

ME 8111 - Multiphase Systems Analysis

Course Lecture Notes

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Dispersions

Dispersion: a mixture of two materials, with one material (the continuous phase) surrounding discrete quantities of the other material (the dispersed phase)

Types of dispersions:

- Colloids: particles in a liquid
- Aerosols: droplets or particles in a gas
- Bubble suspensions: gas bubbles in a liquid
- Emulsions: liquid droplets in another (immiscible) liquid
- Granular systems: high volume fraction of particles in a fluid
- Foams: high volume fraction of gas bubbles in a liquid or solid

Terminology:

Dilute: small volume fraction of dispersed phase (3-way collisions insignificant)

Polydisperse: wide range of particle size for dispersed phase

Monodisperse: uniform particle size for dispersed phase

Size Distributions

Consider a simple polydisperse dispersion:

- spherical particles with a wide range of diameters
- a concentration density for any given range of particle diameter

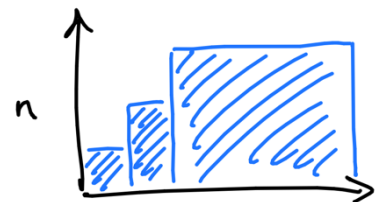
How can we characterize this dispersion?

Nomenclature:

d_p	particle diameter (units of length)
n	number density (units of particles/volume)
Δ	finite interval or difference
δ	differentially small interval or difference

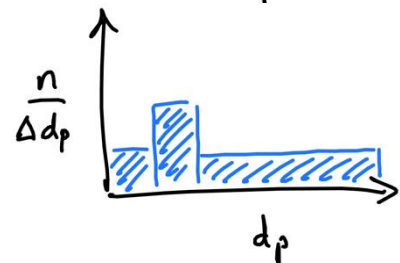
Naively we could collect a finite sample of particle sizes and construct a histogram of number density, binning by particle size:

bin area = ???



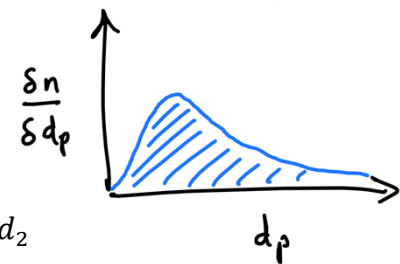
Normalizing the vertical axis by bin width Δd_p causes area to faithfully represent number density in the sample:

bin area = $(n/\Delta d_p)\Delta d_p = n$ for bin



Extending this idea to continuous data from an infinite sample size, differentially small bins of width δd_p make differentially small contributions to density δn :

$$\text{area slice} = \int_{d_1}^{d_2} (\delta n / \delta d_p) \delta d_p = n \text{ for } d_1 < d_p < d_2$$



This is the number concentration **size distribution function**:

$$\frac{\partial n}{\partial d_p} = \text{marginal particle number concentration per unit change in } d_p$$

Size Distribution Function

$\partial n / \partial d_p$ has units of length^{-4}

The size distribution function $\partial n / \partial d_p$ can be used to find:

- the total volumetric concentration of the dispersion

$$n_{tot} = \int \partial n = \int_0^{\infty} \left(\frac{\partial n}{\partial d_p} \right) \partial d_p$$

- the volumetric concentration of particles of a given size $d_1 < d_p < d_2$

$$n_{d_1 \rightarrow d_2} = \int_{d_1}^{d_2} \left(\frac{\partial n}{\partial d_p} \right) \partial d_p$$

- the total number of particles in a given sample volume V

$$N_{tot} = V n_{tot}$$

- the number of particles of a given size in a given sample volume V

$$N_{d_1 \rightarrow d_2} = V n_{d_1 \rightarrow d_2}$$

- the total volume fraction of the dispersion

$$v_{tot} = \int \frac{\pi}{6} d_p^3 \partial n = \frac{\pi}{6} \int_0^{\infty} \left(\frac{\partial n}{\partial d_p} \right) d_p^3 \partial d_p$$

- the volume fraction of particles of a given size

$$v_{d_1 \rightarrow d_2} = \frac{\pi}{6} \int_{d_1}^{d_2} \left(\frac{\partial n}{\partial d_p} \right) d_p^3 \partial d_p$$

Common Distribution Functions

Gaussian (normal) distribution:

Two parameters: mean $\overline{d_p}$ and standard deviation σ

$$\frac{\partial n}{\partial d_p} = \frac{n_{tot}}{\sigma\sqrt{2\pi}} \text{Exp} \left[-\frac{1}{2} \left(\frac{d_p - \overline{d_p}}{\sigma} \right)^2 \right]$$

Where:

$$\overline{d_p} = \frac{\int_0^\infty d_p \frac{\partial n}{\partial d_p} \partial d_p}{n_{tot}}$$

$$\sigma = \left[\frac{\int_0^\infty (d_p - \overline{d_p})^2 \frac{\partial n}{\partial d_p} \partial d_p}{n_{tot}} \right]^{\frac{1}{2}}$$

*The normal distribution has an unbounded domain, allowing negative d_p !

Rosin-Rammler (Weibull) distribution:

Two fit parameters: A and B (mean value and size uniformity are independent)

$$\frac{\partial n}{\partial d_p} = A B d_p^{B-1} \text{Exp}[-A d_p^B]$$

Exponential distribution:

One fit parameter: A (mean value and size uniformity are dependent)

$$\frac{\partial n}{\partial d_p} = A \text{Exp}[-A d_p]$$

Log-Normal (Galton) Distribution

We will be using the log-normal distribution for most of this course

The normal distribution doesn't work for dispersions:

- particle size is bounded below at zero, since negative sizes are impossible
- particle sizes often span orders of magnitude (*e.g.* 3 OOMs)

Using $\ln(d_p)$ in place of d_p in a Gaussian-like distribution alleviates both problems:

$$\frac{\partial n}{\partial d_p} = \frac{n_{tot}}{\ln(\sigma^*) \sqrt{2\pi} d_p} \text{Exp} \left[-\frac{1}{2} \left(\frac{\ln(d_p/\bar{d}_p^*)}{\ln(\sigma^*)} \right)^2 \right]$$

Note: $\ln(d_p)$ has a normal distribution.

