Chapter 7. Transport Phenomena of Nanoparticles

7.1 Drag force

(1) Stokes' law

** Drag force, F_D:*

- net force exerted by the fluid on the spherical particle in the direction of flow

$$F_D = C_D \left(\frac{\pi}{4} d_p^2 \right) \frac{\rho_f U^2}{2}$$

Area exerted by friction	Kinetic energy of unit-mass fluid

where U : relative velocity between particle and fluid

C_D: drag coefficient

cf. For pipe flow

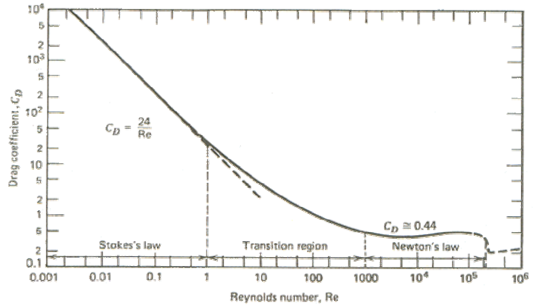
$$\tau_w = f \frac{\rho_f U^2}{2} \rightarrow F_w = f(\pi DL) \frac{\rho_f U^2}{2}$$

where f: Fanning friction factor

* C_D *vs.* Re_p

where $\mathrm{Re}_p = \dfrac{d_p U \rho_f}{\mu}$

ρ, μ: *density and viscosity of fluid*



\- *For* $Re_p < 1$ *(creeping flow region)*

$$F_D = 3\pi d_p \mu U \qquad \textit{Stokes' law}$$

$$F_D = \left(\frac{24}{\mathrm{Re}_p}\right)\left(\frac{\pi}{4} d_p^2\right)\frac{\rho_f U^2}{2}$$

$$\therefore C_D = \frac{24}{\mathrm{Re}_p}$$

cf. for pipe flow $f = \dfrac{16}{\mathrm{Re}}$

\- *For* $500 < Re_p < 200{,}000$ $\qquad C_D = \sim 0.44$

For $1 < Re_p < 500$ $\qquad C_D = \dfrac{24}{\mathrm{Re}_p}\left(1 + 0.15\,\mathrm{Re}_p^{0.687}\right)$

(2) Non-continuum Effect

** Mean-free path of fluid*

$$\lambda = \frac{1}{\sqrt{2} n_m \pi d_m^2}$$

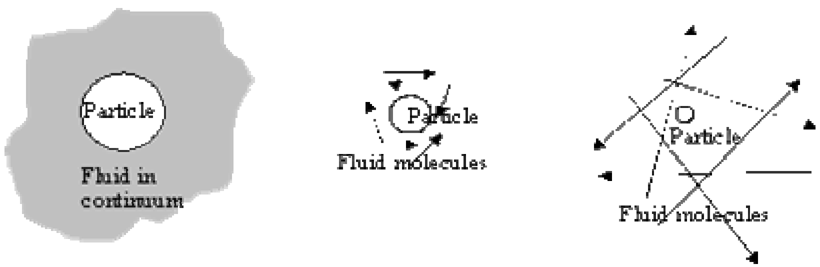
where n_m *: number concentration of molecules*

