Characterisation of Soil Colloids (10 points)

Colloidal science is useful for characterising soil particles because many of them can be regarded as colloidal particles of micrometre size. For example, Brownian motion (random motion of colloidal particles) can be used to measure particle sizes.

Part A. Motions of colloidal particles (1.6 points)

We analyse the one-dimensional Brownian motion of a colloidal particle with mass M. The equation of motion for its velocity $v(t)$ reads:

$$M\dot{v} = -\gamma v(t) + F(t) + F_{\text{ext}}(t), \tag{1}$$

where γ is the friction coefficient, $F(t)$ is a force due to random collisions with water molecules, and $F_{\text{ext}}(t)$ is an external force. In Part A, we assume $F_{\text{ext}}(t) = 0$.

A.1	Consider that a water molecule collides with the particle at $t = t_0$, giving impulse I_0, and $F(t) = 0$ afterwards. If $v(t) = 0$ before the collision, $v(t) = v_0 e^{-(t-t_0)/\tau}$ for $t > t_0$. Determine v_0 and τ, using I_0 and necessary parameters in Eq.(1).	0.8pt

In the following, you may use τ in your answers.

A.2	In reality, water molecules collide with the particle one after another. Suppose that the ith collision gives the impulse I_i at time t_i and determine $v(t)$ with the condition that $t > 0$ and $v(0) = 0$. Also, give the inequality that specifies the range of t_i that needs to be considered for a given t. In the answer sheet, it is not necessary to specify this range in the expression for $v(t)$.	0.8pt

Part B. Effective equation of motion (1.8 points)

The results so far imply that particle velocities $v(t)$ and $v(t')$ may be regarded as uncorrelated random quantities if $|t - t'| \gg \tau$. On this basis, we introduce a theoretical model to approximately describe the one-dimensional Brownian motion, where the velocity changes randomly at each time interval δ $(\gg \tau)$, i.e.,

$$v(t) = v_n \quad (t_{n-1} < t \leq t_n), \tag{2}$$

with $t_n = n\delta$ $(n = 0, 1, 2, \cdots)$ and a random quantity v_n. It satisfies

$$\langle v_n \rangle = 0, \quad \langle v_n v_m \rangle = \begin{cases} C & (n = m), \\ 0 & (n \neq m), \end{cases} \tag{3}$$

with a parameter C depending on δ. Here $\langle X \rangle$ indicates the expectation value of X. That is, if you draw random numbers X infinitely many times, the mean will be $\langle X \rangle$.

Now, we consider the particle displacement $\Delta x(t) = x(t) - x(0)$ for $t = N\delta$ with an integer N.

B.1	Determine $\langle \Delta x(t) \rangle$ and $\langle \Delta x(t)^2 \rangle$ using C, δ, and t.	1.0pt

B.2	The quantity $\langle \Delta x(t)^2 \rangle$ is called the mean squared displacement (MSD). It is a characteristic observable of the Brownian motion, which corresponds to the limiting case $\delta \to 0$. From this, we can show that $C \propto \delta^\alpha$ and $\langle \Delta x(t)^2 \rangle \propto t^\beta$. Determine the values of α and β.	0.8pt

Part C. Electrophoresis (2.7 points)

Here we discuss electrophoresis, i.e., the transport of charged particles by an electric field. A suspension of colloidal particles with mass M and charge $Q\ (>0)$ is put in a narrow channel with a cross-section A (Fig.1(a)). We ignore the interaction between particles, the effects of the wall, the fluid, the ions therein, and gravity.

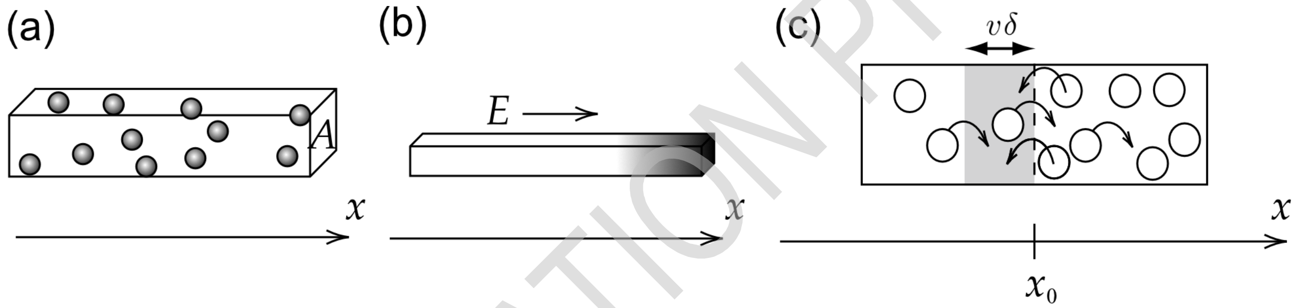


Fig.1: Setting for Part C.

