Colloidal attraction induced by a temperature gradient

R. Di Leonardo, F. Ianni, and G. Ruocco
1 CNR-INFM, CRS SOFT c/o Dipartimento di Fisica, Università di Roma “La Sapienza”, I-00185, Roma, Italy
2 Dipartimento di Fisica, Università di Roma “La Sapienza”, I-00185, Roma, Italy

Colloidal crystals are of extreme importance for applied research, such as photonic crystals technology, and for fundamental studies in statistical mechanics. Long range attractive interactions, such as capillary forces, can drive the spontaneous assembly of such mesoscopic ordered structures. However, long range attractive forces are very rare in the colloidal realm. Here we report a novel strong and long ranged attraction induced by a thermal gradient in the presence of a wall. Switching on and off the thermal gradient we can rapidly and reversibly form stable hexagonal 2D crystals. We show that the observed attraction is hydrodynamic in nature and arises from thermal induced slip flow on particle surfaces. We used optical tweezers to directly measure the force law and compare it to an analytic prediction based on Stokes flow driven by Marangoni forces.

Colloidal particles, dispersed in a homogeneous solvent, undergo unbiased Brownian motion unless an external body force, such as gravity, drives them along a particular direction. Directed colloidal transport can also be induced, in the absence of a net body force, by a gradient in some external field such as electric potential (electrophoresis), temperature (thermophoresis) or concentration of a solute molecule (diffusiophoresis). In phoretic transport, due to the absence of a net body force acting on the particle, and the thin interface layer around it, the surrounding fluid is perturbed with a flow field decaying as \(1/r^3\), compared with the leading term of order \(1/r\) for sedimentation. As a consequence, hydrodynamic interactions, which are crucial for sedimentation problems, are usually negligible in phoretic transport. The opposite situation may occur when particles transport is impeded by an external wall. While sedimentsing particles become stationary as a result of a force balance between gravity and wall repulsion, phoretic particles have a zero velocity despite the presence of a non-zero body force (wall repulsion) acting on them. In such peculiar condition, gradients in the external field will produce a flow field around a stationary particle which will be long ranged (\(1/r\)) determining strong hydrodynamic couplings to nearby particles. Such hydrodynamic interactions have been predicted by Squires and are expected to manifest as an effective attractive potential when phoretic particles are pinned on a wall. Here we report the direct observation of strong attraction between colloidal particles confined at a solid interface by thermophoresis. The induced force is strong enough to lead to the formation of stable close packed structures and can be efficiently exploited to drive quick self assembly of colloidal crystal. Evidences for such a “hydrodynamic attraction” in temperature gradients have been independently reported by Weinert and Braun. We propose an analytic expression for the effective force and validate it by direct force measurement with optical tweezers.

A thin (\(\sim 15 \mu m\)) sample cell is obtained by sandwiching a small drop of sample solution (2 \(\mu m\) diameter silica beads in a glycerol/water mixture) between a coverslip and an absorbing yellow filter as the microscope slide. High temperature gradients (\(\sim 1K/\mu m\)) can be produced by focusing a laser beam on the absorbing ceiling of the sample cell (Fig. 1). The same microscope objective (100x NA 1.4 in a Nikon TE2000U inverted microscope) is used both for focusing the heating beam and for bright field imaging. As soon as the laser is turned on, the particles move towards colder regions under the effect of thermophoresis, following the direction of the negative thermal gradient, as expected for thermophobic behavior. We used a finite element method (COMSOL Multiphysics) to solve the stationary heat equation, with a heat source term modeled as a Gaussian beam, that propagates in an absorbing medium (top coverslip). The distribution of the isothermal surfaces (black lines) and the temperature gradient direction (white lines), due to the absorption of a laser beam by the optical filter at the top, are depicted in Fig. 1. Once the particles reach the bottom wall, a strong interparticle interaction manifests leading to the formation of closed packed clusters. In order to reduce the radial components of temperature gradient we focused on the top absorbing wall an array of 20 traps along a circumference of 30 \(\mu m\) diameter. Isolated particles in the inner ring region are pushed against the bottom wall and then perform unbiased 2D Brownian motion. On the other hand thermophobic particles in the outer region are prevented to enter the heated region. In this way we can have a small number of particles in the inner region and record the dynamics of cluster formation. Each cluster was able to find the closest packing structure in a few tens of seconds. A few sample clusters are shown in (Fig. 2 a). These clusters are completely reversible and disgregate as soon as the temperature gradient is turned off (Fig. 2 b). At higher concentrations particles assemble in stable, two dimensional crystal (Fig. 3 c).

