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Thermal Forces from a Microscopic Perspective

Pietro Anzini, Gaia Maria Colombo, Zeno Filiberti, and Alberto Parola[*]
Dipartimento di Scienza e Alta Tecnologia, Università degli Studi dell'Insubria, Via Valleggio 11, 22100 Como, Italy

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Thermal gradients lead to macroscopic fluid motion if a confining surface is present along the gradient. This fundamental nonequilibrium effect, known as thermo-osmosis, is held responsible for particle thermophoresis in colloidal suspensions. A unified approach for thermo-osmosis in liquids and in gases is still lacking. Linear response theory is generalized to inhomogeneous systems, leading to an exact microscopic theory for the thermo-osmotic flow, showing that the effect originates from two independent physical mechanisms, playing different roles in the gas and liquid phases, reducing to known expressions in the appropriate limits.

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When a uniform bulk fluid is placed in a thermal gradient, mechanical equilibrium quickly sets in via the force balance condition, implying constant pressure throughout the system. In the absence of external forces, the steady state is characterized by a space dependent density profile and a constant heat flux not associated with mass current [1]. The action of a thermal gradient on a fluid then resembles the effect of a fictitious "thermal force" [2], which has been known to play also a *dynamic* role since the first studies in gases [3]. The onset of a stationary fluid flow induced by temperature gradients (in the absence of symmetry breaking forces like gravity, when convection dominates) is named "thermo-osmosis" [10] and only occurs due to the presence of a confining surface parallel to the thermal gradient, as already pointed out both in gases [5–7] and in liquids [11–13]. Thermo-osmosis is believed to be the driving mechanism for thermophoresis, i.e., the motion of a colloidal particle in a solvent due to a temperature gradient [14–16], where the slip of the fluid in the boundary layer close to the particle's surface gives rise to momentum transfer and eventually to particle motion. Thermo-osmosis is therefore one of the most fundamental manifestations of thermal forces and its physical origin is deeply rooted in nonequilibrium statistical mechanics. At the same time, it is of great interest for applications as a mechanism for governing a particle's motion at the nanoscale [17,18].

A unified description of thermo-osmosis is still lacking. The phenomenon was theoretically investigated mainly in the gas phase, where the fluid moves from the cold to the hot side and the characteristic length scale is of the order of the molecular mean free path [19]. The kinetic theory of gases has been used in this framework since the seminal work by Maxwell [7], who showed that the thermal creep is due to the tangential stress exerted by the gas on the fixed confining surface in the direction opposite of the temperature gradient. Such a stress, however, requires some exchange of energy and tangential momentum in the wall-particle scattering process and therefore depends on the modeling of fluid-surface interactions. Thermo-osmosis in the liquid regime is considerably less studied, both theoretically [13,20–22] and experimentally [13,23–25]. In addition, as shown in a recent review [26], experiments often disagree even about the direction of the thermo-osmotic flow. Nonequilibrium irreversible thermodynamics, based on the concept of local thermal equilibrium, was first used by Derjaguin *et al.* to relate the thermo-osmotic velocity in liquids to the change of the local enthalpy of the fluid near the confining surface [13,27]. Then, according to this macroscopic approach, the physical origin of the fluid motion is due to the modification in the local thermodynamic properties of the fluid induced by the presence of a wall, as pointed out in Refs. [28,29]. Clearly, in the rarefied limit, which Derjaguin *et al.* do not consider, the argument must fail because the effects of a hard wall on the (local) equilibrium properties of the gas disappear at low density. Only recently have numerical simulations directly tackled this subtle nonequilibrium problem in the liquid regime [30–35], but a clear numerical evidence of the correctness of the Derjaguin formula has not been established yet. Rather, in Ref. [32] it was pointed out that the Derjaguin expression cannot be correct because neither the enthalpy density nor the tangential pressure close to a surface is well defined on microscopic grounds.