d_m*: diameter of molecules*

For air at 1 atm and 25°C, $\lambda = 65.1nm$

For water at 25°C, $\lambda = ?$

** Particle-fluid interaction*



Continuum regime   transition regime   free-molecule regime

* *Knudsen number* $K_n = \dfrac{\lambda}{d_p}$

-*Continuum regime* $K_n \sim 0$ *(<0.1)*

-*Transition regime* $K_n \sim 1$ *(0.1~10)*

-*Free-molecular regime* $K_n \sim \infty$ *(>10)*

- *Particles in water is always in continuum regime…*

* *Corrected drag force*

$$F_d = \frac{3\pi d_p \mu U}{C_C}$$

where C_c*: Cunnigham correction factor*

$$C_C = 1 + K_n\left[20514 + 0.8\exp\left(-0.55/K_n\right)\right]$$

- *Particles in water do not need noncontinuum correction…*

In air at 1atm and 25°C

d_p, μm	C_c
0.01	22.7
0.05	5.06
0.1	2.91
1.0	1.168
10	1.017

(3) Nonspherical particles χ

* *Shape correction factor,* $\chi = \dfrac{F_D}{3\pi d_\upsilon \mu U}$

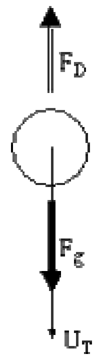
Dynamic shape factors of powders

Powders	Dynamic shape factor
sphere	1.00
cube	1.08
Cylinder (L/D=4)	
axis horizontal	1.32
axis vertical	1.07
bituminous coal	1.05–1.11
quartz	1.36
sand	1.57
talc	2.04

7.2 Migration in Gravitational Force Field

For the particle suspending in the fluid

- *Force balance* $F_D = F_g - F_B$



$$\therefore C_D\left(\frac{\pi}{4}d^2{}_p\right)\frac{\rho_f U^2}{2} = \frac{\pi}{6}\left(\rho_p - \rho_f\right)d^3{}_p g$$

$$\therefore U_T = \left[\frac{4}{3}\frac{gd_p}{C_D}\left(\frac{\rho_p - \rho_f}{\rho_f}\right)\right]^{1/2}$$

Terminal settling velocity

- *For Stokes' law regime*

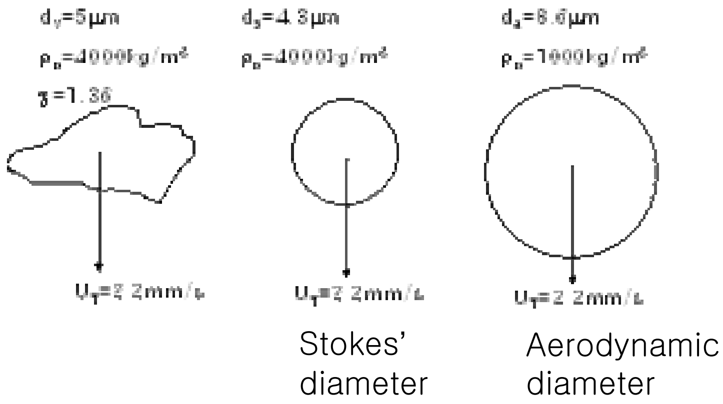
$$\frac{3\pi d_p \mu U}{C_c} = \frac{\pi}{6}\left(\rho_p - \rho_f\right)d^3{}_p g$$

$$\therefore U^T = \frac{\left(\rho_p - \rho_f\right)g d^2{}_p C_c}{18\mu}$$

[a]*For unit density particle in air at 1atm and 25°C*

d_p, μm	U_T, cm/s[a]
0.1	8.8×10^{-5}
0.5	1.0×10^{-3}
1.0	3.5×10^{-3}
5.0	7.8×10^{-2}
10.0	0.31

** Dynamic equivalent diameters – calculated in air*



Irregular particles and its equivalent spheres

In general

** Migration velocity*

$$F_{ext} = F_D \left(= \frac{3\pi\mu d_p}{C_c} U_m \right)$$

where U_m: migration or drift velocity in the fields

Note gravitational migration velocity: terminal settling velocity, U_T

** Number flux by migration*

$$\vec{J} = n\vec{U}_m$$

where n: particle number concentration

Centrifugal migration

$$F_c = m_p\left(1-\frac{\rho_f}{\rho_p}\right)\frac{U^2{}_t}{r} = m_p\left(1-\frac{\rho_f}{\rho_p}\right)r\omega^2$$

Acceleration of centrifugation>>g

$$\therefore U_{cf} = \frac{\left(\rho_p - \rho_f\right)d^2{}_p U^2{}_t C_c}{18\mu r}$$

Electrical Migration

$$\vec{F} = q\vec{E} = n_e eE$$

where q: charge of particles

E : strength of electric field

e: charge of electron (elementary unit of charge)

n_e : number of the units

$$\therefore U_e = \frac{n_e eEC_c}{3\pi\mu d_p}$$

* Charging of particles

- Applied to electrostatic precipitation

7.3 Electrical Migration

$$\vec{F} = q\vec{E} = n_e eE$$

where *q: charge of particles*

E : strength of electric field

e: charge of electron (elementary unit of charge)

n_e *: number of the units*

$$\therefore U_e = \frac{n_e eEC_c}{3\pi\mu d_p}$$ *Electrical migration velocity*

