Coulomb-Like Diffusiophoretic Interaction Between Catalytic Particles

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We calculate the concentration fields of solutes A and B around a sphere whose surface can catalyze the interconversion reaction \( A \rightleftharpoons B \) which is maintained out of equilibrium by controlling the bulk concentrations of the solutes. We use the results to compute the interaction between two such catalytic spheres in the limit when their separation \( r \) is much larger than their radius \( R \) and show that the resulting diffusiophoretic force on each particle is Coulomb-like: it decreases as \( 1/r^2 \), can be attractive or repulsive, and is screened on length scales larger than some penetration depth \( \xi \). The relevance of our results to experiments on catalytic colloids is discussed.

Diffusiophoresis refers to the drift of a colloidal particle (or a liquid droplet) in a solvent, induced by gradients in the concentration of chemical species (solute) \[1\] \[10]. The phenomenon is driven by short-range interactions between the surface of the particle and the solute molecules which results in different energies of a solute molecule close to the surface of the particle and away from it and, depending on the sign of the interaction, it leads to the motion of the particle along or opposite to the direction of the concentration gradient. Recently, diffusiophoresis has been proposed as a non-equilibrium, non-motor protein mechanism for metabolism-dependent transport of protein filaments, plasmoids, storage granules, and foreign particles of different sizes in cells \[5\] \[6\]. Related cross-diffusion and chemotaxis effects \[7\] have been also implicated in the aggregation of enzymes and the formation of metabolons in regions of high substrate concentrations \[8\].

One simple way to create solute concentration gradients is to have colloidal particles catalyzing the reaction \( A \rightleftharpoons B \) between substrates (“fuel”) \( A \) and products (“exhaust”) \( B \), provided that substrates are supplied to the system, while products are washed away. The goal of the present article is to point out that catalytic particles in this situation will experience a long range interaction force, behaving like \( 1/r^2 \) at long distances, much like electrostatic Coulomb interaction. The sign of the force, attractive or repulsive, depends on the short range interactions between the surface of each colloidal particle and solute molecules \( A \) and \( B \). Furthermore, it is predicted to exhibit other Coulomb-like properties, such as Debye screening \[9\], Wigner crystals \[10\], etc. We will start by briefly reviewing the situation with one spherically symmetric catalyst, then consider the force of interaction between two such symmetric or non-symmetric colloids, and finally discuss the many-catalysts systems.

Solute density profile around a single catalytic sphere. To set a stage and establish the notations, consider a dilute solution of molecules \( A \) (there could be several species \( A_i \)) and \( B \) (or \( B_j \)) of concentrations (molecules per unit volume) \( c_{A_i} \) and \( c_{B_j} \), respectively. In the following we will assume that \( A \) and \( B \) can interconvert via the reaction \( \sum_i \nu_{A_i} A_i \rightleftharpoons \sum_j \nu_{B_j} B_j \), where \( \nu_{A_i} \) and \( \nu_{B_j} \) are the corresponding stoichiometric coefficients. We will also assume that the energy barrier for the reaction is sufficiently high so that the system can be maintained indefinitely out of equilibrium and therefore \( c_{A_i} \) and \( c_{B_j} \) are externally controlled parameters. We now introduce a spherical particle of radius \( R \) which can catalyze the reaction \( A \rightleftharpoons B \) on its surface by reducing the energy barrier to a value comparable to \( k_B T \). Assuming for simplicity that concentrations are sufficiently small, the steady state rate of catalytic reaction can be written as

\[
J = v k_{\rightarrow} \prod_i [c_{A_i}(R)]^{\nu_{A_i}} - v k_{\leftarrow} \prod_j [c_{B_j}(R)]^{\nu_{B_j}},
\]

with \( k_{\rightarrow} \) and \( k_{\leftarrow} \) forward and backward rate constants, \( c(R) \) the corresponding concentrations at the surface of the catalyst, and \( v \) the volume where reaction takes place (for instance, if catalysis occurs uniformly along spherical surface, then \( v = 4\pi R^2 d \), with \( d \) molecular length scale). Since solute particles \( A \) and \( B \) have to be delivered to and from the catalyst surface by diffusion, their steady state concentration profiles must be found from the appropriate diffusion equation. For a spherically symmetric catalyst, the concentration fields of all solutes \( A \) and \( B \) are spherically symmetric:

\[
c_{A_i}(r) = c_{A_i} - \frac{\nu_{A_i} J}{4\pi D_{A_i} r}; \quad c_{B_j}(r) = c_{B_j} + \frac{\nu_{B_j} J}{4\pi D_{B_j} r}.
\]

