ARTICLE

Simulation of diffusio-phoretic motion of colloidal particle suppressed by bound solutes within adsorption shell

Jiachen Wei^{a,b}

^aInstitute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China; ^bDepartment of Chemistry, University of Cambridge, CB21EW, UK

ARTICLE HISTORY

Compiled January 15, 2020

ABSTRACT

Colloidal particle submerged in non-equilibrium fluid with a concentration gradient of solutes experiences diffusio-phoresis. Such directional transport originates from the driving forces that exert on fluid in a microscopic boundary layer surrounding the colloid. Based on a simple model of spherical colloid fixed in a concentration gradient of solutes, molecular dynamics simulations are performed to determine the interaction parameters that maximize the diffusio-phoretic mobility, which cannot be properly measured by conventional continuum theory. The diffusio-phoretic mobility is found to depend non-monotonically on the strength of the interaction between the colloid and solutes, due to the presence of bound solutes within adsorption shell that cannot contribute to diffusio-phoresis. The results also show that the phoretic mobility depends sensitively on the density of solutes in bulk, due to the uneven distribution of excess particles surrounding the colloid at microscopic level. The simulations suggest that diffusio-phoresis may in principle be applied to the selective transport, separation and purification for colloidal systems. By substituting the spherical colloid with other realistic macromolecules, the model could provide results that are quantitatively comparable with experiments.

KEYWORDS

diffusio-phoresis, molecular dynamics, colloid, phoretic transport

1. Supplementary information



Figure S1. The radial distribution function g(r) at three different $\epsilon_{\beta c}$, with solute density $\rho_{\beta}^{bulk} = 0.05$. we find $\rho(r)$ barely changes as $\epsilon_{\beta c}$ is increased from 1.0 to 2.6, although the local composition of the fluid is changed: as $\epsilon_{\beta c}$ is increased, solute particles tend to displace the solvent particles surrounding the colloid. However, for a still larger value $\epsilon_{\beta c} = 5.0$, the total density of adsorbed fluid increases significantly, indicated by the blue arrow.



Figure S2. The number density of fluids, ρ , and force density in x direction, F_x , as a function of distance to the fixed colloid, r, for $\epsilon_{\beta c} = 2.6$ and $\epsilon_{\beta c} = 5.0$. The density of solute in bulk is $\rho_{\beta}^{bulk} = 0.05$. While the shape of $\rho(r)$ is barely changed by increasing $\epsilon_{\beta c}$ from 1.0 to 2.6, its first peak at r = 3.0 grows sharply for $\epsilon_{\beta c} = 5.0$. The aggregated solutes at r = 3 form a sticky shell-region that reduces the phoretic effect: for $\epsilon_{\beta c} = 2.6$, the magnitude of diffusiophoretic flow reaches maximum (i.e.), and F_x is negative at r = 3.0; for $\epsilon_{\beta c} = 5.0$, the attraction between solute and colloid becomes so strong that F_x becomes positive at r = 3.0and a peak around $r \sim 3.2$ is observed. Although the aggregation of solutes increases the magnitude of force density around $r \sim 2.8$, the formation of the sticky shell generates the second peak of F_x that counterbalances the interior phoretic force by reducing the slip length. More importantly, for $\epsilon_{\beta c} = 2.6$, F_x is always negative at the peaks of $\rho(r)$. For $\epsilon_{\beta c} = 5.0$, however, the peaks of $\rho(r)$ slightly shifted, resulting in the counterbalance effect.



Figure S3. The force density in x direction for fluids (F_x) , solutes (F_x^{β}) and solvents (F_x^{α}) , as a function of distance to the fixed colloid, r, for $\epsilon_{\beta c} = 2.6$. It shows that there are regions where the sign of F_x changes. Except at short distances (r < 2.65), this effect cannot be due to a local accumulation of solvent because the only difference between solvent and solute is the strength of their interaction with the colloid. Hence, the sign changes of the local force density at larger distances are due to the restoring force that results from the overall deformation of the density distribution around the colloid. This deformation becomes larger for larger values of $\epsilon_{\beta c}$, because then a shell of solute particles is effectively trapped around the colloid. The net effect of this polarization is that the overall phoretic flow decreases for larger values of $\epsilon_{\beta c}$ (immobilised solute shells do not contribute to diffusio-phoresis).