- Electrical mobility

$$Z_i = \frac{U_0}{E} = \frac{n_e eC_c}{3\pi\mu}$$

- Applied to electrostatic precipitation in gas

** Charging of particles in gas (Later for the case of liquid)*

- Direct ionization

- Static electrification: electrolyte, contact, spray, tribo, flame)

- Collision with ions or ion cluster

** Diffusion charging*

- Collision by ions and charged particles in Brrownian motion

$$n(t) = \frac{d_p kT}{2K_E e^2} \ln\left[1 + \frac{\pi K_E d_p \overline{c_i} e^2 N_i t}{2kT}\right]$$

Where $\overline{c_i}$ *: mean thermal speed of the ions(=240m/s at SC)*

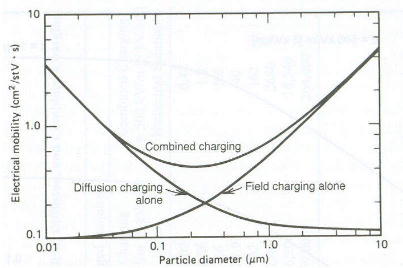
N_i*: ion concentration*

K_E*: proportionality factor depending on unit used…* $K_E = \frac{1}{4\pi\varepsilon_0}$

** Field charging*

- Charging by unipolar ions in the presence of a strong electric field

$$n(t) = \left(\frac{3\varepsilon}{\varepsilon + 2}\right)\left(\frac{E d_p^{\ 2}}{4K_E e}\right)\left(\frac{\pi K_E e Z_i N_i t}{1 + \pi K_E e Z_i N_i t}\right)$$



Where ε_r*: relative permissibility of the particle*

Z_i*: mobility of ions(=0.00015m2/V s*

- Saturated after sufficient time…

** Charge limit*

- By electron ejection from mutual repulsion on the surface

$$n_{\max} = \frac{{d_p}^2 E_L}{4 K_E e}$$

where E_L: surface field strength required for spontaneous emission of electrons(=9.0×10^8 V/m)

- Rayleigh limit

If mutual repulsion > surface tension force for liquid droplets

$$n_{\max} = \left(\frac{2\pi\sigma {d_p}^3}{K_E e^2} \right)^{1/2}$$

** bipolar charging: Kr_{85}*

Electrophoresis

- Movement of nanoparticles in liquid medium

** Zeta potential : potential at the slip plane**

- Plane that separates the tightly bound liquid layer from the rest of liquid

- ~Stern layer

- determines the stability of colloidal dispersion or a sol

- requires >25mV for the stability

$$\zeta = \frac{q}{2\pi\varepsilon_0\varepsilon_r d_p(1+\kappa d_p/2)}$$

** Electrical migration velocity*

$$U_E = \frac{2\varepsilon_0\varepsilon_r\zeta E}{3\pi\mu}$$

** Electrical mobility*

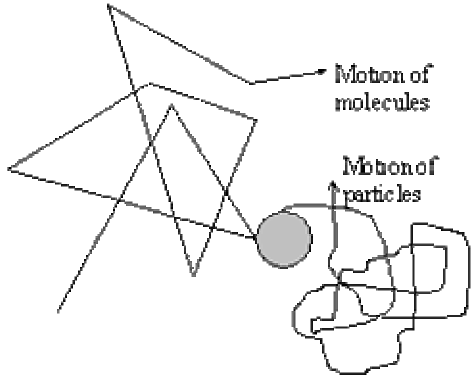
$$B_E = \frac{U_0}{E} = \frac{2\varepsilon_0\varepsilon_r\zeta}{3\pi\mu}$$

7.3 Migration by Interaction with Fluids

(1) Diffusion

* *Brownian motion*

: Random wiggling motion of particles by collision of fluid molecules on them



* *Brownian Diffusion* :