By applying a uniform electric field E in the x-direction, particles are transported and their concentration $n(x)$ (particle number per unit volume) becomes non-uniform (Fig.1(b)). When E is removed, this non-uniformity gradually disappears. This is due to the Brownian motion of particles. If $n(x)$ is not uniform, the numbers of right-going and left-going particles may differ (Fig.1(c)). This generates a particle flux $J_D(x)$, the mean number of particles flowing at x along the x-axis per unit cross-sectional area and unit time. This flux is known to satisfy:

$$J_D(x) = -D\frac{dn}{dx}(x), \tag{4}$$

where D is called the diffusion coefficient.

Now let's assume, for simplicity, that half of the particles have velocity $+v$ and the other half have velocity $-v$. Let $N_+(x_0)$ be the number of particles with velocity $+v$ that cross x_0 from left to right per unit cross-sectional area and unit time. For particles with velocity $+v$ to cross x_0 in the time interval δ, they should be within the shaded region of Fig.1(c). Since δ is small, we have $n(x) \simeq n(x_0) + (x - x_0)\frac{dn}{dx}(x_0)$ in this region.

C.1	Express $N_+(x_0)$ using necessary quantities from $v,\ \delta,\ n(x_0)$, and $\frac{dn}{dx}(x_0)$.	0.5pt

We define $N_-(x_0)$ as the counterpart of $N_+(x_0)$ for the velocity $-v$. With this, we have $J_D(x_0) = \langle N_+(x_0) - N_-(x_0) \rangle$. According to Eq.(3), we have $\langle v^2 \rangle = C$.

C.2	Determine $J_D(x_0)$ using necessary quantities out of C, δ, $n(x_0)$, and $\frac{dn}{dx}(x_0)$. Use this and Eq.(4) to express D in terms of C and δ, and $\langle \Delta x(t)^2 \rangle$ in terms of D and t.	0.7pt

Now we discuss the effect of osmotic pressure Π. It is given by $\Pi = \frac{n}{N_A} RT = nkT$ with the Avogadro constant N_A, the gas constant R, temperature T, and the Boltzmann constant $k = \frac{R}{N_A}$. Let us consider the non-uniform concentration formed under the electric field E (Fig.1(b)). Since $n(x)$ depends on x, so does $\Pi(x)$. Then, the forces due to $\Pi(x)$ and $\Pi(x+\Delta x)$ must be balanced with the total force from the field E acting on the particles (Fig.2). Here, we consider a small Δx so that $n(x)$ can be regarded as constant over this range, while $n(x+\Delta x) - n(x) \simeq \Delta x \frac{dn}{dx}(x)$.

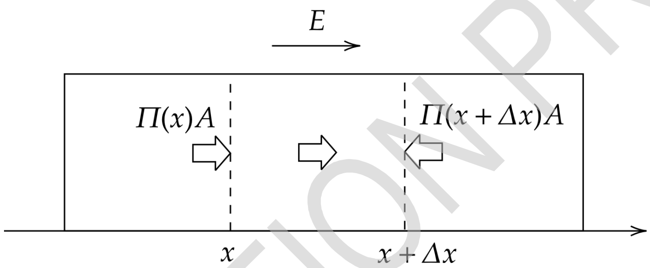


Fig.2: Force balance.

C.3	Express $\frac{dn}{dx}(x)$ using $n(x)$, T, Q, E, and k.	0.5pt

Let us now discuss the balance of the flux. Besides the flux $J_D(x)$ due to the Brownian motion, there is also a flux due to the electric field, $J_Q(x)$. It is given by

$$J_Q(x) = n(x)u, \tag{5}$$

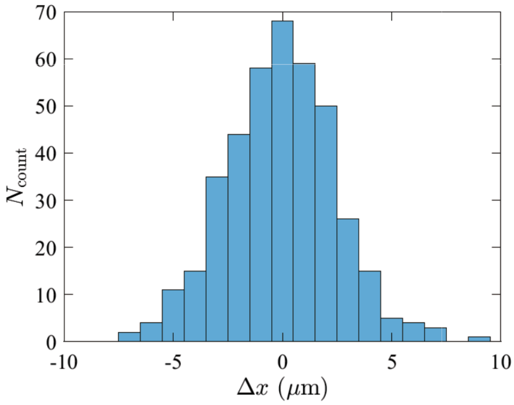
where u is the terminal velocity of particles driven by the field.