Geometric mean diameter (units of length) is \bar{d}_p^* (or \bar{d}_g):

$$\bar{d}_p^* = \text{Exp} \left[\frac{\int_0^\infty \frac{\partial n}{\partial d_p} \ln(d_p) \partial d_p}{n_{tot}} \right]$$

Geometric standard deviation (dimensionless) is σ^* (or σ_g):

$$\sigma^* = \text{Exp} \left[\left(\frac{\int_0^\infty \frac{\partial n}{\partial d_p} [\ln(d_p/\bar{d}_p^*)]^2 \partial d_p}{n_{tot}} \right)^{\frac{1}{2}} \right]$$

Values of σ^* :

- $\sigma^* \geq 1$ by definition
- if perfectly monodisperse, then $\sigma^* = \text{Exp}[0] = 1$
- usually considered monodisperse if $\sigma^* \leq 1.1$
- usually considered polydisperse if $\sigma^* > 1.1$
- distribution shape is very sensitive to even small changes in σ^*

Probability Distribution Functions

Some students may have previously encountered probability density function (PDF):

$$f(d) = \frac{1}{n_{tot}} \frac{\partial n}{\partial d_p} \quad \text{evaluated at } d_p = d$$

...or cumulative distribution function (CDF):

$$F(d) = \int_0^d f(x) dx$$

PDF and CDF are often used if particle size matters but particle concentration is inconsequential, *e.g.* using droplet size to evaluate the performance of an atomizer.

More About the Log-Normal Distribution

To show: if d_p has log-normal distribution, then $\ln(d_p)$ has normal distribution.

As previously introduced, the log-normal size distribution function is given by:

$$\frac{\partial n}{\partial d_p} = \frac{n_{tot}}{\ln(\sigma^*) \sqrt{2\pi} d_p} \text{Exp} \left[-\frac{1}{2} \left(\frac{\ln(d_p) - \ln(\overline{d_p^*})}{\ln(\sigma^*)} \right)^2 \right]$$

Let's investigate this distribution in terms of $\ln(d_p)$. In general:

$$\frac{\partial n}{\partial \ln(d_p)} = \frac{\partial n}{\partial d_p} \frac{\partial d_p}{\partial \ln(d_p)} = \frac{\partial n}{\partial d_p} \left(\frac{\partial \ln(d_p)}{\partial d_p} \right)^{-1} = \frac{\partial n}{\partial d_p} \left(\frac{1}{d_p} \right)^{-1} = d_p \frac{\partial n}{\partial d_p}$$

So for the log-normal distribution $\partial n / \partial d_p$ above we have:

$$\frac{\partial n}{\partial \ln(d_p)} = d_p \frac{\partial n}{\partial d_p} = \frac{n_{tot}}{\ln(\sigma^*) \sqrt{2\pi}} \text{Exp} \left[-\frac{1}{2} \left(\frac{\ln(d_p) - \ln(\overline{d_p^*})}{\ln(\sigma^*)} \right)^2 \right]$$

This is a normal distribution of $\ln(d_p)$ with mean $\ln(\overline{d_p^*})$ and standard deviation $\ln(\sigma^*)$.

Volume- and Surface Area Concentration Size Distributions

Our previous size distributions $\partial n / \partial d_p$ were expressed in terms of particle number concentration per unit volume ∂n .

Particle volume per unit total volume for each size class is:

$$\partial v = \frac{\pi}{6} d_p^3 \partial n$$

Note: Each d_p contributes only ∂v and ∂n . The expression $v = \frac{\pi}{6} d_p^3 n$ is not well-defined for a polydisperse dispersion (see next section Representative Diameters).

Therefore:

$$\begin{aligned} \frac{\partial v}{\partial d_p} &= \frac{\pi}{6} d_p^3 \frac{\partial n}{\partial d_p} \\ v_{d_1 \rightarrow d_2} &= \int_{d_1}^{d_2} \frac{\pi}{6} d_p^3 \frac{\partial n}{\partial d_p} \partial d_p \\ v_{tot} &= \int_0^{\infty} \frac{\pi}{6} d_p^3 \frac{\partial n}{\partial d_p} \partial d_p \end{aligned}$$

Particle surface area per unit total volume for each size class is:

$$\partial s = \pi d_p^2 \partial n$$

Therefore:

$$\begin{aligned} \frac{\partial s}{\partial d_p} &= \pi d_p^2 \frac{\partial n}{\partial d_p} \\ s_{d_1 \rightarrow d_2} &= \int_{d_1}^{d_2} \pi d_p^2 \frac{\partial n}{\partial d_p} \partial d_p \\ s_{tot} &= \int_0^{\infty} \pi d_p^2 \frac{\partial n}{\partial d_p} \partial d_p \end{aligned}$$

Representative Diameters

In the previous section we desired an expression like $v_{tot} = \frac{\pi}{6} d_v^3 n_{tot}$.