Figure S4. The dependence of particle flux in x direction J_x on r, at x = 0 plane. When $\epsilon_{\beta c}$ is increased from 1.0 to 2.6, the magnitude of $J_x(r)$ near the colloid (r < 4.0) increases, indicating an increase of the phoretic force. However, when $\epsilon_{\beta c}$ is further increased to 5.0, the magnitude of $J_x(r)$ decreases due to the fact that strongly adsorbed solute particles are less mobile. For r > 4.0, the flux is roughly constant at a value: $J_x = -3.52$ for $\epsilon_{\beta c} = 2.6$, and $J_x = -1.68$ for $\epsilon_{\beta c} = 5.0$, both of which are determined by averaging the value of J_x in bulk at z > 8.0 and z < -8.0. For $\epsilon_{\beta c} = 1.0$, there is no phoretic effect. Hence the observed variations in J_x give an indication of the statistical noise.



Figure S5. The dependence of velocity of fluids v_x on the scaled coordinate number N_c/N_c^0 for simulations based on implicit gradient. The coordinate number N_c is defined as the number of bound solutes trapped by colloid within the distance $r_{ic} < 4.5$, where an excess distribution of solute particles is determined. N_c^0 denotes the coordinate number determined at $\epsilon_{\beta c} = 1.0$. The results indicate that at about $N_c = 2N_c^0$ the maximum v_x is reached.



Figure S6. The dependence of v_x on $\epsilon_{\beta c}$ for different strengths of the colloid-solvent interaction, $\epsilon_{\alpha c}$. To compare original Morse potential U^M introduced in Eq.2 of the main text with purely repulsive colloid-fluid interactions, a Morse potential that is truncated and shifted at r = 3.0 (with $\epsilon_{\alpha c} = 1.0$), U^{MTS} , is used, and the corresponding results are indicated by the blue curve with triangles. The strength of this interaction has only a weak effect on v_x . The maximum velocity $v_x^m \sim -0.0045$ are obtained for all three cases. However, with a decrease of interaction strength between solvent and colloid, $\epsilon_{\alpha c}$, from 1.0 to 0.2, the maximum v_x^m is reached at lower $\epsilon_{\beta c}$. If the attractive part of solvent-colloid interaction is completely removed, v_x^m is reached at $\epsilon_{\beta c} \sim 1.0$.



Figure S7. The difference of solute density of left (x < 0) and right (x > 0) part of the system, $\delta \rho_{\beta} = \rho_{\beta}(x < 0) - \rho_{\beta}(x > 0)$, as a function of distance to the fixed colloid, r, at different solute density in bulk ρ_{β}^{bulk} . The interaction strength between solute and colloid is fixed at $\epsilon_{\beta c} = 2.6$. By increasing ρ_{β}^{bulk} from 0.05 to 0.25, the peak value at r = 3.0 drops, while for r > 4.0 the shape of $\delta \rho_{\beta}(r)$ is kept. When ρ_{β}^{bulk} is further increased to 0.50, the magnitude of both the first and second peak of $\delta \rho_{\beta}$ decreases significantly. This indicates that the polarization of the distribution of bound solutes close to the fixed colloid is reduced with the increase of ρ_{β}^{bulk} .



Figure S8. The dependence of velocity of fluids v_x on the distance between colloids d for system containing two adjacent colloidal particles that are either vertically (black) or horizontally (red) aligned. The dashed line indicates v_x for system with a single colloid. The solute-colloid interaction is fixed at $\epsilon_{\beta c} = 2.4$. For $d \leq 6$, the magnitude of v_x is smaller for system that contains horizontally aligned colloids, and larger for system contains vertically aligned colloids. This difference in v_x decreases with the increase of d, and becomes negligible for $d \geq 12$.