This unsatisfactory setting calls for a first principle approach to the phenomenon, able to quantitatively evaluate the extent of the thermo-osmotic slip in terms of well-defined properties of the fluid, which can be measured in experiments and calculated in numerical simulations. In this Letter, we present a microscopic description of thermo-osmosis on the basis of statistical physics: linear response theory generalized to inhomogeneous and anisotropic environments. In the case of an imposed uniform thermal gradient, the use of conservation laws allow us to evaluate the velocity profile of the fluid and the thermo-osmotic slip in terms of both the static and the dynamic equilibrium properties of the fluid near the surface. In the appropriate limits the well-known expressions obtained within kinetic theory and nonequilibrium thermodynamics (Derjaguin) are recovered by retaining each of these terms, showing that the gas and liquid regimes are indeed governed by different physical mechanisms.

The Green-Kubo formalism for linear response theory [36,37] was generalized by Mori to deal with the thermal transport coefficients [38,39]. The starting point, as in the nonequilibrium thermodynamics framework, is the concept of local equilibrium (LE) mathematically defined by the many-body distribution function

$$F^{\mathrm{LE}} = \mathcal{Q}^{-1} e^{-\int d\boldsymbol{r}\beta(\boldsymbol{r})\hat{\mathcal{E}}(\boldsymbol{r})}, \tag{1}$$

where $\mathcal{Q}$ is the partition function and the local energy density $\hat{\mathcal{E}}(\boldsymbol{r})$ is expressed in terms of the conserved densities as

$$\hat{\mathcal{E}}(\boldsymbol{r}) = \hat{\mathcal{H}}(\boldsymbol{r}) - \boldsymbol{u}(\boldsymbol{r}) \cdot \hat{\boldsymbol{j}}(\boldsymbol{r}) - \mu(\boldsymbol{r})\hat{\rho}(\boldsymbol{r}).$$

Here $\beta(\boldsymbol{r})$, $\boldsymbol{u}(\boldsymbol{r})$, and $\mu(\boldsymbol{r})$ are external fields governing the temperature profile, the fluid velocity, and the local chemical potential blue (per unit mass), respectively. $\hat{\mathcal{H}}(\boldsymbol{r})$ is the microscopic many-body Hamiltonian density

$$\hat{\mathcal{H}}(\boldsymbol{r}) = \sum_i \delta(\boldsymbol{q}_i - \boldsymbol{r})\left(\frac{p_i^2}{2m} + \frac{1}{2}\sum_{j(\neq i)} v(|\boldsymbol{q}_i - \boldsymbol{q}_j|) + V(\boldsymbol{q}_i)\right), \tag{2}$$

which describes a system of interacting point particles of mass m confined by hard walls represented by the external potential $V(\boldsymbol{r})$. The operators

$$\hat{\rho}(\boldsymbol{r}) = m\sum_i \delta(\boldsymbol{q}_i - \boldsymbol{r}),$$
$$\hat{j}^{\alpha}(\boldsymbol{r}) = \sum_i \delta(\boldsymbol{q}_i - \boldsymbol{r}) p_i^{\alpha} \tag{3}$$

define the local mass and momentum densities, which, together with the Hamiltonian density $\hat{\mathcal{H}}(\boldsymbol{r})$ introduced in Eq. (2), satisfy microscopic conservation equations of the general form

$$\frac{d\hat{A}(\boldsymbol{r})}{dt} + \partial_{\alpha}\hat{J}^{\alpha}_{A}(\boldsymbol{r}) = 0, \tag{4}$$

where $\hat{A}(\boldsymbol{r})$ is the conserved density, and $\hat{J}^{\alpha}_{A}(\boldsymbol{r})$ is the corresponding current operator. Here and in the following, Greek indices represent spatial components of vectors and tensors and Einstein summation convention is understood. In our case $\hat{J}^{\alpha}_{A}(\boldsymbol{r})$ represents the mass current $\hat{j}^{\alpha}_{\rho}(\boldsymbol{r})$, the momentum $\hat{J}^{\alpha\gamma}_{j}(\boldsymbol{r})$, and the energy flux $\hat{J}^{\alpha}_{\mathcal{H}}(\boldsymbol{r})$, respectively. The explicit expressions for the current operators in terms of the coordinates and momenta of the particles [40] are reported in the Supplemental Material [43].