We can find a single representative diameter for this expression by working backward from the integral form of v_{tot} :

$$v_{tot} = \int_0^\infty \frac{\pi}{6} d_p^3 \frac{\partial n}{\partial d_p} \partial d_p$$

$$\Rightarrow$$

$$v_{tot} = \frac{\pi}{6} d_v^3 n_{tot} \quad \text{where} \quad d_v = \left(\frac{\int_0^\infty d_p^3 \frac{\partial n}{\partial d_p} \partial d_p}{n_{tot}} \right)^{\frac{1}{3}}$$

Similarly for surface area concentration:

$$s_{tot} = \pi d_{surf}^2 n_{tot} \quad \text{where} \quad d_{surf} = \left(\frac{\int_0^\infty d_p^2 \frac{\partial n}{\partial d_p} \partial d_p}{n_{tot}} \right)^{\frac{1}{2}}$$

A common notation for distribution mean diameters is:

$$d_{ij} = \left(\frac{\int_0^\infty d_p^i \frac{\partial n}{\partial d_p} \partial d_p}{\int_0^\infty d_p^j \frac{\partial n}{\partial d_p} \partial d_p} \right)^{\frac{1}{i-j}}$$

The most common of these are d_{10} (arithmetic mean) and d_{32} (Sauter mean diameter).

Sauter mean diameter is often used in spray measurements due to its relation to the overall droplet surface-area-to-volume ratio:

$$d_{32} = \frac{\int_0^\infty d_p^3 \frac{\partial n}{\partial d_p} \partial d_p}{\int_0^\infty d_p^2 \frac{\partial n}{\partial d_p} \partial d_p} = \frac{d_v^3 n_{tot}}{d_{surf}^2 n_{tot}} = \frac{\frac{6}{\pi} v_{tot}}{\pi s_{tot}} = 6 \frac{v_{tot}}{s_{tot}}$$

For a finite set of droplet measurements, $d_{32} = \Sigma d_p^3 / \Sigma d_p^2$.

Hatch-Choate Equations

From Hatch & Choate (1929), d_{surf} and d_v of a log-normal distribution can be expressed using geometric mean and geometric standard deviation of d_p :

$$d_{surf}^2 = \text{Exp}[2 \ln(\bar{d}_p^*) + 2 \ln^2(\sigma^*)]$$

$$d_v^3 = \text{Exp}[3 \ln(\bar{d}_p^*) + 4.5 \ln^2(\sigma^*)]$$

Size Distributions by Particle Volume

Instruments often measure and report $\partial n / \partial d_p$ (per unit change in particle diameter).

When doing theoretical analysis it might be easier to track changes in size distributions using $\partial n / \partial v_p$ (per unit change in particle volume).

What can change a size distribution in time?

- coagulation (particle joining)
- fragmentation (particle splitting)
- deposition on walls

Joining and splitting are processes that directly influence particle volume.

We can translate a size distribution from d_p to v_p using the identity $v_p = \frac{\pi}{6} d_p^3$.

$$\frac{\partial n}{\partial v_p} = \frac{\partial n}{\partial d_p} \frac{\partial d_p}{\partial v_p} = \frac{\partial n}{\partial d_p} \left(\frac{\partial v_p}{\partial d_p} \right)^{-1} = \frac{\partial n}{\partial d_p} \left(\frac{\partial}{\partial d_p} \left[\frac{\pi}{6} d_p^3 \right] \right)^{-1} = \frac{2}{\pi d_p^2} \frac{\partial n}{\partial d_p}$$

Rearranging this result slightly we have:

$$\boxed{\frac{\partial n}{\partial v_p} = \frac{d_p}{3 v_p} \frac{\partial n}{\partial d_p}}$$

Recall: a log-normal $\partial n / \partial d_p$ is given by:

$$\frac{\partial n}{\partial d_p} = \frac{n_{tot}}{\ln(\sigma^*) \sqrt{2\pi} d_p} \text{Exp} \left[-\frac{1}{2} \left(\frac{\ln(d_p / \bar{d}_p^*)}{\ln(\sigma^*)} \right)^2 \right]$$

Thus a **volumetric concentration size distribution function** for log-normal d_p is:

$$\begin{aligned}
 \frac{\partial n}{\partial v_p} &= \frac{d_p}{3 v_p} \frac{\partial n}{\partial d_p} \\
 &= \frac{d_p}{3 v_p} \left(\frac{n_{tot}}{\ln(\sigma^*) \sqrt{2\pi} d_p} \text{Exp} \left[-\frac{1}{2} \left(\frac{\ln(d_p/\bar{d}_p^*)}{\ln(\sigma^*)} \right)^2 \right] \right) \\
 &= \frac{n_{tot}}{3 \ln(\sigma^*) \sqrt{2\pi} v_p} \text{Exp} \left[-\frac{1}{2} \left(\frac{\ln(v_p^{1/3}/\bar{v}_p^{*1/3})}{\ln(\sigma^*)} \right)^2 \right] \\
 &= \frac{n_{tot}}{3 \ln(\sigma^*) \sqrt{2\pi} v_p} \text{Exp} \left[-\frac{1}{2} \left(\frac{\frac{1}{3} \ln(v_p/\bar{v}_p^*)}{\ln(\sigma^*)} \right)^2 \right] \\
 &= \frac{n_{tot}}{3 \ln(\sigma^*) \sqrt{2\pi} v_p} \text{Exp} \left[-\frac{1}{18} \left(\frac{\ln(v_p/\bar{v}_p^*)}{\ln(\sigma^*)} \right)^2 \right]
 \end{aligned}$$

$$\begin{aligned}
 \frac{\partial n}{\partial d_p} &= \frac{n_{tot}}{\ln(\sigma^*) \sqrt{2\pi} d_p} \text{Exp} \left[-\frac{1}{2} \left(\frac{\ln(d_p/\bar{d}_p^*)}{\ln(\sigma^*)} \right)^2 \right] \\
 \frac{\partial n}{\partial v_p} &= \frac{n_{tot}}{3 \ln(\sigma^*) \sqrt{2\pi} v_p} \text{Exp} \left[-\frac{1}{18} \left(\frac{\ln(v_p/\bar{v}_p^*)}{\ln(\sigma^*)} \right)^2 \right]
 \end{aligned}$$

Note that:

- we have already seen that \bar{d}_p^* is the geometric mean d_p
- it can be shown that $\bar{v}_p^* = (\pi/6) \bar{d}_p^{*3}$ is also the geometric mean v_p
- the geometric standard deviation σ^* is unchanged and equal in both expressions $\partial n/\partial d_p$ and $\partial n/\partial v_p$

Whether expressed in terms of d_p or v_p , any log-normal distribution is fully defined by three parameters: n_{tot} , a geometric mean, and a geometric standard deviation.

