surface. This includes two contributions: i) direct interactions between the particles and the surface which are represented by the potential energy $u(z)$, and ii) the change in the particle-particle interaction energy resulting from the variations in the local density of the fluid *that are due to the particles-surface interactions.* The latter contribution must be calculated in a statistical manner, *i.e.* by averaging over all the particles configurations with the Boltzmann statistical weights of the isobaric-isothermal ensemble. Taken together, the "effective" surface energy per particle can be represented by a potential of mean force (PMF), $\phi(z)$, which is related to the local density by

$$\rho(z) = \rho_0 e^{-\phi(z)/k_B T(x)}. \qquad (19)$$

The last equation (19) invokes the LTE approximation (see discussion in sect. 3).

A subtle, yet important, point to mention is that in principle the PMF depends on the local density and temperature, but the approximation that the fluid has no thermal expansion implies a temperature-independent PMF. This can be understood from the following argument: The lack of thermal expansivity means that the density of the bulk fluid is insensitive to the temperature. This is an ideal situation in which a small change in the temperature causes changes in the intramolecular interactions energy and entropy that exactly cancel each other. The fact that the fluid has no thermal expansivity does not mean that the density is uniform throughout the *entire system* (as, otherwise, there will be no thermo-osmotic effect). Variations in the local density are encountered at the interfacial layer as a result of surface interactions (direct and indirect) that are fully accounted for by eq. (19) that defines the PMF. This form represents a mechanical balance between the average mechanical forces experienced by particles within a thin layer of width dz ($z < z' < z + dz$) and the thermal forces associated with the mixing entropy of the non-uniform distribution in the layer. In the absence of thermal expansivity, no other thermal effects need to be considered, which means that $\phi(z)$ (just like ρ_0), has no temperature dependence.

With the above considerations in mind, we now wish to calculate the thermo-osmotic and the mechano-caloric Onsager coefficients, and demonstrate their equivalence. The former is calculated by assuming that the temperature along the x-direction (parallel to surface) is given by $T(x) = T_0 + T'x$, and that the pressure is uniform. Similarly to the case studied in sect. 3, the particle flux in the z direcron vanishes to linear order in T'. The particle flux per unit volume in the x-direction is given by $\boldsymbol{j}_n \cdot \hat{x} = -D(x,z)\partial \rho(x,z)/\partial x$, where $D(x,z)$ is a coordinate-dependent Fickian diffusion coefficient. The z-dependence of D arises from the influence of the surface on the (collective) diffusive dynamics of the particles. The x-dependence, on the other hand, arises from the temperature gradient and, therefore, is unimportant if one wishes to calculate the flux j_n *to linear order* in T'. We thus arrive at the following result:

$$\boldsymbol{j}_n(z) = -\hat{x} D(z) \frac{\partial[\rho_0 e^{-\phi(z)/k_B T(x)}]}{\partial x}$$
$$= -\hat{x} \left(\frac{T'}{T_0}\right) \rho_0 D(z) \frac{\phi(z)}{k_B T_0} e^{-\phi(z)/k_B T_0} + \mathcal{O}\left[(T')^2\right].$$
(20)

The total particle flux (per unit length in the y-direction) is obtained by integration: $j_n = \int_0^\infty j_n(z)dz$, and by comparison with eq. (7), we conclude that

$$L_{nh} = -\int_0^\infty \rho_0 D(z) \frac{\phi(z)}{k_B T_0} e^{-\phi(z)/k_B T_0} dz. \quad (21)$$

Before proceeding to the calculation of the mechano-caloric coefficient, L_{hn}, it is important to dwell shortly on the difference between the Fickian diffusion coefficient,

$D(z)$, appearing in the previous paragraph and the diffusion coefficient, D_0, which is related to the solute mobility in sect. 3 via Einstein's relation: $D_0 = \mu_0 k_B T_0$. The latter is a single-particle quantity since each solute particle is treated (in sect. 3) as an independent Brownian particle. Single-particle diffusion, however, is not the same as Fickian (collective, or chemical) diffusion, which is the process relevant to the problem discussed in this section. In single-component fluids the motion of the particles is strongly correlated and, clearly, the particles interact with each other via short-range molecular forces. The confusion between single-particle and Fickian collective diffusion arises because both processes are represented by the same diffusion equation. The former describes the random thermal motion arising from the collisions of a colloidal particle with the molecules of an embedding fluid medium. The later, on the other hand, describes the response of a fluid medium to density inhomogeneities. Of course, in the absence of an external potential, the fluid would relax to uniform distribution, but this occurs via random collisions of the fluid particles with each other.