Particle migration due to concentration gradient by Brownian motion

$$\vec{J} = -D_p \vec{\nabla} n$$

Fick's law

where D_p*: diffusion coefficient of particles,* cm^2/s

n *: particle concentration by number*

cf. Diffusion of molecules

* Coefficient of Diffusion

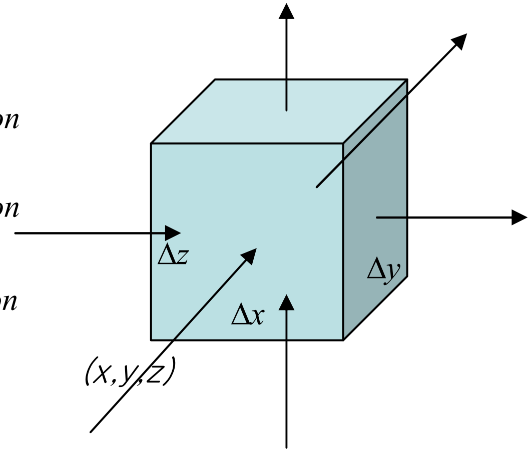
$$D_p = \frac{kTC_c}{3\pi\mu d_p}$$

Diffusion Coefficient of Unit-density sphere at 20°C in air

Particle diameter,	Diffusion coefficient, cm^2/s
0.00037(air molecule)	0.19
0.01	5.2×10^{-4}
0.1	6.7×10^{-6}
1.0	2.7×10^{-7}
10	2.4×10^{-8}

cf. Liquid diffusivity $10^{-5} cm^2/s$

- *Mass balance for the cube in the fluid*



$$\frac{\partial n}{\partial t}\Delta x\Delta y\Delta z = [J_x - (J_x + \Delta J_x)]\Delta y\Delta z$$ *Net input in x direction*

$$+[J_y - (J_y + \Delta J_y)]\Delta x\Delta z$$ *Net input in y direction*

$$+[J_z - (J_z + \Delta J_z)]\Delta x\Delta y$$ *Net input in z direction*

$$\therefore \frac{\partial n}{\partial t}\Delta x\Delta y\Delta z = -\Delta J_x\Delta y\Delta z - \Delta J_y\Delta x\Delta z - \Delta J_z\Delta x\Delta y$$

$$/\,\Delta x\Delta y\Delta z \quad \textit{and} \quad \Delta x, \Delta y, \Delta z \to 0$$

$$\therefore \frac{\partial n}{\partial t} = -\left(\frac{\partial J_x}{\partial x} + \frac{\partial J_y}{\partial y} + \frac{\partial J_z}{\partial z}\right) = -\vec{\nabla}\cdot\vec{J}$$

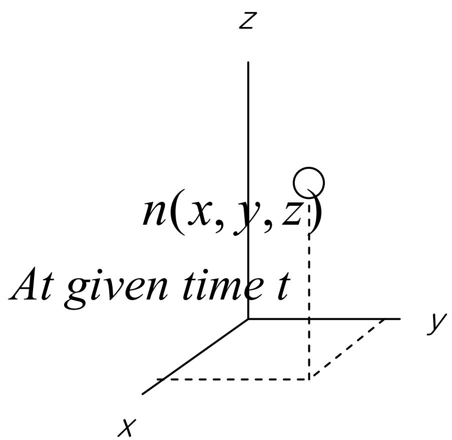
- *Introducing Fick's law*

$$\frac{\partial n}{\partial t} = \vec{\nabla}\cdot\left(D_p\vec{\nabla}n\right) = D_p\nabla^2 n \qquad B.C. \quad n = 0$$

Constant D_p

- *Integration (or solution) gives: n=n (x,y,z,t),*

or particle number concentration at (x,y,z) at t



* *One-dimensional diffusion from the origin*

$$\frac{\partial n}{\partial t} = \vec{\nabla} \cdot \left(D_p \vec{\nabla} n \right) = D_p \nabla^2 n \longrightarrow \therefore \frac{\partial n}{\partial t} = D_p \frac{\partial^2 n}{\partial x^2}$$

At t=0 n=0 for all x except x=0

At x=0, n=n_0 for all t and $\left(\frac{\partial n}{\partial x} \right)_{x=0} = 0$