Distribution Moments

****Moments are in the top 5 important ideas of the course****

The k th moment of a volumetric size distribution function is:

$$M_k = \int_0^\infty \frac{\partial n}{\partial v_p} v_p^k \partial v_p$$

For example:

$$M_0 = \int_0^\infty \frac{\partial n}{\partial v_p} v_p^0 \partial v_p = \int_0^\infty \frac{\partial n}{\partial v_p} \partial v_p = n_{tot}$$

$$M_1 = \int_0^\infty \frac{\partial n}{\partial v_p} v_p \partial v_p = v_{tot}$$

The moments of a log-normal distribution can be related to n_{tot} , $\overline{v_p^*}$, and σ^* :

$$M_k = n_{tot} \overline{v_p^*}^k \text{Exp} \left[\frac{9}{2} k^2 \ln^2(\sigma^*) \right]$$

$$n_{tot} = M_0$$

$$\overline{v_p^*} = \frac{M_1^2}{M_0^{3/2} M_2^{1/2}}$$

$$\ln^2(\sigma^*) = \frac{1}{9} \ln \left(\frac{M_0 M_2}{M_1^2} \right)$$

That is, knowledge of M_0 , M_1 , and M_2 is equivalent to knowledge of n_{tot} , $\overline{v_p^*}$, and σ^* .

****Thus we can track the time evolution of a log-normal size distribution function using only a subset of its moments.**

Particle Coagulation Physics

Suppose two incompressible particles having individual volumes v_i and v_j collide and stick together, forming a single sphere. The volume of the new particle is:

$$v_k = v_i + v_j$$

The volumetric collision rate R_{ij} (collisions per unit volume per unit time) occurring due to random motion is characterized by a collision rate coefficient (or collision kernel) β_{ij} that makes R_{ij} directly proportional to the number concentrations of colliding species:

$$R_{ij} = \beta_{ij} n_i n_j$$

This same rate equation format is also typically used for chemical reactions and other phenomena resulting from the collisions of particles or molecules.

Particle volume bins ∂v_i and ∂v_j in a continuous size distribution contribute differentially small ∂n , so we write:

$$\partial R_{ij} = \beta_{ij} \partial n_i \partial n_j = \beta_{ij} \frac{\partial n}{\partial v_i} \partial v_i \frac{\partial n}{\partial v_j} \partial v_j$$

We will use this expression for ∂R_{ij} in a later section.

Time Evolution of Distribution Moments (Coagulation)

In the Distribution Moments section we saw that knowing n_{tot} , $\overline{v_p^*}$, and σ^* for log-normal distribution at time $t = 0$ implies knowledge of its moments M_0 , M_1 , and M_2 .

For complete knowledge of the size distribution evolution in time, we now seek expressions for $\partial M_0/\partial t$, $\partial M_1/\partial t$, and $\partial M_2/\partial t$.

Considering the single coagulation event $v_k = v_i + v_j$:

Moment	Before collision	After collision	Change per collision
$M_0 = n_{tot}$	2	1	-1
$M_1 = v_{tot}$	$v_i + v_j$	$v_i + v_j$	0
M_2	$v_i^2 + v_j^2$	$(v_i + v_j)^2$	$2 v_i v_j$
M_k	$v_i^k + v_j^k$	$(v_i + v_j)^k$	$(v_i + v_j)^k - v_i^k - v_j^k$

For convenience in the following work, abbreviate the change in moment M_k per $v_i + v_j$ collision as $\Delta_{kij} = (v_i + v_j)^k - v_i^k - v_j^k$. In other words, $\Delta_{kij} = \partial(\partial M_k/\partial t)/\partial R_{ij}$.

Using integration to sum all possible $v_i + v_j$ collisions occurring at rate ∂R_{ij} :

$$\frac{\partial M_k}{\partial t} = \int \partial \left(\frac{\partial M_k}{\partial t} \right) = \frac{1}{2} \iint_{i,j} \frac{\partial(\partial M_k/\partial t)}{\partial R_{ij}} \partial R_{ij} = \frac{1}{2} \iint_{i,j} \Delta_{kij} \partial R_{ij}$$

Note that the factor $1/2$ appears here because R_{ij} and R_{ji} double-count identical collisions.

So we have:

$$\frac{\partial M_k}{\partial t} = \frac{1}{2} \iint_0^\infty \Delta_{kij} \left[\beta_{ij} \frac{\partial n}{\partial v_i} \partial v_i \frac{\partial n}{\partial v_j} \partial v_j \right] = \frac{1}{2} \iint_0^\infty \beta_{ij} \Delta_{kij} \frac{\partial n}{\partial v_i} \frac{\partial n}{\partial v_j} \partial v_i \partial v_j$$

Therefore:

$$\begin{aligned} \frac{\partial M_0}{\partial t} &= \frac{-1}{2} \iint_0^\infty \beta_{ij} \frac{\partial n}{\partial v_i} \frac{\partial n}{\partial v_j} \partial v_i \partial v_j \\ \frac{\partial M_1}{\partial t} &= 0 \\ \frac{\partial M_2}{\partial t} &= \iint_0^\infty \beta_{ij} v_i v_j \frac{\partial n}{\partial v_i} \frac{\partial n}{\partial v_j} \partial v_i \partial v_j \end{aligned}$$