Furthermore, the application of a linear potential (constant force, F) in the fluid results in an exponential Boltzmann equilibrium distribution if the system is closed. If, one the other hand, the fluid is found in an open system, the force will cause it to flow with a velocity field which is linear in the force:

$$v(z) = \mu(z)F. \quad (22)$$

The coefficient of proportionality in this linear velocity-force relationship (22), $\mu(z)$, is called Fickian mobility. As μ_z is proportional to the velocity field arising from the application of a constant force like a uniform pressure gradient, it essentially characterizes the hydrodynamic response of the system. In the simplest example of a Newtonian Newtonian incompressible fluid with no-slip boundary conditions, $\mu(z)$ has the form of a laminar Poiseuille flow. However, eq. (22) is not limited to this example only, but is a far more general relation that can be assumed whenever the driving force F is sufficiently weak (linear response). It is, therefore, also relevant to other boundary conditions (*e.g.*, slip) and, furthermore, not even limited to the NS continuum description but can be used in molecular models. These models are essential for understanding osmosis in systems where the range of the interaction interfacial regime is of order of several molecular layer [13, 22]. Molecular simulations take into account the variations in the fluid viscosity at the interfacial layer, which are typically ignored when solving the NS equation.

The key point to note now is the fact that $\mu(z)$ is related to the Fickian diffusion coefficient, $D(z)$, via the Nernst-Einstein equation

$$D(z) = \mu(z)k_B T_0. \quad (23)$$

The fact that this relationship takes a similar form to the Einstein relation for single-particle diffusion is not surprising. It follows from the fact that the governing diffusion equations in both cases have the same form (see

discussion and derivation in ref. [23], sect. 11.3). Equation (23) allows us to continue with the calculation of the mechano-caloric coefficient in a fashion similar to the derivation of its counterpart in the solvent-solute case, eq. (10). Thus, we consider a system with constant temperature $T(x) = T_0$ and a small uniform pressure gradient along the x-direction: $P(x) = P_0 + P'x$. The fluid density, $\rho(z)$, is given by eq. (19). The pressure gradient causes a steady-state flow of the fluid, with a local (z-dependent) flux given by $\boldsymbol{j}_n(z) = -\mu(z)P'\hat{x}$. The excess heat flow is associated with the interfacial free energy that the moving particles carry which, by definition, is characterized by the PMF, $\phi(z)$. Thus, the excess heat (enthalpy) density flux is $\boldsymbol{j}_h(z) = -\mu(z)\rho(z)\phi(z)P'\hat{x}$, and by using the Nernst-Einstein relation this result can be also written as

$$\boldsymbol{j}_h(z) = -\hat{x}P'\rho_0 D(z)\frac{\phi(z)}{k_B T_0}e^{-\phi(z)/k_B T_0}. \qquad (24)$$

The heat density flux per unit length in the y-direction is $j_h = \int_0^\infty j_h(z)\mathrm{d}z$, and from eq. (7) we find that

$$L_{hn} = -\int_0^\infty \rho_0 D(z)\frac{\phi(z)}{k_B T_0}e^{-\phi(z)/k_B T_0}\mathrm{d}z, \qquad (25)$$

which is identical to L_{nh} in eq. (21).

5 Discussion and conclusions

Derjaguin theory of thermo-osmosis (material flow resulting from a temperature gradient) is based on Onsager's reciprocity principle relating thermo-osmotic flows to the mechano-caloric effect (heat flux due to a pressure gradient). It is formulated in macroscopic non-equilibrium thermodynamics terms, but its interpretation at the molecular level in not entirely clear. Here, we took such an approach and used statistical-mechanical tools to directly verify the equivalence between the thermo-osmotic and mechano-caloric transport coefficients. We considered two very distinct models: i) an incompressible (structerless) solvent containing non-interacting solute particles, and ii) a single-component fluid without thermal expansivity. While the calculation of the thermo-osmotic coefficient, L_{nh}, was somewhat complicated, the derivation of the mechano-caloric coefficient, L_{hn}, was simple and straightforward. In both cases, it followed the same simple logic recognizing that the excess interfacial heat transport is nothing but the product of the volume material flux arising from the application of a pressure gradient force and the surface interaction free energy of the moving particles. The latter can be associated with the potential of mean force of the surface, which is directly related to the equilibrium distribution of the solute (case model i) and the fluid particles (case model ii). The only difference between expressions (10) and (25) for the cross-coefficients in both cases, is the particle mobility relevant to the situation. In the solvent-solute model, we assumed a constant single-particle mobility, μ_0, since each solute particle was treated as an independent Brownian particle.