The solution is :

$$n(\eta) = 1 - \frac{2}{\pi} \int_0^{\eta} e^{-\eta^2} d\eta \equiv 1 - erf(\eta) \equiv erfc(\eta)$$

Where $\eta \equiv \frac{z}{2\sqrt{D_p t}}$

Differentiating with respect to x

$$n(x,t) \frac{dn(x,t)}{n_0} = \frac{1}{(4\pi D_p t)^{1/2}} \exp\left(\frac{-x^2}{4 D_p t} \right) dx$$

Normal distribution with respect to x-axis

- *Mean displacement:* $\bar{x} = 0$

- *Standard deviation or root-mean square displacement*

$$\sigma = x_{rms} = \sqrt{2D_p t}$$

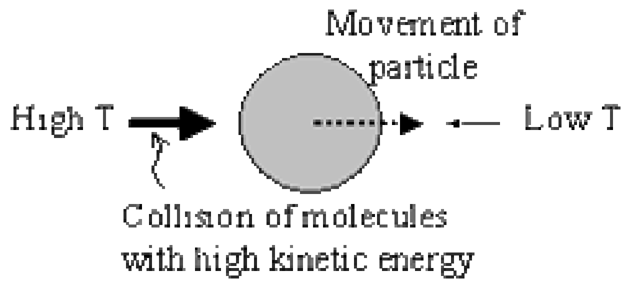
- *represent particle movement (displacement) by diffusion*

Net displacement in 1s due to Brownian motion and gravity for standard-density spheres at standard conditions

Particle diameter, μm	x_{rms} in 1s(m)	Settling in 1s(m)	x_{rms} / x_{sett}
0.01	3.3×10^{-4}	6.9×10^{-8}	4800
0.1	3.7×10^{-5}	8.8×10^{-7}	42
1.0	7.4×10^{-6}	3.5×10^{-6}	0.21
10	2.2×10^{-6}	3.1×10^{-3}	7.1×10^{-4}

(2) Thermophoresis

- *Discovered by Tyndall in 1870*



- *Examples of thermophoresis*

    - *Dust free surface on radiator or wall near it*
    - *Movement cigarette smoke to cold wall or window*
    - *Spoiling of the surface of the cold wall*
    - *Scale formation on the cold side in the heat exchanger*

** In free molecular regime*

Waldmann and Schmidt(1966) $\vec{F}_{th} = -p\lambda d^2{}_p \frac{\vec{\nabla} T}{T}$

$$\therefore \vec{U}_{th} = -\frac{3\nu\vec{\nabla} T}{4\left(1+\frac{\pi\alpha}{8}\right)T} = \sim 0.55\nu\frac{\vec{\nabla} T}{T}$$

- *independent of* d_p

** Correction for continuum fluid-particle interaction*

Brock(1962)

$$\vec{F}_{th} = \frac{-9\pi\mu^2 d_p H\vec{\nabla}T}{2\rho_G T}$$

where $$H \sim \frac{1}{1+6Kn}\left(\frac{\frac{k_G}{k_p}+4.4Kn}{1+2\frac{k_G}{k_p}+8.8Kn}\right)$$

$$\therefore \vec{U}_{th} = \frac{-3\mu C_c H\vec{\nabla}T}{2\rho_G T}$$

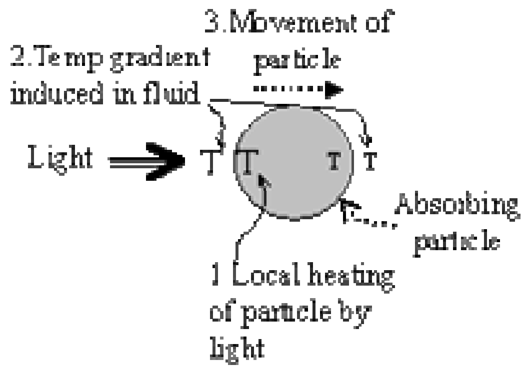
Terminal settling and thermophoretic velocities in a temperature gradient of 1°C/cm at 293K