The potential dependence of β_{ij} on v_i and v_j is the only dependency between the nested integrals. So **if we have constant $\beta_{ij} = A$** , the integrals are separable and the resulting differential equations in time are easy to solve:

$$M_0 = \left(\frac{1}{M_{0,t=0}} + \frac{A}{2} t \right)^{-1}$$

$$M_1 = M_{1,t=0}$$

$$M_2 = M_{2,t=0} + A M_{1,t=0}^2 t$$

We can also substitute these results into the previous equations for $\overline{v_p^*}$ and σ^* :

$$\overline{v_p^*} = \frac{M_1^2}{M_0^{3/2} M_2^{1/2}} = \frac{M_{1,t=0}^2 \left(\frac{1}{M_{0,t=0}} + \frac{A}{2} t \right)^{3/2}}{(M_{2,t=0} + A M_{1,t=0}^2 t)^{1/2}}$$

$$\ln^2(\sigma^*) = \frac{1}{9} \ln \left(\frac{M_0 M_2}{M_1^2} \right) = \frac{1}{9} \ln \left(\frac{M_{2,t=0} + A M_{1,t=0}^2 t}{M_{1,t=0}^2 \left(\frac{1}{M_{0,t=0}} + \frac{A}{2} t \right)} \right)$$

Interestingly, the geometric standard deviation displays asymptotic behavior in time:

$$\lim_{t \rightarrow \infty} [\ln^2(\sigma^*)] = \lim_{t \rightarrow \infty} \left[\frac{1}{9} \ln \left(\frac{M_{2,t=0} + A M_{1,t=0}^2 t}{M_{1,t=0}^2 \left(\frac{1}{M_{0,t=0}} + \frac{A}{2} t \right)} \right) \right] = \frac{1}{9} \ln(2)$$

Therefore:

$$\lim_{t \rightarrow \infty} (\sigma^*) \approx 1.32$$

The mean size will continue to increase, but the relative distribution width is preserved.

Depending on the physics (this is coagulation only), the asymptotic value may be different but this general behavior is called a **self-preserving size distribution**.

Unary Reactions

Unary: involving only one particle

Example unary processes for dispersions:

- deposition
- condensation
- evaporation

Deposition rate (units of particles deposited per second per unit volume) can be written:

$$R_{dep} = \beta_{dep} n \quad \text{and} \quad \partial R_{dep} = \beta_{dep} \partial n = \beta_{dep} \frac{\partial n}{\partial v_p} \partial v_p$$

where β_{dep} is a rate coefficient similar to that used for coagulation.

For deposition the size dependence of β_{dep} is commonly characterized by the fit:

$$\beta_{dep} \approx \beta_0 v_p^x$$

for some constants β_0 and x . (Note:.)

We can then show:

$$\left(\frac{\partial M_k}{\partial t} \right)_{dep} = -\beta_0 \int_0^\infty v_p^x v_p^k \frac{\partial n}{\partial v_p} \partial v_p = -\beta_0 M_{k+x}$$

However: x is often non-integer and $x < 0$, so how can we express M_{k+x} in terms of the first three moments? (for use in a system of three differential equations for M_0, M_1, M_2)

Non-Integer Moments

We just derived an expression containing M_{k+x} where x is usually not a positive integer.

Recall that in earlier sections we saw:

$$M_k = n_{tot} \overline{v_p^*}^k \text{Exp} \left[\frac{9}{2} k^2 \ln^2(\sigma^*) \right]$$

$$n_{tot} = M_0$$

$$\overline{v_p^*} = \frac{M_1^2}{M_0^{3/2} M_2^{1/2}}$$

$$\ln^2(\sigma^*) = \frac{1}{9} \ln \left(\frac{M_0 M_2}{M_1^2} \right)$$

Combining these four equations, after simplification we obtain:

$$M_{k+x} = n_{tot} \overline{v_p^*}^{k+x} \text{Exp} \left[\frac{9}{2} (k+x)^2 \ln^2(\sigma^*) \right] = M_0^A M_1^B M_2^C$$

$$A = 1 - \frac{3}{2} (k+x) + \frac{1}{2} (k+x)^2$$

$$B = 2(k+x) - (k+x)^2$$

$$C = \frac{-1}{2} (k+x) + \frac{1}{2} (k+x)^2$$

This representation of M_{k+x} can now be used in systems of differential equations tracking changes to a log-normal distribution through M_0, M_1, M_2 .

N-ary Reactions

For unary reactions (*e.g.* deposition) we saw the forms:

$$\partial R_1 = \beta \frac{\partial n}{\partial v_1} \partial v_1$$

$$\left(\frac{\partial M_k}{\partial t} \right)_1 = \int_0^\infty \beta \Delta_k \frac{\partial n}{\partial v_1} \partial v_1$$

And for binary reactions (*e.g.* coagulation) we used:

$$\partial R_{12} = \beta \frac{\partial n}{\partial v_1} \frac{\partial n}{\partial v_2} \partial v_1 \partial v_2$$

$$\left(\frac{\partial M_k}{\partial t} \right)_{12} = \frac{1}{2} \iint_0^\infty \beta \Delta_k \frac{\partial n}{\partial v_1} \frac{\partial n}{\partial v_2} \partial v_1 \partial v_2$$

In general, for a process involving $N > 0$ particles we will encounter:

$$\partial R_{12 \dots N} = \beta \frac{\partial n}{\partial v_1} \frac{\partial n}{\partial v_2} \dots \frac{\partial n}{\partial v_N} \partial v_1 \partial v_2 \dots \partial v_N$$

$$\left(\frac{\partial M_k}{\partial t} \right)_{12 \dots N} = \frac{1}{2^{N-1}} \iint \dots \int_0^\infty \beta \Delta_k \frac{\partial n}{\partial v_1} \frac{\partial n}{\partial v_2} \dots \frac{\partial n}{\partial v_N} \partial v_1 \partial v_2 \dots \partial v_N$$

Note that in general the rate coefficient β and moment rate effect $\Delta_k = \partial(\partial M_k / \partial t) / \partial R$ may be and usually are functions of v_1, v_2, \dots, v_N .