Plugging this (at \( r = R \)) back to Eq. \[1\] which serves as a boundary condition for the diffusion equation, produces an equation for current \( J \) which, as one can show, always has a unique solution. To be specific, consider the simplest case with only one species of \( A \) and of \( B \), assume catalysis taking place in a narrow layer around the catalyst surface, \( v = 4\pi R^2 d \), and write rate constants in the
form \( k_{\alpha} = \frac{1}{\tau} e^{\beta (\varepsilon_{\alpha} - \varepsilon_{\ell})} \) and \( k_{\infty} = \frac{1}{\tau} e^{\beta (\varepsilon_{\infty} - \varepsilon_{\ell})} \), where \( 1/\tau \) is the attempt rate, \( \beta = 1/k_{B}T \), while \( \varepsilon_{\alpha}, \varepsilon_{\infty}, \) and \( \varepsilon_{\ell} \) are energies of \( A, B, \) and transition state of the catalytic surface reaction. This yields

\[
\frac{J}{4\pi R^{2}d} = \frac{c_{A}e^{\beta \varepsilon_{A}} - c_{B}e^{\beta \varepsilon_{B}}}{\frac{\hbar d}{D_{A}}e^{\beta \varepsilon_{A}} + \varepsilon_{\ell} + \frac{\hbar d}{D_{B}}e^{\beta \varepsilon_{B}}} \tag{3}
\]

As expected, the flux vanishes in equilibrium due to detailed balance. In fact, the entire effect is proportional to \( c_{A}e^{\beta \varepsilon_{A}} - c_{B}e^{\beta \varepsilon_{B}} \), which is a measure of chemical imbalance: the process is driven by the difference in chemical potentials of \( A \) and \( B \); it can run on energy if \( \varepsilon_{A} > \varepsilon_{B} \), or on entropy if \( c_{A} > c_{B} \), or on any combination of these two. Thus, the numerator of the last expression is like a voltage driving a current, while the denominator consists of three resistances connected in series: diffusion of reagent to the catalyst (first term), catalytic reaction (second term), and diffusion of product from the catalyst (third term).

**Interaction energy and force between catalytic spheres.** We now consider two catalytic spheres, some distance \( r \) apart, such that \( r \gg R \); the catalyst spherical symmetry assumption will be relaxed later on. Because of the short-range interactions between solute particles \( A \) and \( B \) and catalyst, and because steady state concentrations of \( A \) and \( B \) are non-uniform in space, energies of these two spheres depend on the distance \( r \) between them, i.e., there is an interaction force between them. This problem can be treated, in the first approximation, by thinking of one droplet located in the origin, while the other, positioned distance \( r \) away, interacting with concentration fields \( c_{A}(r), c_{B}(r) \) Eq. (2) created by the first. “Interference” effect does exist, when the concentrations of the two spheres are subtracted such that the entire phenomenon is of non-equilibrium nature. It is driven by the supply of “fuel” \( A \) molecules as well as removal of “exhaust” \( B \) molecules at infinity, and by the catalytic ability of the spheres to transform \( A \) to \( B \).

For instance, if we model short range interactions of \( A \) and \( B \) with the catalytic surface as some layer of thickness \( d \) in which our particles have energies \( \varepsilon_{A}^{*} \) and \( \varepsilon_{B}^{*} \), different from their bulk values \( \varepsilon_{A} \) and \( \varepsilon_{B} \), then \( \sigma_{A} = d\varepsilon_{A}e^{-\beta \varepsilon_{A}} \) and \( \sigma_{B} = d\varepsilon_{B}e^{-\beta \varepsilon_{B}} \), with \( \varepsilon_{A} = \varepsilon_{A}^{*} - \varepsilon_{\ell} \) and \( \varepsilon_{B} = \varepsilon_{B}^{*} - \varepsilon_{\ell} \). In this approximation,

\[
\frac{f}{4\pi R^{2}} = \frac{J d}{4\pi r^{2}} \left[ \frac{\varepsilon_{B}}{D_{B}}e^{-\beta \varepsilon_{B}} - \frac{\varepsilon_{A}}{D_{A}}e^{-\beta \varepsilon_{A}} \right] \tag{6}
\]

with \( J \) given by Eq. (3).

