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Forces induced by nonequilibrium fluctuations: The Soret-Casimir effect

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Abstract. – The notion of fluctuation-induced forces is generalized to the cases where the fluctuations have nonequilibrium origin. It is shown that a net force is exerted on a single flat plate that restricts scale-free fluctuations of a scalar field in a temperature gradient. This force tends to push the object to the colder regions, which is a manifestation of thermophoresis or the Soret effect.

In his pioneering work in 1948, Casimir introduced the notion of fluctuation-induced forces for macroscopic bodies when he showed that quantum fluctuations of the electromagnetic fields can generate measurable long-ranged forces between conducting plates [1]. The idea, however, has been subsequently generalized to various cases where: i) the fluctuations are of classical thermal origin, ii) the fluctuating media are complex fluids, and iii) the boundaries are moving [2–7].

In light of the extensive development of the original idea of fluctuation-induced interactions, it may seem quite natural to ask what happens if the fluctuations that cause the interaction are of nonequilibrium nature. A first attempt towards answering this question was made by Taylor already in 1951, when he was studying the swimming mechanism of flagella (tails of spermatozoa) and the theoretically challenging question of the possibility of "swimming at low Reynolds number" [8]. In this classic work, Taylor has shown that two flagella undergoing wavelike harmonic deformations have a tendency to attract each other, because their undulations introduce (nonequilibrium) hydrodynamic fluctuations in the surrounding viscous fluid that could induce an effective interaction between them. Another related work is that of Lifshitz [3], where he obtains the force between dissipative dielectric materials by considering the frequency-dependent random forces. More recently, a generalization has been introduced where localized sources drive the fluctuating medium out of equilibrium [9]. We also note that the idea of depletion forces [10], which are also fluctuation-induced in origin, has been generalized to systems driven out of equilibrium [11].

A particularly interesting way of driving a thermally fluctuating system out of equilibrium is by imposing spatial or temporal variations in the temperature profile. Many interesting phenomena are known to appear under such conditions, ranging from anomaly in diffusion to

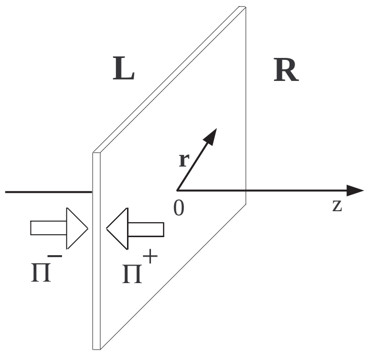

Fig. 1 – A single plate immersed in a fluctuating medium. As denoted, $\Pi^{\pm}$ represent the stresses exerted on the plate from the right- or the left-hand side of it.

the old problem of thermophoresis or Soret effect [12, 13]. In this effect, whose microscopic mechanism is still a subject for debate [14], solutions of colloidal particles [15] or polymers [16] that are placed in a temperature gradient experience separation, which signals the appearance of a net driving force on particles as a result of the temperature gradient. It has also been recently shown that inhomogeneity in the temperature profile could lead to deviation of the self-diffusion coefficient of a tracer undergoing Brownian motion from the simplistic local Einstein's relation [17].

Here, we attempt to generalize the notion of Casimir forces for nonequilibrium systems in which temperature profile is not uniform [18]. We consider a near-equilibrium fluctuating system in which we can define local and instantaneous temperature. We study the dynamics of a classical scalar field governed by a Langevin equation, in which the strength of the noise is proportional to the local and instantaneous temperature in the system. We consider external objects that restrict the fluctuations of the scalar field and calculate the resulting fluctuation-induced stress on these objects. We concentrate on the example of a single flat plate, as depicted in fig. 1, immersed in various temperature profiles. We find that a net force is exerted on the plate due to the imbalance of the fluctuation-induced forces from the two sides, which has a tendency to push it to the colder regions.

Our approach has a similar structure to the original work of Lifshitz [3], where he presents a theory for the force between dissipative dielectric materials by considering the frequency-dependent random force. While the noise amplitude is set by temperature profile in our case, it is given by the dissipative (imaginary) part of the dielectric function in Lifshitz theory.