We could, in fact, correct this result to account for the particle's hydrophobic interactions with the surface, by using Brenner's theory [24]. In contrast, the mobility in the single-component fluid model, is dominated by the particle-particle interactions and, thus, one has to consider the collective Fickian mobility $\mu(z) = D(z)/k_B T_0$ that, in principle, depends on the fluid density. Thus, the major difficulty in evaluating the transport cross-coefficients in simple fluids is to determine the mobility as a function of the distance from the surface. Derjaguin circumvented this problem by considering the hydrodynamic flow profile rather than the local mobility, but this continuum picture is relevant only when the range of the surface potential energy is much larger than several molecular layers.

We conclude by considering yet another classical example, which is a 1:1 electrolyte such as sodium chloride interacting with a uniformly charged surface. This problem resembles the solvent-solute model discussed in the this paper, with two important differences: First, in the electrolyte problem we have two types of particles (cations and anions) suspended in the solvent (water), rather than one. Second, the ions have Coulomb interactions not only with the charged surface but also with each other. The equilibrium distribution of the ions can be found from the solution of the Poisson-Boltzmann equation. In the Debye-Hückel approximation, the electrostatic potential is exponentially screened by the ions in the diffusive electric double layer [25]

$$\psi(z) = \psi_s e^{-z/\lambda_D}, \qquad (26)$$

where ψ_s is the surface potential, and

$$\lambda_D = \sqrt{\frac{\epsilon k_B T}{2c_0 e^2}} \qquad (27)$$

is the Debye screening length, where ϵ is the water permittivity ($\epsilon \simeq 78\epsilon_0$), and e is the electron charge. The anions and cations distributions, c_- and c_+ respectively, are related to $\psi(z)$ via relations similar to eq. (9):

$$c_\mp(z) = c_0 e^{\pm e\psi(z)/k_B T}. \qquad (28)$$

The excess electrostatic free energy density is given by

$$f_{\mathrm{el}}(z) = \frac{\epsilon}{2}\left(\frac{\mathrm{d}\psi}{\mathrm{d}z}\right)^2 + k_B T \sum_{i=\pm}\left[c_i \ln\left(\frac{c_i}{c_0}\right) - c_i + c_0\right]$$
$$= \frac{\epsilon\psi_s^2 e^{-2z/\lambda_D}}{\lambda_D^2} = 2c_0\frac{(e\psi_s)^2}{k_B T}e^{-2z/\lambda_D}. \qquad (29)$$

In the Debye-Hückel limit ($e\psi_s \ll k_B T$), this electrostatic free energy density can be equally divided between the anions and cations. To leading order, we can assume that their densities in the boundary layer are nearly identical and, thus, the relevant mobility for the transportation of f_{el} under the action of a constant pressure gradient is $(\mu_- + \mu_+)/2$. The mechano-caloric coefficient is thus given

by

$$L_{hn} = \frac{\mu_- + \mu_+}{2} \int_0^\infty f(z) \mathrm{d}z$$
$$= \frac{\mu_- + \mu_+}{2} c_0 \lambda_D \frac{(e\psi_s)^2}{k_B T}. \qquad (30)$$

Notice the unusual dependence on the bulk concentration $L_{hn} \sim c_0 \lambda_D \sim c_0^{1/2}$, which is an manifestation of the collective nature of the screening effect. This is a major difference from the example of non-interacting solute particles discussed in sect. 3, which also complicates the calculation of the thermo-osmotic coefficient L_{nh}. Further complications in the analysis of the thermo-osmotic effect in electrolytes arise from the temperature-dependence of the permitivity of the water [19,26].

Author contribution statement

OF conducted the research and wrote the manuscript.

Appendix A. Hydrodynamic considerations

In sect. 3 we considered the model of an incompressible liquid containing a small concentration of solute molecules. We derived identical expressions (10) and (18) for the cross-coefficients, relating them to equilibrium properties of the solute. The only quantity in these expressions that depends on properties of the solvent is the mobility of the solute-particles which, presumably, also depends on the viscosity, η, of the embedding medium. As already discussed above, Onsager reciprocity establishes a relationship between the mechano-caloric and thermo-osmotic flows, but it does not provide sufficient information from which the thermo-osmotic force on the surface and the slip-velocity can be derived. In order to calculate the latter, one must consider the solvent flow, which is done by invoking the NS equation for the flow of an incompressible fluid with constant viscosity η:

$$\eta \nabla^2 \boldsymbol{v} = \boldsymbol{\nabla} \Pi(x,z) - \boldsymbol{f}_{\text{body}}, \qquad (A.1)$$

where v is the solvent velocity, f_{body} is the body force exerted on a volume element by the solute-surface interactions, and Π is the fluid hydrodynamic pressure, which is not identical to the solute osmotic pressure that enters into the above calculation of Onsager cross-coefficients.