Particle diameter(μm)	Terminal settling velocity (m/s)	Thermophoretic velocities in a temperature gradient of 1°C/cm at 293K[a]
0.01	6.7×10^{-8}	2.8×10^{-6}
0.1	8.6×10^{-7}	2.0×10^{-6}
1.0	3.5×10^{-5}	1.3×10^{-6}
10.0	3.1×10^{-3}	7.8×10^{-7}

[a] $k_p = 10k_a$

(3) Phoresis by Light

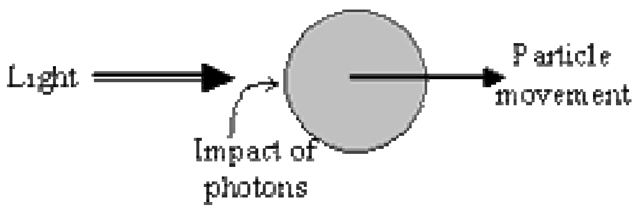
<u>Photophoresis</u>



- *Where to be heated depends on the refractive index of the particle*

  e.g. submicron particles in the upper atmosphere

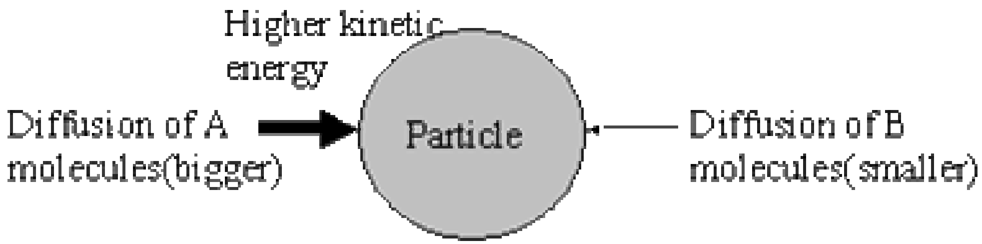
<u>Radiation pressure</u>



e.g. tails of comet, laser-lift of particles

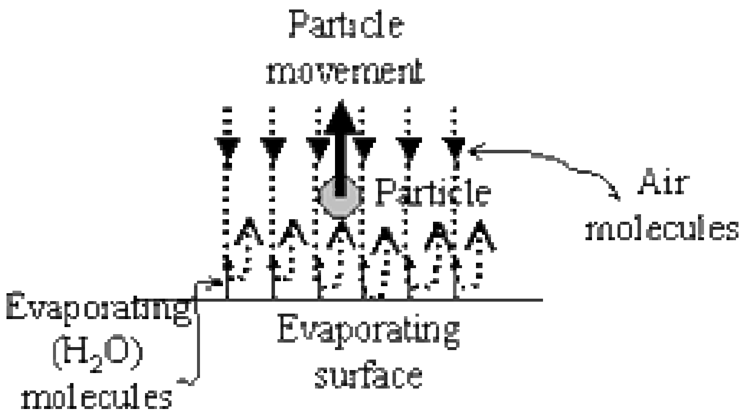
(4) Diffusion of medium

Diffusiophoresis

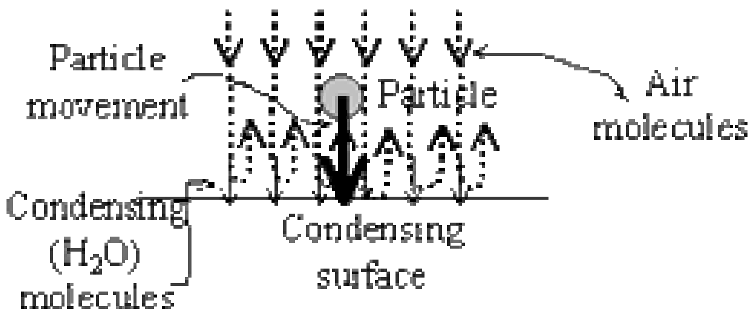


Stefan flow

- *For evaporating surface*



- *For condensing surface*



e.g. Venturi scrubber

7.4 Inertial Motion and Impact of Particles

(1) Inertial motion

- For Stokesian particles

Momentum (force) balance for a single sphere

Neglecting buoyancy force

$$\therefore \frac{\pi}{6} d^3{}_p \rho_p \frac{dU}{dt} = -\frac{3\pi\mu d_p U}{C_c}$$