Let us consider an equilibrium system described by a scalar field $\phi(\boldsymbol{R}, t)$ that undergoes thermal fluctuations in a space that is bounded by a number of external objects. The field could represent a component of the electromagnetic field(1) in a dielectric medium or vacuum [1,2,4], an order parameter field for a critical binary mixture or a magnetic system [5](2), a massless Goldstone mode arising from a continuous symmetry breaking such as nematic liquid crystals or superfluid helium, an elastic deformation field for fluctuating membranes and

(1)The electromagnetic field can be decomposed into TE and TM modes and those modes can be described by two scalar field theories in 4-dimensional spacetime, one having Dirichlet and the other one Neumann boundary conditions [19].

(2)A binary mixture can only be tuned to its critical point at one temperature, so it will not be possible to maintain an infinitely large correlation length over the entire system. However, since the Soret pressure is found to depend only locally on the temperature profile (see eq. (13)), one can safely neglect the mass term in the Hamiltonian if the object is placed in the neighborhood where the field is critical.

surfaces, or the electrostatic potential in charged fluids at very low salt concentrations [6]. In all of the above systems, it is possible to write down a Hamiltonian for the fluctuations around the equilibrium state, which in Gaussian approximation reads

$$\mathcal{H} = \frac{K}{2} \int \mathrm{d}^3\boldsymbol{R}\ [\nabla\phi(\boldsymbol{R})]^2 , \tag{1}$$

where K is an elastic modulus describing the stiffness of the system for the fluctuations around equilibrium state.

We consider the situation where temperature has a slowly varying profile such that thermal equilibrium can be achieved locally. This means that we have many heat reservoirs locally in contact with our system, which have different temperatures. The temperature difference between neighboring reservoirs should be sufficiently small so that the condition of local equilibrium is fulfilled [20,21]. Similarly, we can consider a temperature profile with temporal variations that are sufficiently slow such that instantaneous equilibrium state can be defined. We would like to drive the system described by the Hamiltonian in eq. (1) out of equilibrium by imposing such temperature profiles and examine the corresponding fluctuation-induced forces exerted on external boundaries in the medium.

Our specific choice of boundaries is sketched in fig. 1, where we consider the case of a single plate of area A immersed in a fluctuating medium. We choose the z-axis to be the normal direction to the plate, such that the three-dimensional position vector can be represented as $\boldsymbol{R} = (\boldsymbol{r}, z)$. We assume the Dirichlet boundary condition, which means that the fluctuating field ϕ is restricted to vanish on the plate. The vanishing of the electric field on the conducting plates, the strong homeotropic anchoring of the nematogens in the nematic liquid crystal [22], or the enhanced screening of the electrostatic potential near the macroions due to counterion condensation in the case of charged fluids [6], will be the physical realizations of the Dirichlet boundary condition. The case of Neumann boundary condition can also be considered and our choice is just meant to be an example to show the possible effects.

The physical quantity that we would like to calculate for such a system is the pressure or the normal force per unit area exerted on the plate from the fluctuating medium. In the prescribed geometry, this will be Π_{zz} —the zz component of the stress tensor. Using the Hamiltonian in eq. (1), one can calculate the components of the stress tensor in terms of the two-point correlation functions of the field. For example, the local pressure exerted from the right side on the plate that is located at $z = 0$ is given as [23]

$$\Pi^{+}_{zz}(\boldsymbol{r}, t) = \frac{K}{2} \partial_z \partial_{z'} \left\langle \phi(\boldsymbol{r}, z, t)\phi(\boldsymbol{r}, z', t) \right\rangle |_{z,z' \to 0^+} . \tag{2}$$

A similar definition and expression can be given for the pressure from the left side Π^{-}_{zz}, and the total normal force per unit area

$$\Pi_{\mathrm{tot}} = \Pi^{-}_{zz} - \Pi^{+}_{zz} , \tag{3}$$

exerted on the plate in the positive z-direction. Note that due to the translational symmetry of the infinite plate in the parallel directions, the lateral forces are all zero, even for the case where temperature is not uniform.