Moment Transport Equations (Nonzero Mean Velocity Fields)

In fluid mechanics class, we learned control volume balance equations such as:

$$\text{mass balance: } 0 = \frac{\partial}{\partial t} \int_{CV} \rho \, \partial V + \int_{CS} \rho \, \mathbf{u} \cdot d\mathbf{A}$$

$$\text{energy balance: } \dot{Q} \pm \dot{W} = \frac{\partial}{\partial t} \int_{CV} \rho \, e \, \partial V + \int_{CS} \mathbf{q}'' \cdot d\mathbf{A}$$

Transport of a moment M_k through a homogeneous control volume of finite size is described by:

$$V \left[\sum_{processes} \left(\frac{\partial M_k}{\partial t} \right)_{process} \right] = \frac{\partial}{\partial t} \int_{CV} M_k \, \partial V + \int_{CS} \mathbf{j}_k'' \cdot d\mathbf{A}$$

where \mathbf{j}_k'' is the surface flux of total moment (same units as $M_k \mathbf{u}$). Remember that for a volumetric size distribution, we have M_k per unit volume, so that is why we multiply by volume V or ∂V here.

For a differentially small control volume, we obtain the transport equation for M_k :

$$\sum_{processes} \left(\frac{\partial M_k}{\partial t} \right)_{process} = \frac{\partial M_k}{\partial t} + \nabla \cdot \mathbf{j}_k''$$

It might be confusing to have multiple $\partial M_k / \partial t$ in the same equation. Those appearing in the summation term on the lefthand side are process-specific contributions to change in M_k , while the $\partial M_k / \partial t$ appearing alone on the righthand side of the equation is the total Eulerian rate of change at a fixed point in space.

For a divergence-free flow ($\nabla \cdot \mathbf{u} = 0$) with $\mathbf{j}_k'' = M_k \mathbf{u} + \mathbf{j}_{k,nf}''$ where the subscript nf indicates moment flux from other non-fluid effects (*e.g.* diffusion, gravitational settling):

$$\sum_{processes} \left(\frac{\partial M_k}{\partial t} \right)_{process} = \frac{\partial M_k}{\partial t} + \nabla \cdot (M_k \mathbf{u} + \mathbf{j}_{k,nf}'') = \frac{\partial M_k}{\partial t} + \mathbf{u} \cdot \nabla M_k + \nabla \cdot \mathbf{j}_{k,nf}''$$

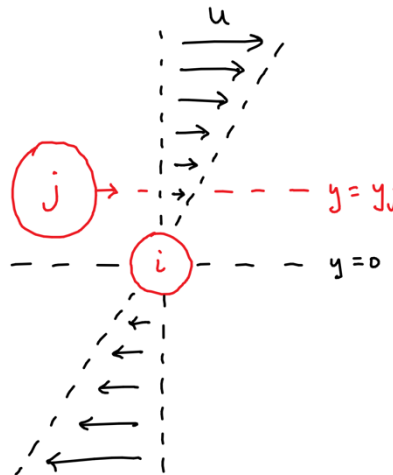
$$\frac{\partial M_k}{\partial t} + \mathbf{u} \cdot \nabla M_k = \sum_{processes} \left(\frac{\partial M_k}{\partial t} \right)_{process} - \nabla \cdot \mathbf{j}_{k,nf}''$$

Orthokinetic Coagulation (Velocity Gradients)

Historical experimental observation: a suspension at rest with an equilibrium size distribution may suddenly coagulate if stirred or passed through a small tube.

Velocity gradients lead to relative motion between particles.

Suppose a laminar planar shear flow is given by $u(y) = u_0 + Gy$, where u_0 and G are constants, and consider two particles i and j moving with the local fluid velocity. Using the center of particle i as our coordinate frame of reference, the flow looks like:



The relative velocity of the two particles is Gy_j , so this velocity gradient could cause particles i and j to collide if $y_j \leq a_i + a_j$, where a_i and a_j are the particle radii.

Even in laminar planar shear, particles with different local velocities may collide due to finite particle size.

In cylindrical coordinates (r, θ, x) with the origin in the center of particle i and the x direction oriented parallel to velocity u , the relative velocity of particles i and j is:

$$u_{rel} = Gr_j |\cos \theta_j|$$

Any j particles intersecting the $x = 0$ plane at $r_j \leq a_i + a_j$ will collide with particle i .

The volumetric flow rate of fluid moving through this collision area is:

$$\dot{V}_{collide} = \int_0^{2\pi} \int_0^{a_i+a_j} u_{rel} r \partial r \partial \theta = \int_0^{2\pi} \int_0^{a_i+a_j} G r^2 |\cos \theta| \partial r \partial \theta = \frac{4}{3} G (a_i + a_j)^3$$

The rate of j particles colliding with the single i particle is then:

$$R_j = n_j \dot{V}_{collide}$$

And our overall ij collision rate is:

$$R_{ij} = n_i n_j \dot{V}_{collide}$$

Comparing the general form of the collision rate equation $R_{ij} = \beta_{ij} n_i n_j$, we can see that:

$$\beta_{ij} = \dot{V}_{collide} = \frac{4}{3} G (a_i + a_j)^3$$

Thus for orthokinetic coagulation in laminar planar shear, we have:

$$\begin{aligned} R_{ij} &= \beta_{ij} n_i n_j \\ \beta_{ij} &= \frac{4}{3} G (a_i + a_j)^3 = \frac{1}{6} G (d_i + d_j)^3 = \frac{G}{\pi} (v_i^{1/3} + v_j^{1/3})^3 \end{aligned}$$

Saffman & Turner (1956) on Canvas discusses this problem for turbulent flows.

Moment Methods with Orthokinetic Coagulation

Consider an incompressible dispersion with log-normal d_p coagulating due to a laminar planar shear G .