The previously defined local equilibrium distribution function (1) is not a solution of the Liouville equation and therefore it cannot describe a stationary state. Even if the system is initially set in a LE state, its distribution function changes in time in order to reach full thermodynamic equilibrium. External constraints may, however, keep the system out of equilibrium, for instance, by enforcing different temperatures at the boundaries, leading instead to a nonequilibrium stationary state characterized by constant fluxes of particles and/or energy and momentum. Accordingly, F^{LE} cannot be used to evaluate averages in the resulting stationary state, rather we have to include a correction term coming from the ensuing dynamics. It is precisely such a contribution that defines the microscopic expressions of the standard transport coefficients [37,39,52]. Within linear response theory, the formal expression of the distribution function is known and reads

$$F = F^{\mathrm{LE}} + F^{\mathrm{eq}} \int_0^t dt' \int d\boldsymbol{r}\beta(\boldsymbol{r})[\partial_{\alpha}\hat{J}^{\alpha}_{\mathcal{H}}(\boldsymbol{r},t') - u^{\alpha}(\boldsymbol{r})\partial_{\gamma}\hat{J}^{\alpha\gamma}_{j}(\boldsymbol{r},t') - \mu(\boldsymbol{r})\partial_{\alpha}\hat{j}^{\alpha}_{\rho}(\boldsymbol{r},t')], \tag{5}$$

where F^{eq} is the underlying grand canonical equilibrium distribution function defined by the average value of the (inverse) temperature β and of the chemical potential (per unit mass) μ, and the time dependence of the current operators means that they are evaluated after a time lapse t' from the initial configuration. Averages in the stationary state can be formally evaluated starting from Eq. (5), performing an integration by parts and taking the $t \to \infty$ limit [53]. Here we stress that the dynamic corrections in (5) only involve the divergence of the fluxes introduced in (4) and the resulting physical averages can be evaluated without ambiguity, even if the microscopic definition of the current operators is not unique [40]. For future reference, we report the final result for the momentum density $\langle\hat{\boldsymbol{j}}(\boldsymbol{r})\rangle$ to linear order in the velocity field $\boldsymbol{u}(\boldsymbol{r})$ and in the spatial derivatives of the temperature and the chemical potential

$$\langle\hat{j}^{\alpha}(\boldsymbol{r})\rangle = \langle\hat{j}^{\alpha}(\boldsymbol{r})\rangle_{\mathrm{LE}} + \int_0^{\infty} dt \int d\boldsymbol{r}'[\langle\hat{j}^{\alpha}(\boldsymbol{r},t)\hat{J}^{\gamma}_{\mathcal{H}}(\boldsymbol{r}')\rangle_0\partial_{\gamma}\beta(\boldsymbol{r}') - \langle\hat{j}^{\alpha}(\boldsymbol{r},t)\hat{j}^{\gamma}_{\rho}(\boldsymbol{r}')\rangle_0\partial_{\gamma}[\beta\mu](\boldsymbol{r}') - \langle\hat{j}^{\alpha}(\boldsymbol{r},t)\hat{J}^{\nu\gamma}_{j}(\boldsymbol{r}')\rangle_0\partial_{\gamma}[\beta u^{\nu}](\boldsymbol{r}')]. \tag{6}$$

The averages $\langle\ldots\rangle_0$ have been evaluated by means of the underlying equilibrium distribution F^{eq}, and, to linear order in the velocity field, the LE distribution (1) gives $\langle\hat{j}^{\alpha}(\boldsymbol{r})\rangle_{\mathrm{LE}} = \rho(\boldsymbol{r})u^{\alpha}(\boldsymbol{r})$. Equation (6) is the formal expression of the thermo-osmotic slip in the presence of a nonuniform temperature field. Notice that (6) also involves *odd-rank* tensors, forbidden by space isotropy, because this general theoretical framework also applies for a fluid close to an external surface, e.g., a hard wall, which breaks isotropy defining a preferred direction.

Similar formulas can be derived for the averages of other physical quantities. The LE average of the momentum flux operator $\hat{J}_j^{\alpha\gamma}(\boldsymbol{r})$ gives the pressure tensor at equilibrium evaluated at the local temperature and chemical potential, but may also include a nonvanishing off-diagonal contribution, as detailed in the Supplemental Material [43].