The existence of a confinement-induced long range attraction between particles of like charge has been observed and debated during the past ten years. Such
interaction is also found to increase when the like charged particles penetrate the electric double layer at the interface [5,7]. One could think that the only role of the thermal gradient is that of pushing the particles against the double layer of the bottom interface and that the observed interactions are ultimately electrostatic in nature. However like-charge attraction disappears on a metallic surface [8,9]. We then checked (Fig. 2 d) that the attraction observed in our experiment persists on a metallic surface obtained through a gold coating 10 nm thick over the glass surface. The position of the laser beam inducing the thermal gradient is indicated by the brighter particle at the bottom, trapped by the beam and displaced from the bottom wall. Close-packed structures form both on a dielectric charged surface, i.e. the cover glass (visible as the clearer band), and on a metallic surface (darker band). Neither we can attribute the observed attraction to an imaging artifact [10], as the formation and stability of small clusters clearly evidences the presence of a strong attractive force. Another candidate for the origin of the attraction could be the distortion of the isothermal surfaces in the fluid, due to the different thermal conductivity of the particles and to the spatial asymmetry induced by presence of the wall. As, in our case, thermophoresis drives particles along the negative thermal gradient, this effect may induce an attraction between particles touching a colder wall, when thermal conductivity is higher than the solvent’s one, or a repulsion in the inverse case. However we always observe attraction in both cases of a higher (silica) and lower (polystyrene) thermal conductivities.

We suggest, in accordance to [8], that the underlying mechanism is hydrodynamic in nature. The basic idea is that even if the particles stop when they reach the bottom wall there’s a non zero net force acting on them, provided by electrostatic repulsion from the wall (the net force and torque produced by thermal gradients on the interface are always zero [11]). At large enough particle separations the ambient flow produced by one particle at the location of the other can be obtained as the flow propagating from a point force. In the absence of the wall

such a flow would be described by the so called Stokeslet [12] which wouldn’t have any attractive component on the other particle. When the no-slip condition imposed by the wall is taken into account, image singularities appear (Stokeslet, source doublet and Stokes doublet [11]) contributing a flow component \( u_x \) pulling the the two particles together. The streamlines of the flow produced by a Stokeslet pointing away from the wall are reported in Fig. 3. Such a flow will have, on the center of a second particle touching the wall at a distance \( s \), a component parallel to the wall given by [2]:

\[
 u_x = \frac{-3F}{2\pi\eta} \frac{h^3}{(s^2 + 4h^2)^{3/2}} 
\]  

(1)
where \( F \) is the force exerted by the wall on the particle and \( h \) is the distance between the particle center and the wall. In the limit of large interparticle distances \( s \) (with respect to the distance \( h \) between particles’ centers and the wall), the flow component parallel to the wall decays as \( 1/s^4 \). The slowly decaying components \( (1/s^2) \) coming from the image singularity sister consisting of a Stokeslet, a Stokes dipole and a source dipole \([11]\). 

The particles will then perform Langevin dynamics under the action of such interaction forces in addition to the usual drag and stochastic forces. Such an effective force on the second particle will be undistinguishable from an attractive force of intensity:

\[
f = 6\pi \eta a \lambda u_x = -9\lambda F \frac{ah^3s}{(s^2 + 4h^2)^{5/2}} \tag{2}
\]

where \( \lambda = \lambda(a/h) \) is an adimensional correction factor on the Stokes drag due to the presence of the wall \([12]\). The particles will then perform Langevin dynamics under the action of such interaction forces in addition to the usual drag and stochastic forces. Such an effective force field is derivable from a potential function and therefore particle statistics will be governed by Boltzmann statistics with an effective interaction potential:

\[
V(s) = -3\lambda F \frac{ah^3}{(s^2 + 4h^2)^{3/2}} \tag{3}
\]

The force \( F \) needed to hold a particle in a temperature gradient can be evaluated along the same lines suggested by Würger \([13]\) for the calculation of the thermophoretic speed \( U \). In that paper the author solves Stokes equations for a homogeneous fluid imposing the three boundary conditions given by: i) a vanishing net force is applied to the particle, ii) the tangential component of the stresses on the particle surface cancel out the Marangoni force. iii) a zero normal component of fluid velocity relative to the particle surface, which in the lab frame gives:

\[
v_{\tau}|_{r=a} = U \cdot \hat{n} \tag{4}
\]

In order to satisfy the above conditions one gets a value for the thermophoretic speed given by \([14]\)

\[
U = -\frac{a\gamma_T \kappa}{3\eta} \nabla T \tag{5}
\]

where \( \eta \) is the solvent viscosity, \( \gamma_T = \partial \gamma/\partial T \) is the partial derivative with respect to temperature of the interfacial energy \( \gamma \), and \( \kappa = 3\kappa_S/(2\kappa_S + \kappa_P) \) is a dimensionless combination of particle and solvent thermal conductivities.