We have:

$$\begin{aligned}\frac{\partial M_0}{\partial t} &= \frac{1}{2} \iint_{i,j} \frac{\partial(\partial M_0 / \partial t)}{\partial R_{ij}} \partial R_{ij} \\ \frac{\partial(\partial M_0 / \partial t)}{\partial R_{ij}} &= (v_i + v_j)^0 - (v_i^0 + v_j^0) = -1 \\ \partial R_{ij} &= \beta_{ij} \frac{\partial n}{\partial v_i} \frac{\partial n}{\partial v_j} \partial v_i \partial v_j = \frac{G}{\pi} (v_i^{1/3} + v_j^{1/3})^3 \frac{\partial n}{\partial v_i} \frac{\partial n}{\partial v_j} \partial v_i \partial v_j\end{aligned}$$

Therefore we substitute and solve:

$$\begin{aligned}\frac{\partial M_0}{\partial t} &= \frac{-G}{2\pi} \iint_0^\infty (v_i^{1/3} + v_j^{1/3})^3 \frac{\partial n}{\partial v_i} \frac{\partial n}{\partial v_j} \partial v_i \partial v_j \\ &= \frac{-G}{2\pi} \iint_0^\infty (v_i + 3v_i^{2/3}v_j^{1/3} + 3v_i^{1/3}v_j^{2/3} + v_j) \frac{\partial n}{\partial v_i} \frac{\partial n}{\partial v_j} \partial v_i \partial v_j \\ &= \frac{-G}{2\pi} (M_1 M_0 + 3M_{2/3} M_{1/3} + 3M_{1/3} M_{2/3} + M_0 M_1)\end{aligned}$$

$$\frac{\partial M_0}{\partial t} = \frac{-G}{\pi} (M_0 M_1 + 3M_{1/3} M_{2/3})$$

The fractional moments like $M_{1/3}$ can be expressed in terms of M_0, M_1, M_2 by using previous formulas either for $M_k, \bar{v}_p^*, \sigma^*$ (combined) or the result already derived for M_{k+x} (using for example $k+x = 1/3$).

And of course:

$$\frac{\partial M_1}{\partial t} = \frac{\partial v_{tot}}{\partial t} = 0$$

Characterization of $\partial M_2 / \partial t$ is an exercise left to the reader.

Integrals with Log-Normal Distributions

Whenever evaluating an integral involving log-normal $\partial n / \partial d_p$ or $\partial n / \partial v_p$, it will likely be easier to integrate with respect to $\ln(d_p)$ or $\ln(v_p)$ instead of d_p or v_p .

For example:

$$\int \partial n = \int \frac{\partial n}{\partial d_p} \partial d_p = \int \frac{\partial n}{\partial \ln(d_p)} \partial \ln(d_p)$$

Or:

$$\int \partial d_p = \int \frac{\partial d_p}{\partial \ln(d_p)} \partial \ln(d_p) = \int d_p \partial \ln(d_p) = \int e^{\ln(d_p)} \partial \ln(d_p)$$

If it is a definite integral, be sure to adjust the limits accordingly:

$$\int_0^\infty \partial d_p = \int_{\ln(0)}^{\ln(\infty)} d_p \partial \ln(d_p) = \int_{-\infty}^\infty d_p \partial \ln(d_p)$$

Following these suggestions will somewhat simplify the exponential terms, but probably only to the point where the expression can be more easily typed into Mathematica, Wolfram Alpha, or any other software solver.

Fragmentation

For some physical processes (coagulation, deposition) the reaction product is self-evident (two particles combining into one, one particle attaching to a wall).

For fragmentation, there are an infinite number of possible outcomes when a particle breaks into two or more pieces (how many new particles are formed, and what sizes?). Suppose we collect many independent observations of a particle of size v_ℓ fragmenting:

Initial volume	Product volumes
v_ℓ	$v_a + v_b$
v_ℓ	$v_c + v_d + v_e$
v_ℓ	$v_f + v_g$
\vdots	\vdots

The average product of this fragmentation (average observation) can be written as:

$$v_\ell \rightarrow \sum_i f_i v_i$$

where on average f_i particles of volume v_i are created. In this case we have:

$v_\ell = \sum_i f_i v_i$ $\bar{N} = \sum_i f_i$	valid for a deterministic outcome
--	---

where \bar{N} is the average number of product particles. If an infinite number of fragmentation observations were made, a continuous distribution of product particle volumes could emerge, in which case:

$v_\ell = \int_0^{v_\ell} \frac{\partial f}{\partial v_i} v_i \partial v_i$ $\bar{N} = \int_0^{v_\ell} \frac{\partial f}{\partial v_i} \partial v_i$	valid for a probabilistic outcome
--	---

where $\partial f / \partial v_i$ is a probability density function (PDF) of product particles. Its value depends on not only v_i but also v_ℓ (initial particle size influences the product size).

Note: moving from a finite number of known fragmentation products to a probabilistic distribution is very similar to our motivation for considering the continuous size distribution function $\partial n / \partial v_p$.

Moments of Fragmentation Product Particles

The k -th moment of the product particles from a single fragmentation event is:

$$M_{k,\text{product}} = \sum_i f_i v_i^k = \int_0^{v_\ell} \frac{\partial f}{\partial v_i} v_i^k \partial v_i$$

where the (Σ) is for a deterministic outcome and the (\int) is for a probabilistic outcome.