Eq. (6) together with Eq. (3) is convenient for making numerical estimates, showing that forces in question are quite large. Assume, for instance, that the reaction is diffusion limited (the barrier energy is of order \( k_{B}T \)) which allows us to neglect the \( \tau \)-term in the denominator of Eq. (3); furthermore, take \( \varepsilon_{A} \gg \varepsilon_{B} \) and assume \( D_{A} = D_{B} = D \). This yields \( J = 4\pi R D \varepsilon_{A} \) and in this case \( c_{A}(R) = 0 \) which means that all \( A \) molecules arriving at the surface of the sphere are converted into \( B \) molecules. As a specific numerical example, we take the separation between spheres to be \( r = 10R \), the molecular scale \( d = 1 \text{ nm} \) and \( R = 1 \mu \text{m} \), a size typical of colloidal particles. We further take the bulk concentrations of the solutes to be \( c_{A} = 10^{7} \text{ molecules/} \mu \text{m}^{3} \) and \( c_{B} = 0 \), and assume all the energies to be of order \( k_{B}T \). With all these approximations Eqs. (3) and (6) yield

\[
f \approx 10^{3} f_{\text{th}}, \tag{7}
\]

where \( f_{\text{th}} = k_{B}T/R \) is the thermal (Brownian) force on the sphere. Thus, diffusiophoretic force is easily three orders of magnitude larger than thermal force. This should lead to deterministic motion of the two spheres along the line that connects them and should be readily observable.

Encouraged by our promising estimate of the force between colloidal catalysts, we proceed to make a similar estimate for the force between biological catalysts, i.e., enzymes (closing for a moment our eyes on the fact that they are not spherically symmetric). Since enzymes are proteins, taking \( r = 10R \), \( c_{A} = 10^{7} \text{ molecules/} \mu \text{m}^{3} \), \( c_{B} = 0 \) and \( R = 10d = 10 \text{ nm} \), yields \( f/f_{\text{th}} \approx 10 \) and we conclude that the attractive force between enzymes should exceed thermal force at separations smaller than a few hundred nanometers. Such forces can lead to the formation of enzyme aggregates (metabolons) [6].

Our consideration so far was restricted to spherically symmetric catalytic particles. This idealization is per-
The region where interaction force is repulsive, in other areas it is attractive. The plot is constructed for $D_A = D_B$; the only modification required in the case $D_A \neq D_B$ is change of scales along axes.

Many catalysts. We now return from considering the force between two catalytic particles to the case when there are many catalysts. Consider a crowd of catalytic particles, with density of $\rho(r)$ catalysts per unit volume. On the mean field level, overall behavior should be described by the volume fraction of catalytic centers in space, $\phi(r) = v\rho(r)$, where $v$ is the volume of the region in which catalysis takes place on the surface of the particle. Now, let $c_A(r)$ and $c_B(r)$ be the concentration fields of “fuel” and “exhaust” molecules $A$ and $B$, coarse grained over distances large compared to the typical distance between catalysts, $\ell (\ell^{-3} \sim \rho)$. Then mean field equations for concentrations of $A$ and $B$ read

$$
\dot{c}_A(r) = D_A \nabla^2 c_A(r) - \phi(r) [k_{\to} c_A(r) - k_{\to} c_B(r)] 
$$

$$
\dot{c}_B(r) = D_B \nabla^2 c_B(r) + \phi(r) [k_{\to} c_A(r) - k_{\to} c_B(r)]
$$

(for simplicity we here consider only one species of $A$ and one for $B$; generalization is straightforward). In steady state, time derivatives vanish, and, combining Eqs. [6] with proper weights, we find that the “field of chemical imbalance” $\psi(r) \equiv k_{\to} c_A(r) - k_{\to} c_B(r)$ satisfies

$$
\nabla^2 \psi(r) - \xi^{-2} \psi(r) = 0,
$$

meaning that the field $\psi(r)$ is screened on distances $\xi$ such that

$$
\xi^{-2} = \left[ \frac{k_{\to}}{D_A} + \frac{k_{\to}}{D_B} \right] \phi. \tag{10}
$$

Note that the distance $\xi$ can be also described as the scale at which the so-called Damköhler number is of order unity (see, e.g., [23]). For instance, if catalysts are distributed inside a sphere of radius $L$ while fuel molecules are delivered by diffusion from infinity, and exhaust molecules $B$ are absorbed also in infinity, then $\psi(x)$ penetrates up to distance $\xi$ into the catalysts-occupied domain. Accordingly, $\xi$ can be called penetration depth. This is sketched in Fig. 2.

Note that it is only the field $\psi(r)$ that is being screened, penetrating a distance $\xi$ into the crowd of catalysts; concentration fields $c_A(r)$ and $c_B(r)$ are not screened at all, and in fact $D_A c_A(r) + D_B c_B(r)$ satisfies the Laplace equation $\nabla^2 [\ldots] = 0$ and thus it is typically (except some special boundary conditions, domain topology, etc) constant throughout space (see plots in the lower part of Fig. 2).

What are the consequences of these electrostatics-like screened forces?