For calculating the correlation functions in the local and instantaneous near-equilibrium states resulted from a prescribed temperature profile, we use the fact that such states could be reached via an equilibrium dynamical relaxation. We assume a dynamical Langevin equation as

$$\gamma \partial_t \phi(\boldsymbol{R}, t) = K \nabla^2 \phi(\boldsymbol{R}, t) + \eta(\boldsymbol{R}, t), \tag{4}$$

with the boundary condition $\phi(\boldsymbol{R},t)|_{\boldsymbol{R}\text{ on boundary}} = 0$. Here, γ is the friction coefficient of the system, and the random force $\eta(\boldsymbol{r},t)$ is a Langevin noise whose spectrum is given by the local and instantaneous fluctuation-dissipation theorem:

$$\langle\eta(\boldsymbol{R},t)\eta(\boldsymbol{R}',t')\rangle = 2\gamma k_{\mathrm{B}}T(\boldsymbol{R},t)\delta^3(\boldsymbol{R}-\boldsymbol{R}')\delta(t-t'), \tag{5}$$

where $T(\boldsymbol{R},t)$ is the temperature profile in the system. The condition of sufficiently slowly varying temperature profile is realized in imposing the cutoffs of $q_{\max} = 1/a$ and $\omega_{\max} = K/(\gamma a^2)$ on the wave vectors and frequencies of the Fourier transform of $T(\boldsymbol{R},t)$, where a is a relevant microscopic length scale (see below). This guarantees that a continuum Langevin description is applicable to each local neighborhood.

For solving the above Langevin equation, we define the appropriate Green's function as the solution of the following equation:

$$(\gamma\partial_t - K\nabla^2)G(\boldsymbol{R},t;\boldsymbol{R}',t') = \delta^3(\boldsymbol{R}-\boldsymbol{R}')\delta(t-t'), \tag{6}$$

with the boundary conditions $G(\boldsymbol{R},t;\boldsymbol{R}',t')|_{\boldsymbol{R}\text{ on boundary}} = 0$, for each value of $\boldsymbol{R}'$. The solution of the Langevin equation can then be written as

$$\phi(\boldsymbol{R},t) = \int \mathrm{d}^3\boldsymbol{R}'\,\mathrm{d}t'\; G(\boldsymbol{R},t;\boldsymbol{R}',t')\;\eta(\boldsymbol{R}',t'), \tag{7}$$

which yields the two-point correlation function of the field as

$$\begin{aligned}\langle\phi(\boldsymbol{R},t)\phi(\boldsymbol{R}',t')\rangle &= 2\gamma k_{\mathrm{B}}\int \mathrm{d}^3\boldsymbol{R}_1\,\mathrm{d}t_1\; T(\boldsymbol{R}_1,t_1)\times \\ &\qquad \times G(\boldsymbol{R},t;\boldsymbol{R}_1,t_1)\; G(\boldsymbol{R}',t';\boldsymbol{R}_1,t_1).\end{aligned} \tag{8}$$

Note that the fluctuations in the ϕ-field are affected by the entire temperature profile through the scale-free relaxation dynamics governed by eq. (4).

To obtain the form of the Green's function for the specific geometry discussed above, we proceed by direct solution of the differential equation. Because of the translational symmetry in time, as well as the space direction parallel to the plates, we introduce the Fourier transformation

$$G_{\boldsymbol{q},\omega}(z,z') = \int \mathrm{d}^2\boldsymbol{r}\;\mathrm{d}t\; e^{i\boldsymbol{q}\cdot(\boldsymbol{r}-\boldsymbol{r}')-i\omega(t-t')}\; G(\boldsymbol{r},z,t;\boldsymbol{r}',z',t'), \tag{9}$$

which satisfies the following equation: $(Q_-^2 - \partial_z^2)G_{\boldsymbol{q},\omega}(z,z') = \delta(z-z')/K$, where $Q_\pm = \sqrt{q^2 \pm i\gamma\omega/K}$. We can divide the space into two distinct half-spaces: left (L) and right (R), as shown in fig. 1, and label the Green's function in each subspace with the corresponding indices: L or R.