$$m_p \frac{dU}{dt} = -F_D$$

Integrating once, defining relation time as $\tau = \dfrac{\rho_p d^2{}_p C_c}{18\mu}$

$$U = U_0 e^{-t/\tau}$$

Integrating twice $\quad x = U_0 \tau \left(1 - e^{-t/\tau}\right)$

$$As \ \frac{t}{\tau} \to \infty, \qquad x \sim U_0 \tau = \frac{\rho_p d^2{}_p U_0 C_c}{18\mu} \equiv s$$

stop distance

Net displacement in 1s due to Brownian motion and gravity for standard-density spheres at standard conditions

Particle diameter, μm	Re_0	S at U_0=10m/s	time to travel 95% of S
0.01	0.0066	7.0×10^{-5}	2.0×10^{-8}
0.1	0.066	9.0×10^{-4}	2.7×10^{-7}
1.0	0.66	0.035	1.1×10^{-5}
10	6.6	2.3*	8.5×10^{-4}*
100	66	127*	0.065*

** out of Stokes' range*

(2) ***Simiulitude Law for Impaction*** *: Stokesian Particles*

** Impaction: deposition by inertia*

- For Re < 1

Force balance around a particle

$$m_p \frac{d\overrightarrow{U_p}}{dt} = -3\pi\mu d_p \left(\overrightarrow{U_p} - \overrightarrow{U_f}\right)$$

Defining dimensionless variables $\overrightarrow{U_1} \equiv \frac{\vec{U}}{L}$, $\overrightarrow{U_{f1}} \equiv \frac{\overrightarrow{U_f}}{L}$ *and* $\theta \equiv \frac{tU}{L}$

where U , L *: characteristic velocity and length of the system*

$$\frac{\pi}{6} d_p^{\ 3} \frac{Ld\overrightarrow{U_1}}{(L/U)d\theta} = -3\pi\mu d_p \left(L\overrightarrow{U_1} - L\overrightarrow{U_{f1}}\right)$$ *(subscript p: omitted)*

$$\frac{\rho_p d_p^{\ 2} U}{18\mu L} \frac{d\overrightarrow{U_1}}{d\theta} = -\left(\overrightarrow{U_1} - \overrightarrow{U_{f1}}\right)$$

,

Define Stokes number

$$St \equiv \frac{\rho_p d^2{}_p U}{18\mu L} = \frac{\tau U}{L} \equiv \frac{\text{particle persistence}}{\text{size of obstacle}}$$

$$\therefore St \frac{d\overrightarrow{U_1}}{d\theta} = -\left(\overrightarrow{U_1} - \overrightarrow{U_{f1}}\right)$$

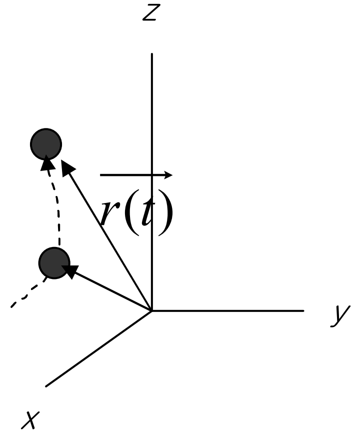
Or in terms of displacement

$$St\frac{d^2\vec{r_1}}{d\theta^2}+\frac{d\vec{r_1}}{d\theta}=\overrightarrow{U_{f1}}$$

$\uparrow$ *Re*

where $\vec{r}_1 \equiv \frac{\vec{r}}{L}$, $\vec{r}$ *: displacement vector*

- The solution gives $\overrightarrow{r_1(\theta)}$, $\overrightarrow{r(t)}$ *or where the particle is at time t…*



** Particle trajectory* $\therefore \overrightarrow{r_1(\theta)} = f\left(St, \mathrm{Re}, R\right)$

$\uparrow$ Geometric similarity

where $R = \frac{d_p}{L}$

- *Two particle impaction regimes are similar*

  when the geometric, hydrodynamic and particle trajectories are the same…

- *Applications*

  - *Cyclone, particle impactor, filter*