However, in any experiment, the external fields $\beta(\boldsymbol{r})$, $\boldsymbol{u}(\boldsymbol{r})$, and $\mu(\boldsymbol{r})$ appearing in Eq. (6) cannot be fixed from the outset but are rather self-consistently determined by the system, while the experimental setup just defines the appropriate boundary conditions. Only pressure, temperature, and velocity at the boundaries are given, while the spatial variation of the same quantities throughout the sample follow from the conservation equations. In steady-state conditions, the divergence of the *average* particle, momentum, and energy flux must therefore vanish. These constraints provide five differential equations for the five external fields appearing in the LE distribution function (1) leading to the formal solution of the problem.

To proceed further, let us consider a simple "slab geometry," where the fluid is confined between two infinite hard walls placed at a distance h along the z direction. The equilibrium density profile $\rho(\boldsymbol{r})$ is z dependent and the only nonvanishing components of the equilibrium pressure tensor define the transverse $p^{xx}(z) = p^{yy}(z) = p_T(z)$ and the normal pressure $p^{zz}(z) = p_N(z) = p$, which is constant and equals the bulk pressure p. Furthermore, the width h is chosen sufficiently large to guarantee that the fluid in the central region can be considered to a good approximation unaffected by the presence of the walls (in practice, a few molecular diameters are sufficient).

A solution to the continuity equations is given by constant values of $\partial_x\beta$ and $\partial_x[\beta\mu]$, while the velocity field $\boldsymbol{u}(z)$ is directed along the x axis. Under these assumptions and within this simple geometry, the stationary continuity equations for the average mass density $\langle\hat{\rho}(\boldsymbol{r})\rangle$, the energy density $\langle\hat{\mathcal{H}}(\boldsymbol{r})\rangle$, and the y component of the average momentum density $\langle\hat{j}^y(\boldsymbol{r})\rangle$ are identically satisfied. Furthermore, the conservation law for the normal (z) component of the momentum density $\langle\hat{j}^z(\boldsymbol{r})\rangle$ gives rise to the well-known hydrostatic equilibrium condition

$$\partial_\alpha\langle\hat{J}_j^{\alpha z}(\boldsymbol{r})\rangle = \partial_z p_N(z)|_{\beta(x),\mu(x)} = 0,$$

where the normal pressure is evaluated at the local temperature and chemical potential. The only nontrivial continuity equation comes from the conservation of the x component of the momentum density, which must be solved imposing that no pressure gradient is present far from the walls ("open channel"). The latter condition implies that $\partial_x[\beta\mu]$ can be expressed in terms of the temperature gradient by $\partial_x[\beta\mu] = h_m\partial_x\beta$, where h_m is the enthalpy per unit mass of the fluid in the bulk. The detailed derivation is discussed in the Supplemental Material [43]. Here we report the final integro-differential equation for the velocity profile

$$\int_0^h dz'\mathcal{K}(z,z')\partial_{z'}u^x(z') = \partial_x\beta\mathcal{S}(z). \tag{7}$$

The kernel $\mathcal{K}(z,z')$ is related to the local viscosity of the fluid

$$\mathcal{K}(z,z') = \beta\int_0^\infty dt\int d\boldsymbol{r}'_\perp\langle\hat{J}_j^{xz}(\boldsymbol{r},t)\hat{J}_j^{xz}(\boldsymbol{r}')\rangle_0,$$

and the source term $\mathcal{S}(z)$ can be written as the sum of two distinct contributions $\mathcal{S}(z) = \mathcal{S}_s(z) + \mathcal{S}_d(z)$, depending on the static and dynamic equilibrium correlations, respectively,

$$\mathcal{S}_s(z) = \int_{h/2}^{z} dz'\frac{\partial p_T(z')}{\partial\beta}\bigg|_p - \int d\boldsymbol{r}'(x-x')\langle\hat{J}_j^{xz}(\boldsymbol{r})\hat{\mathcal{P}}(\boldsymbol{r}')\rangle_0, \tag{8}$$

$$\mathcal{S}_d(z) = \int_0^\infty dt\int d\boldsymbol{r}'\langle\hat{J}_j^{xz}(\boldsymbol{r},t)\hat{J}_Q^x(\boldsymbol{r}')\rangle_0, \tag{9}$$