Using the Dirichlet boundary conditions, we can solve the above equation and directly obtain the closed form for the Green's function in the left part of the space as

$$G^{\mathrm{L}}_{\boldsymbol{q},\omega}(z,z') = \begin{cases} -\sinh[Q_-z]\,\frac{\exp[Q_-z']}{KQ_-}, & z > z', \\ -\sinh[Q_-z']\,\frac{\exp[Q_-z]}{KQ_-}, & z < z', \end{cases} \tag{10}$$

and the Green's function in the right side, namely $G^{\mathrm{R}}_{\boldsymbol{q},\omega}(z,z')$, can be obtained by symmetry.

The above expressions for the Green's function can be used to calculate the normal stresses exerted on the plates for arbitrarily given temperature profiles. While the equilibrium-fluctuation–induced forces are universal, it appears that forces induced by nonequilibrium fluctuations are not universal and do depend on microscopic details, as will be shown in the next discussion. This kind of dynamical behavior is a special case of the solution of a more general problem related to surface critical dynamics [24].

We now focus on the example of a single plate that is embedded in a fluctuating background with nonuniform temperature. When the temperature profile is uniform, the stress resulted from the field configurations on the left side cancels exactly with the corresponding counterpart coming from the right side, and the plate experiences no net force. However, when temperature is not uniform, the strength of the fluctuations are also not uniform, and we expect a force imbalance due to the asymmetry caused by the temperature gradient. To further simplify the problem, we assume that temperature only depends on the z coordinate, *i.e.* it is independent of time and the parallel coordinates. The two contributions to the normal stress at the position of the plate can be written as

$$\Pi^{-} = \frac{\gamma k_{\mathrm{B}}}{K} \int \frac{\mathrm{d}^2\boldsymbol{q}\mathrm{d}\omega}{(2\pi)^3} \int_{-\infty}^{0} \mathrm{d}z\, T(z)\, e^{(Q_{+}+Q_{-})z}, \tag{11}$$

and

$$\Pi^{+} = \frac{\gamma k_{\mathrm{B}}}{K} \int \frac{\mathrm{d}^2\boldsymbol{q}\mathrm{d}\omega}{(2\pi)^3} \int_{0}^{\infty} \mathrm{d}z\, T(z)\, e^{-(Q_{+}+Q_{-})z}. \tag{12}$$

The integrations over wave vector and frequency can be performed, leading to a closed-form expression for the total stress on the plate as

$$\Pi_{\mathrm{tot}} = -\frac{k_{\mathrm{B}}}{12\pi^2} \int_{a}^{\infty} \frac{\mathrm{d}z}{z^4} [T(z) - T(-z)], \tag{13}$$

where the short-distance cutoff a is explicitly included in the integration. We can observe that due to the nonuniformity of the temperature profile, the nonuniversal contributions to the stress on the two sides do not cancel out. Therefore, the forces mediated by nonequilibrium fluctuations are not universal and they also depend on the specific imposed temperature profile.

The observation that a plate in a temperature gradient feels a net force reminds us of the Soret effect, which describes the drift motion of colloidal particles in a medium with a nonuniform temperature profile. The important measurable quantity here is the so-called Soret coefficient, which is defined as $S_T = \frac{D_T}{D}$, where D_T and D are the coefficients of thermal diffusion [13] and self-diffusion, respectively. Thermal diffusion coefficient relates the particles flux to the temperature gradient through the relation $J = -cD_T\nabla T$, where c is the particle density. On the other hand, we can write the current density as $J = cv = c\mu F$, where μ is the mobility of the particle (plate in the present case) and $F = \Pi_{\mathrm{tot}} A$ is the overall force exerted on it. Using these relations, and assuming that the Einstein's relation $D = \mu k_{\mathrm{B}} T$ holds locally, one can extract a relation between the stress on the plate and temperature gradient in terms of the Soret coefficient as

$$\Pi_{\mathrm{tot}} = -\frac{k_{\mathrm{B}}T}{A} S_T \nabla T. \tag{14}$$

The above relation will be used in extracting the values of the Soret coefficient.