Consider first spherically symmetric (and thus not self-diffusiophoretic) catalysts in 3D. We can imagine that they are confined in an osmotic box impermeable for colloidal catalysts but freely permeable for molecules $A$ and $B$. Suppose interactions of $A$ and $B$ with the colloidal surface are such that the force Eq. [6] is attractive. If the size of confining box $L$ is large compared to the penetration length $\xi_0$ corresponding to the overall density of catalysts, the attractive force between catalysts will be significant only in a boundary region of thickness $\sim \xi_0$. For a smaller box with $L < \xi_0$, all catalysts will attract one another and will then tend to aggregate. Although
FIG. 2. Catalytic particles, of diameter 2\(R\) each, are distributed in a sphere of diameter 2\(L\), while “fuel” molecules \(A\) diffuse from outside, and “exhaust” molecules \(B\) diffuse out to infinity. The difference \(k_B c_A(r) - k_B c_B(r) = \psi(r)\), driving the process, is shown in shades of gray. Deep in the crowd of catalysts, there is no chemical imbalance between \(A\) and \(B\), \(\psi(x) \to 0\). In the lower plot, profiles of \(c_A(r) = c_A \left( \frac{k_B}{k_B + \frac{\partial B}{\partial A} \psi(r)} \right) / \left( \frac{k_B}{k_B + \frac{\partial B}{\partial A}} \right)\), and \(c_B(r) = c_A \left[ 1 - \frac{\psi(c_A)}{\psi(\infty)} \right] / \left( \frac{k_B}{k_B + \frac{\partial B}{\partial A}} \right)\), and \(\psi(r)\) are plotted. For this spherical geometry, based on the Eq. [9], along with boundary conditions of continuous function and its derivative and no singularity at the origin, \(\psi(r) = \psi(\infty) \left[ 1 - \frac{\xi}{r} + \frac{\xi}{r} \tanh \frac{r}{\xi} \right]\) at \(r > L\) and \(\psi(r) = \psi(\infty) \frac{\xi}{r} \sinh \frac{r}{\xi} \cosh \frac{L}{\xi}\) at \(r < L\). For plotting, we assumed \(\xi = L/5\), \(\frac{k_B}{k_B + \frac{\partial B}{\partial A}} = \frac{1}{2}\), and \(\frac{\partial B}{\partial A} = 1\).

finding the density of such aggregates is beyond the scope of this paper, because it will be determined by the balance of attractive force Eq. [6] and some short scale repulsion (e.g., excluded volume), we predict that these aggregates (micelles) will not grow beyond a size of the order of penetration depth \(\xi_1 < \xi_0\), set by the aggregate density. This is because attractive interaction inside a bigger aggregate of catalysts will be screened out.

In the opposite case where the force Eq. [6] is repulsive, we again have to prevent catalysts from flying apart, by confining them in a sort of an osmotic bag of the size less than \(\xi_0\), not permeable for catalysts, but permeable for \(A\) and \(B\) molecules. In this case, because of the long range nature of the force, catalysts are predicted to form a Wigner crystal.

An interesting and experimentally relevant case is a quasi-2D system, where catalytic colloids are confined due to gravity within a short distance from the bottom (or from the top if they float) of a container. Note that although colloidal spheres are confined in 2D, the “fuel” \(A\) and “exhaust” \(B\) molecules are diffusing in 3D. If the depth of the container is very large (infinite), the force still obeys the \(1/r^2\) law as in 3D (perhaps with a halved prefactor). Nevertheless, our predictions are very different, because there is no screening in this case. In the attractive case, we expect catalysts in 2D to form a macroscopic aggregate. For repulsive forces we expect a macroscopic 2D Wigner crystal to form (its size is not limited by \(\xi\)).

A more subtle situation exists when the container has a finite depth \(H\). Clearly, on scales less than \(H\) along the surface, catalysts should behave as if the container was very deep, i.e., with no screening. However, on larger scales screening takes over. A naive estimate suggests \(\phi \sim \nu/H^2\), where \(\ell\) is the typical distance between catalysts in 2D. According to Eq. [10], this predicts \(\xi \propto H^{1/2}\), and we expect attractive catalysts to assemble in 2D aggregates of size \(\sim \xi\).

This conclusion is reminiscent of the fact that “live” colloids in the experiments by Theurkauff et al [22] and by Pallaci et al [19] formed 2D aggregates of limited size that did not grow further. These colloids were not spherically-symmetric and exhibited self-diffusiophoretic swimming. Moreover, they were shown [19] to form the so-called “living crystals”, a finding which was interpreted as an experimental confirmation of the theoretically predicted activity-driven condensation [24] [33]. We speculate that the limited size of the aggregates could be due to screening (screening does not require catalysts to be spherically symmetric and is expected to take place even for self-diffusiophoretically driven swimmers).

To summarize, we have presented a very simple schematic theory demonstrating that spherical particles capable of catalyzing some chemical reaction experience peculiar interaction which exists as long as the reaction is maintained out of equilibrium (e.g., by a constant supply of high free energy “fuel” molecules) and which obeys the \(1/r^2\) law for the force.

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