where we have introduced the heat flux operator $\hat{J}_Q^\alpha(\boldsymbol{r}) = \hat{J}_{\mathcal{H}}^\alpha(\boldsymbol{r}) - h_m\hat{j}_\rho^\alpha(\boldsymbol{r})$ [54] and the operator $\hat{\mathcal{P}}(\boldsymbol{r}) = h_m\hat{\rho}(\boldsymbol{r}) - \hat{\mathcal{H}}(\boldsymbol{r})$, whose average in a homogeneous system at equilibrium reduces to the bulk pressure p. Note that both source terms vanish in the bulk, implying $\partial_z u^x(z) = 0$. In the case of a "closed channel," where a pressure gradient along the x direction is present and the integrated mass current must vanish, the boundary condition should be modified and the results differ from those reported here.

The solution of this set of equations provides an expression for the gradient of the velocity field $\partial_z u^x(z)$ independent of the particular definition of the fluxes in (4), because the continuity equations only involve divergences of the fluxes (see [40]). When the result is substituted into Eq. (6), the final formula for the mass current is found,

$$\langle\hat{j}^x(z)\rangle = \rho(z)u^x(z) + \int_0^\infty dt\int d\boldsymbol{r}'[\langle\hat{j}^x(\boldsymbol{r},t)\hat{J}_Q^x(\boldsymbol{r}')\rangle_0\partial_x\beta - \beta\langle\hat{j}^x(\boldsymbol{r},t)\hat{J}_j^{xz}(\boldsymbol{r}')\rangle_0\partial_{z'}u^x(z')]. \tag{10}$$

All the contributions appearing in Eq. (10) vanish for a homogeneous system, showing that the physical origin of thermo-osmosis relies on the existence of a confining surface [55]. However, the mass flux is not fully determined by Eq. (10) because the velocity field (and not only its derivative) appears in the first term. To resolve this ambiguity, we have to know the mass flux at a given height z. This further requirement is not a limitation of the theory but rather a consequence of the Galilean invariance (along the x direction) of the equilibrium system which, in an experimental setup, is broken by the presence of friction between the fluid and the wall [56]. Instead, in the simplified model considered here, the wall is represented by an external confining potential (a hard wall), which does not modify the tangential (x) component of the particles' momenta. Supplementing this solution by a suitable (for instance *no-slip*) boundary condition for the mass flux, Eq. (10), allows us to evaluate the thermo-osmotic flow in slab geometry: We first have to solve Eq. (7) for $u^x(z)$ and then substitute the result into Eq. (10).

The above analysis of a model of a simple fluid close to a wall is exact, within linear response theory, and shows that two distinct mechanisms give rise to thermo-osmosis, both related to interface physics: the presence of anisotropies in the pressure tensor close to the wall [see Eq. (8)] and the effect of a confining surface on the dynamic correlation functions [see Eq. (9)]. We now consider two limiting situations in which these terms play a very different role in order to clarify their relevance in providing the required thermal force.

In liquids, we expect that the correlations can be estimated by their bulk value and the kernel $\mathcal{K}(z,z')$ is taken to be a short-ranged function

$$\mathcal{K}(z,z') \sim \eta\delta(z-z'), \tag{11}$$

where η is the bulk viscosity of the fluid. Under these assumptions, only the local equilibrium terms survive and the thermo-osmotic velocity reduces to $u^x(z)$ given, for $z < h/2$, by

$$u^x(z) = -\frac{\partial_x T}{\eta}\frac{\partial}{\partial T}\bigg|_p \int_0^{h/2} dz' \min(z,z')\Delta p_T(z'), \tag{12}$$

where $\Delta p_T(z) = p_T(z) - p$ and the derivative is evaluated at fixed bulk pressure. This result coincides with the solution of the linearized Navier-Stokes equation for an incompressible fluid in the presence of a gradient in the tangential pressure given by the LE expression [15]. Moreover, Eq. (12) reduces to the generalization of the result of Derjaguin *et al.* [27] recently provided in Ref. [32] in the context of nonequilibrium thermodynamics, where the enthalpy difference $\Delta h(z) = h(z) - \rho(z)h_m$ takes the place of the temperature derivative of $\Delta p_T(z)$. All the details about (12) and the continuum limit can be found in the Supplemental Material [43]. Finally, the temperature derivative of the pressure tensor has been recently evaluated by numerical simulations [29,32] for a Lennard-Jones fluid. Use of the numerical results [32] allows us to estimate that the thermo-osmotic velocity for hard walls is opposite of the thermal gradient and of the order of few micrometer per second.