Examining the behavior of eq. (13) above, we can distinguish between two different general categories depending on whether the temperature profile is continuous or discontinuous on the plate. Each category is examined separately below.

In the case where the temperature is continuous on the plate (see fig. 2(a) for an example), the dominant contribution of the integral in eq. (13) comes from the short distances, where the temperature difference can be written as $T(z) - T(-z) = 2z\nabla T + \mathrm{O}(z^2)$. This yields

$$\Pi_{\mathrm{tot}} = -\frac{1}{3\pi^2} \frac{k_{\mathrm{B}}}{a^2} \nabla T, \tag{15}$$

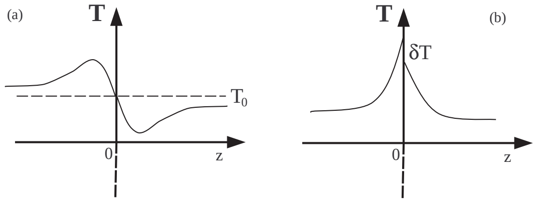

Fig. 2 – (a) Temperature profile is continuous on the plate. (b) Temperature is discontinuous on the plate.

to the leading order. Note that this result is independent of the behavior of the temperature profile at large distances, and, for example, it is not sensitive to whether the asymptotic values of the temperature profile are equal or not. The Soret coefficient can be obtained as

$$S_T = \frac{A}{3\pi^2 a^2 T(0)}\,. \tag{16}$$

If the temperature profile is not continuous and undergoes a jump of δT across the plate (such as the example shown in fig. 2(b)), the leading behavior of the Casimir stress is altered as $\Pi_{\rm tot} = -\frac{k_{\rm B}\delta T}{4\pi^2 a^3}$, to the leading order. Note that due to the discontinuous form of the temperature profile, it is not possible to define a Soret coefficient in this case. The discontinuous case might not be very physical unless the thickness of the plate is sufficiently large, in which case the heat conduction across the plate should be considered.

We have examined the effect of nonequilibrium fluctuations that are modified due to the presence of external objects, and the corresponding pressure imbalance. Despite the equilibrium case where the interactions between immersed objects are universal, nonequilibrium-fluctuation–induced forces do depend on a microscopic length scale a, which depends on the system under consideration. This is also the case for the fluctuations of the fluctuation-induced forces [25]. For example, in the case of the electromagnetic field it is set by the plasma wavelength of the metallic boundaries, which is typically in the 100 nm range for good conductors. For nematic liquid crystals, a is set by the size of the nematogens, which can be anywhere between 2 and 200 nm [22]. For charged fluids, this length is set by the so-called Gouy-Chapman length, which sets the thickness of the layer of condensed counterions near the highly charged macroion surfaces [6]. The dependence on cutoff may suggest at first that the result is somewhat arbitrary, because one can define the cutoff in various ways. We should note, however, that cutoff procedures as exemplified above are always due to certain physical properties, and in each case one should be able to unambiguously find the appropriate way to incorporate the cutoff by considering a sufficiently realistic model. For example, in the case of electrostatic fluctuations, one should use the full profile of the counterions instead of using a simplified artificial one [6]. It should also be mentioned that this length scale is characteristic of the system itself and thus has the same value in the different sides of the plates, such that the stresses from the two sides are guaranteed to cancel at equilibrium.

External objects subject to nonequilibrium-fluctuation–induced forces are shown to exhibit the Soret effect, which causes them to go to the colder region. While the force itself is nonuniversal, the tendency to push them towards the colder region appears to be universal, unlike other manifestations of the Soret effect. This universal tendency has its roots in the fact that by pushing the boundary to the colder region more space can be opened up for the fluctuating medium to gain entropy excess by undergoing wilder fluctuations.

The net force on a single plate (eq. (13)) has naturally appeared to depend only on the asymmetric (odd) part of the temperature profile. One can view the result as a local summation of van der Waals forces between slabs of different temperatures in terms of the scaling of the kernel, $1/z^4$. The kernel also shows that the information from farther distances is screened by the strong algebraic decay, as is the case in any fluctuation-induced interaction.

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