C.4	To determine u, we use Eq.(1) with $F_{\text{ext}}(t) = QE$. Since $v(t)$ is fluctuating, we consider $\langle v(t) \rangle$. Assuming $\langle v(0) \rangle = 0$ and using $\langle F(t) \rangle = 0$, evaluate $\langle v(t) \rangle$ and obtain $u = \lim_{t\to\infty} \langle v(t) \rangle$.	0.5pt

C.5	The flux balance reads $J_D(x) + J_Q(x) = 0$. Express the diffusion coefficient D in terms of k, γ, and T.	0.5pt

Part D. Mean squared displacement (2.4 points)

Suppose we observed the Brownian motion of an isolated, spherical colloidal particle with radius $a = 5.0\ \mu$m in water. Figure 3 shows the histogram of displacements Δx measured in the x-direction at every interval $\Delta t = 60$ s. The friction coefficient is given by $\gamma = 6\pi a \eta$ with water viscosity $\eta = 8.9 \times 10^{-4}$ Pa · s and the temperature was $T = 25\ ^\circ$C.



Δx (μm)	-10	-9	-8	-7	-6	-5	-4
N_{count}	0	0	0	2	4	11	15
Δx (μm)	-3	-2	-1	0	1	2	3
N_{count}	35	44	58	68	59	50	26
Δx (μm)	4	5	6	7	8	9	10
N_{count}	15	5	4	3	0	1	0

Fig.3: Histogram of displacements.

D.1	Estimate the value of N_A without using the fact that it is the Avogadro constant, up to two significant digits from the data in Fig.3. The gas constant is $R = 8.31$ J/K · mol. Do not use the value of the Boltzmann constant k given in the General Instructions. As for the Avogadro constant, you might obtain a value different from that in the General Instructions.	1.0pt

Now, we extend the model in Part B to describe the motion of a particle with charge Q under an electric field E. The particle's velocity $v(t)$ considered in Eq.(2) should be replaced by $v(t) = u + v_n$ $(t_{n-1} < t \leq t_n)$ with v_n satisfying Eq. (3) and u being the terminal velocity considered in Eq.(5).

D.2	Express the MSD $\langle \Delta x(t)^2 \rangle$ in terms of u, D, and t. Obtain approximate power laws for small t and large t, as well as the characteristic time t_* where this change occurs. Draw a rough graph of the MSD in a log-log plot, indicating the approximate location of t_*.	0.8pt

Next, we consider swimming microbes (Fig.4(a)), in one dimension for simplicity (Fig.4(b)). These are spherical particles with radius a. They swim at velocities $+u_0$ or $-u_0$, where the sign is chosen randomly at every time interval δ_0 without correlation. The observed motion is a combination of displacements due to swimming and those due to the Brownian motion of a spherical particle.

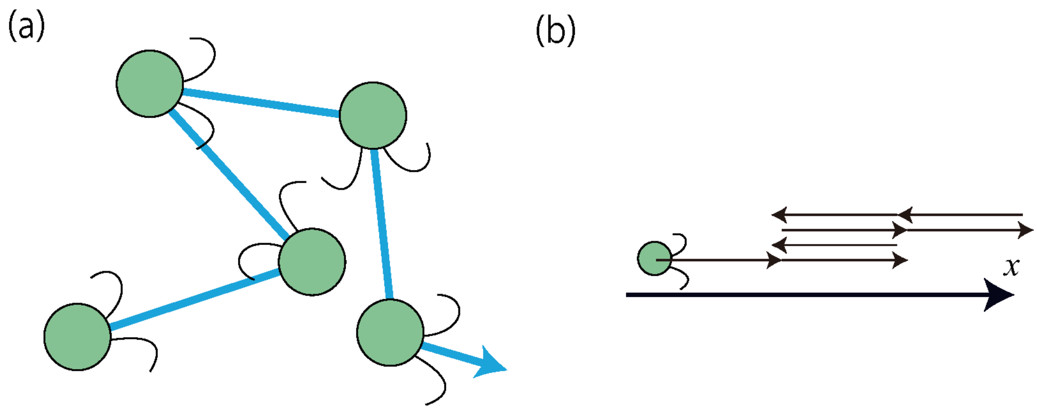


Fig.4: (a) Motion of microbes. (b) Its one-dimensional version.