For the completeness of the discussion, we will calculate the slip velocity here by following the hydrodynamic calculation of Anderson [18] for the diffuso-osmotic slip. The basic assumption is that, within the boundary layer, the normal velocity, v_z, is negligible. Therefore, for the z component the NS equation reads

$$\frac{\partial \Pi}{\partial z} = f_{\text{body}}^z = -c(x,z)u'(z)$$
$$= -u'(z)c_0 \left[1 - \frac{T'x}{T_0}\left(1 - \frac{u(z)}{k_B T_0}\right)\right] e^{-u(z)/k_B T_0}, \qquad (A.2)$$

where eq. (16) for the solute concentration has been used in the last equality of eq. (A.2). This non-linear equation has no simple analytic solution, except in the limit of a weak interaction potential $u(z)/k_B T_0 \ll 1$, in which case the equation simplifies to $\partial_z \Pi = k_B T_0 C_0 (1 - T'x/T_0)\partial_z[\exp(-u/k_B T_0)]$ and, thus,

$$\Pi(x,z) = k_B T_0 c_0 \left[1 - \frac{T'x}{T_0}\right] e^{-u(z)/k_B T_0} + \Pi_0(x). \quad (A.3)$$

From this result, we identify $\Pi_0(x)$ as the difference between the hydrodynamic and osmotic pressures. This component can be found by invoking the requirement that the bulk hydrodynamic pressure away from the surface becomes uniform. Thus, $\Pi_0(x) = -k_B T_0 c_0 (1 - T'x/T_0) + \Pi_0$, and the hydrodynamic pressure is given by

$$\Pi(x,z) = k_B T_0 c_0 \left(1 - \frac{T'x}{T_0}\right)\left[e^{-u(z)/k_B T_0} - 1\right] + \Pi_0, \qquad (A.4)$$

where Π_0 is an unimportant constant.

In order to find the interfacial shear stress, we return to the NS equation for the x component. Here, we assume that v_x varies much more rapidly along the normal z-direction than parallel to the surface in the x-direction. Thus, $\nabla^2 v_x \simeq \partial^2 v_x/\partial z^2$, and considering that $f_{\text{body}}^x = 0$ (since the surface forces on the solute particles are in the z-direction), the NS equation for v_x (A.1) reads

$$\eta \frac{\partial^2 v_x}{\partial z^2} = \frac{\partial \Pi}{\partial x} = -- k_B T' c_0 \left(e^{-u(z)/k_B T_0} - 1\right). \quad (A.5)$$

The shear stress, σ_{xy}, is then found by integrating eq. (A.5) with respect to z

$$\sigma_{xz}(z) = \eta \frac{\partial v_x}{\partial z} = k_B T' c_0 \int_z^\infty \left(e^{-u(z')/k_B T_0} - 1\right) \mathrm{d}z', \qquad (A.6)$$

where the integration constant was determined such that $\sigma_{xz}(z \to \infty) = 0$. The thermo-osmotic force per unit surface area, $\sigma_{\text{t-o}}$, is nothing but the shear stress evaluated at $z = 0$:

$$\sigma_{\text{t-o}} = k_B T' c_0 \int_0^\infty \left(e^{-u(z)/k_B T_0} - 1\right) \mathrm{d}z. \qquad (A.7)$$

Remarkably, it is expressed as a function of only equilibrium properties of the solute, and has no dependence on

the solvent viscosity or the type of boundary conditions (slip/stick) assumed for the fluid flow. The fluid velocity profile, $v_x(z)$, can be obtained by a second integration of eq. (A.5):

$$v_x(z) = \frac{k_B T' c_0}{\eta} \int_0^z \mathrm{d}z' \int_{z'}^\infty \left(e^{-u(z'')/k_B T_0} - 1 \right) \mathrm{d}z'',$$
(A.8)

and the integration constant, in this case, was set to satisfy no-slip boundary conditions: $v_x(z=0) = 0$.

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