We seek here a solution for a spherical particle held stationary in a thermal gradient by a body force. The corresponding boundary conditions become: i) again a zero normal component of fluid flow on particle surface in the particle frame which now coincides with the lab frame, ii) a non vanishing, but unknown in modulus, net force \( F \) on the particle, iii) an off-diagonal stress tensor canceling the Marangoni force. A Stokeslet flow has a zero off diagonal stress tensor, a non vanishing body force \( F \), and a fluid flow projection on the particle surface normal \( \hat{n} \) given by

\[
v_{\tau}|_{r=a} = \frac{F \cdot \hat{n}}{4\pi \eta a} \tag{6}
\]

Comparing (4) to (6) it is easy to satisfy the above conditions by simply adding to the flow obtained above for the freely moving particle, a Stokeslet flow with

\[
F = -4\pi \eta U = \frac{4\pi a^2 \gamma_T \kappa}{3} \nabla T = \frac{1}{3} \nabla \Gamma \tag{7}
\]

where \( \Gamma \) is the total interfacial energy. We can now assume that \( F \) remains a good estimate even in the presence of the wall and get an expression for the force \( f \) by substituting (7) in (2). For spheres almost touching the wall \( (h \sim a \ [15]) \) we get:

\[
f = -f_0 \frac{s/a}{[4 + (s/a)^2]^{5/2}} \tag{8}
\]

\[
f_0 = 12\pi \lambda \kappa \gamma_T \nabla T a^2 \tag{9}
\]

The force depends linearly on the interface energy gradient, increases with the square of particle size but is independent from solvent viscosity.

In order to validate the above expression we used optical micromanipulation to directly measure the force law with interparticle distance.
Holographic optical tweezers allow to isolate a single pair of particles and vary their relative distance while gauging their interaction. In particular, a high intensity optical trap \((P = 42 \text{ mW})\) is focused next to the interface with the top wall in order to produce the thermal gradient, while two traps of lower intensities \((P = 3 \text{ mW})\) are used to hold two particles on the bottom wall. We checked that the intensity of the last traps alone is low enough not to induce further attraction between the particles. In order to avoid fluid instabilities induced by the high thermal gradient \([16]\), we have chosen a high viscosity suspension (a glycerol-water mixture 56% w) and a thin cell gap (13 \(\mu\text{m}\) thick).

The thermal induced interaction tend to push the particles towards each other and out of the optical traps, until the restoring trap force balances the attractive force. By measuring the difference \(\Delta s\) between trap centers distance and interparticle distance, the value of the attractive force can be deduced: \(f = k\Delta s\), where \(k\) is the equivalent elastic strength of the two traps system \([17]\) and may be determined experimentally from the mean square displacement of particle distance: \((\Delta d^2) = K_B T/k\). In the reported experimental conditions we found \(k = 0.1 \text{ pN}/\mu\text{m}\). However an experimental determination of the prefactor \(f_0\) in \([9]\) is very hard because of the strong dependence of \(\lambda\) on the exact value of \(h\) and difficulties in measuring the temperature gradient. On the other side the dependence on interparticle distance only contains particle radius and can be accurately checked. Fig. 4 reports the experimental determination of force as a function of interparticle distance together with a fit to Eq. 8 with \(f_0 = 4.8 \text{ pN}\) as the only fit parameter.

In conclusion, we have shown that a thermal gradient pushing thermophoretic particles against an interface can induce a strong and long ranged attraction between like-charged particles, leading to the prompt formation of stable, ordered structures. We provide a static measurement of this interaction and quantitatively confirm the prediction of a hydrodynamic pseudo-force \([2]\) driven by Marangoni forces on particle surface. The long range nature of the interaction, similarly to capillary forces, may open new routes to fabrication of ordered structures. Already, this mechanism may have enhanced the self-assembling observed under a convective flow and uniquely attributed to a confining effect \([18][19][20]\).

We thank M. Ortolani and the IPN-CNR labs for kindly providing us the gold coated cover glass.

\[\sum_{i=1}^{s} f_i(n) = \sum_{i=1}^{s} \frac{n_i}{2}\]

* Electronic address: roberto.dileonardo@phys.uniroma1.it

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FIG. 4: Intensity of the attractive force as a function of distance. Open symbols are experimental data, solid line is a fit to Eq. (8).

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