D.3 Figure 5 displays the MSD $\langle \Delta x(t)^2 \rangle$ of those microbes, showing different power laws for small, large, and intermediate t, as indicated by dashed lines. Obtain the power law for each time range and express it using necessary quantities from D, u_0, δ_0, and t. 0.6pt

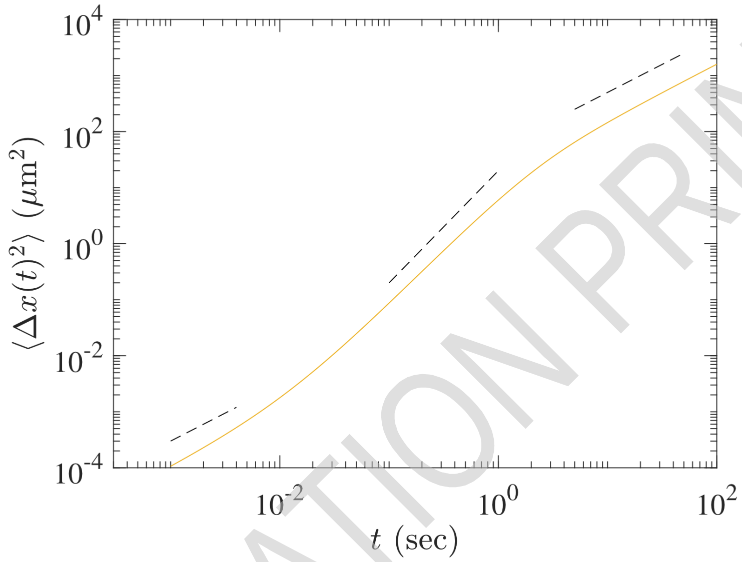


Fig.5: Mean squared displacement of the microbes.

Part E. Water purification (1.5 points)

Here we discuss the purification of water containing colloid-like soil particles, by adding electrolytes to coagulate them. Particles interact through the van der Waals force and the electrostatic force, the latter including effects of both surface charges and the surrounding layer of oppositely charged ions (such ions and their layer are called counter-ions and the electric double layer, respectively; see Fig.6(a)). As a result, the interaction potential for particle separation distance d (Fig.6(b)) is given by

$$U(d) = -\frac{A}{d} + \frac{B\epsilon(kT)^2}{q^2} e^{-d/\lambda}, \tag{6}$$

where A and B are positive constants, ϵ is the dielectric constant of water, and λ is the thickness of the electric double layer. Assuming that charges of ions are $\pm q$, we have

$$\lambda = \sqrt{\frac{\epsilon kT}{2N_A q^2 c}}, \tag{7}$$

where c is the molar concentration of ions.

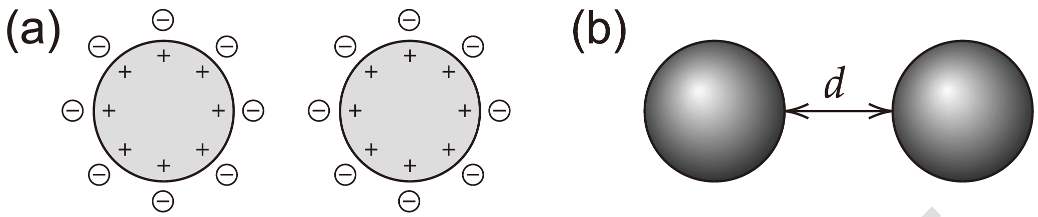


Fig.6: (a) Surface charges of colloidal particles and counter-ions. (b) Definition of the distance d.

E.1	The addition of sodium chloride (NaCl) to the suspension causes colloidal particles to coagulate. Determine the lowest concentration c of NaCl necessary for coagulation. It is sufficient to consider two particles without thermal fluctuations, i.e., $F(t) = 0$ in Eq.(1), and assume that the terminal velocity for the given potential force is reached instantaneously.	1.5pt