In the opposite low density limit, where kinetic theories provide a quantitative interpretation of the phenomenon [19,57], our formalism is also able to reproduce the known results. Taking the ideal gas limit, i.e., ignoring the interparticle interactions, the gas remains homogeneous and isotropic in the z direction also close to the surface, implying that $\mathcal{S}_s(z) = 0$. The dynamic source term $\mathcal{S}_d(z)$ can be estimated introducing a finite relaxation time τ and retaining only the kinetic contribution to the equilibrium average in (9) as

$$\int_0^\tau dt \sum_i \left\langle \delta(\boldsymbol{r}-\boldsymbol{r}_i(t)) \frac{p_i^x p_i^x(t) p_i^z(t)}{m^2}\left[\frac{p_i^2}{2m} - m h_m\right]\right\rangle_0. \tag{13}$$

However, as shown in the Supplemental Material [43], this term vanishes in our model because the averaged operator is odd in p^z and the ballistic kinetics of an ideal gas conserves both the x component of the momentum and the particles' kinetic energy and also when scattering at the confining wall takes place. A nonzero value of the average in (13), and accordingly of the creep velocity, can only be obtained if, during the scattering at the surface, at least one of these two conservation laws are violated, as already known in the literature [7]. The first case corresponds to elastic scattering against rough surfaces, whereas the second case can occur due to inelastic particle-surface collisions. Inspired by the seminal work by Maxwell [7], we assume that, after the collision with the surface, the outgoing particle loses memory of the magnitude and the direction of its momentum before the impact. Within this hypothesis, the time-correlation functions vanish after the scattering and (13) can be evaluated analytically, leading to the following expression for the thermo-osmotic velocity v_∞ far from the surface (the derivation is detailed in the Supplemental Material [43]):

$$v_\infty = \frac{3}{4}\frac{\eta}{\rho}\frac{\partial_x T}{T} = \frac{3}{4}k_B T\frac{\eta}{p}\frac{\partial_x T}{T}, \tag{14}$$

which coincides with the kinetic theory result originally obtained by Maxwell [7,57] and shows how the slip velocity grows at low pressure, as experimentally demonstrated [19].

In summary, our generalization of the linear response theory formalism to inhomogeneous systems, applied to a simple microscopic model of fluid close to a planar smooth wall, has provided the general, exact, expression allowing us to evaluate the thermo-osmotic flow. The emerging picture turns out to be more complex than expected on the basis of the previously adopted theoretical approaches, making use of kinetic theories as regards low pressure and rarefied gases and macroscopic linear irreversible thermodynamics for the liquid phase. The resulting velocity profile of the fluid (10) is valid for all regimes and depends on both static and dynamic equilibrium properties of the system [see Eqs. (7) and (10)]: these expressions will be useful in the interpretation of future experiments and numerical simulations in the whole phase diagram of a fluid. A preliminary comparison with the existing macroscopic approach by Derjaguin *et al.* shows that it closely resembles one of the two contributions found in our general expression. The other, instead, allows us to reproduce the known expressions of the kinetic theory of gases in the appropriate limits.

Although our result is expressed in terms of quantities, like the tangential pressure near the wall and the heat flux, which are not uniquely defined on microscopic grounds, the *combination* of these terms [see, for instance, Eq. (8)] is indeed *independent* of the adopted choice, thereby solving the problem posed in Refs. [32,33].

Our method is general: the results presented in this Letter can be easily extended to a closed channel, where the relevant quantity is the pressure difference between the two ends of the system and can be applied also to other simple geometries, like spherical geometry, where it may provide insights on the microscopic mechanism at the basis of thermophoresis.

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[*] Corresponding author.
alberto.parola@uninsubria.it

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the derivation of the main results in the Letter, which includes Refs. [44–51].

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