Like other unary processes (*e.g.* deposition), for fragmentation we write:

$$R_\ell = K_\ell n_\ell \quad \text{and} \quad \partial R_\ell = K_\ell \frac{\partial n}{\partial v_\ell} \partial v_\ell$$

$$\frac{\partial M_k}{\partial t} = \int \partial \left(\frac{\partial M_k}{\partial t} \right) = \int \frac{\partial(\partial M_k / \partial t)}{\partial R_\ell} \partial R_\ell = \int (M_{k,\text{product}} - M_{k,\text{reactant}}) \partial R_\ell$$

So for the two different fragmentation types (deterministic or probabilistic) we have:

$$\begin{aligned} \frac{\partial M_k}{\partial t} &= \int_0^\infty \left[\left(\sum_i f_i v_i^k \right) - v_\ell^k \right] \left[K_\ell \frac{\partial n}{\partial v_\ell} \partial v_\ell \right] \\ \frac{\partial M_k}{\partial t} &= \int_0^\infty \left[\left(\int_0^{v_\ell} \frac{\partial f}{\partial v_i} v_i^k \partial v_i \right) - v_\ell^k \right] \left[K_\ell \frac{\partial n}{\partial v_\ell} \partial v_\ell \right] \end{aligned}$$

Example: For binary fission, $v_\ell \rightarrow 0.5v_\ell + 0.5v_\ell$, so $M_{k,\text{product}} = 2(0.5v_\ell)^k$.

Equilibrium Size Distributions

We have now seen that:

k	Coagulation	Fragmentation
0	$(\partial M_0/\partial t)_C < 0$	$(\partial M_0/\partial t)_F > 0$
1	$(\partial M_1/\partial t)_C = 0$	$(\partial M_1/\partial t)_F = 0$
2	$(\partial M_2/\partial t)_C > 0$	$(\partial M_2/\partial t)_F < 0$

In each case, $\partial M_k/\partial t$ is opposite signs or both zero, so dispersions with simultaneous coagulation and fragmentation can reach an equilibrium size distribution where:

$$0 = \frac{\partial M_k}{\partial t} = \left(\frac{\partial M_k}{\partial t}\right)_C + \left(\frac{\partial M_k}{\partial t}\right)_F$$

We could then find the equilibrium state by solving the system of equations:

$$\left(\frac{\partial M_k}{\partial t}\right)_C = \left(\frac{-\partial M_k}{\partial t}\right)_F$$

for $k = 0, 1, 2$.

Particle Trajectories

Until now we've usually assumed that reaction rate coefficients like β_{ij} in $R_{ij} = \beta_{ij}n_i n_j$ have some constant value. The next section of the course will introduce particle dynamics to explore what the true values of these coefficients might look like.

For a particle of constant mass m_p we know that:

$$m_p \frac{\partial \mathbf{u}_p}{\partial t} = \sum \mathbf{F}$$

where \mathbf{u}_p is particle velocity and $\sum \mathbf{F}$ is the sum of all forces acting on the particle.

**Many types of force are possible here, but in most dispersions two or three force types dominate, allowing significant simplification of the force balance.

Drag Force on Particles

The drag force on a particle with velocity \mathbf{u}_p is given by:

$$\mathbf{F}_D = \frac{1}{2} \rho_f A_p |\mathbf{u}_f - \mathbf{u}_p|^2 C_D \left(\frac{\mathbf{u}_f - \mathbf{u}_p}{|\mathbf{u}_f - \mathbf{u}_p|} \right)$$

where ρ_f and \mathbf{u}_f are the density and velocity of the surrounding fluid, A_p is the projected area of the particle in the direction of relative velocity, and C_D is drag coefficient. The part in parentheses is a unit vector indicating the correct direction for the drag force.

The Reynolds number associated with this flow over the particle is:

$$\text{Re}_p = \frac{\rho_f |\mathbf{u}_f - \mathbf{u}_p| d_p}{\mu_f}$$

where d_p is the particle diameter and μ_f is the dynamic viscosity of the surrounding fluid.

*Note: Usually Re_p is relatively low compared to macroscale Reynolds numbers, since relative velocity $|\mathbf{u}_f - \mathbf{u}_p|$ decreases as the surrounding fluid accelerates a particle.

For Stokes flow ($\text{Re}_p < 0.1$) we have:

$$C_D = \frac{24}{\text{Re}_p}$$

Combined with the drag force equation above, we obtain Stokes' Law of Resistance:

$$\mathbf{F}_D = 3\pi\mu_f d_p (\mathbf{u}_f - \mathbf{u}_p)$$

Drag is proportional to relative velocity. This can also be written $\mathbf{F}_D = f(\mathbf{u}_f - \mathbf{u}_p)$, where $f = 3\pi\mu_f d_p$ (or sometimes ζ) is a friction coefficient with units of mass flow.

After Stokes, more complex drag analyses have proposed other expressions for f :

	$\text{Re}_p < 0.1$	$\text{Re}_p < 10$	$\text{Re}_p < 10^3$
f	$3\pi\mu_f d_p$ Stokes flow	$3\pi\mu_f d_p \left(1 + \frac{3}{16} \text{Re}_p\right)$ Oseen correction	$3\pi\mu_f d_p (1 + 0.158 \text{Re}_p^{2/3})$ many others exist

*Note: This friction coefficient is different than the dimensionless and more common Fanning or Darcy friction factors.

Continuum and Free-Molecular Scales

Continuum scale: Large particles experience very frequent interaction with the surrounding gas at many locations all over their surface, reacting predominantly to average macroscopic conditions in the fluid.

Free-molecular scale: Small particles intermittently collide with single molecules of the surrounding gas, requiring a statistical knowledge of the size and instantaneous velocity of individual gas molecules in order to predict the outcome.

Aerosols can commonly be encountered at either of these scales, or somewhere in between.

Knudsen number is the length scale ratio of molecular interactions and particle size:

$$\text{Kn} = \frac{\lambda}{a_p}$$

where λ is mean free path in the surrounding gas and a_p is particle radius.

Estimation of mean free path depends on intermolecular forces through ϕ :

$$\lambda = \frac{\mu_f}{\phi \rho_f \bar{c}}$$

$$\bar{c} = \sqrt{\frac{8kT}{\pi m}}$$

$$\phi = \begin{cases} 0.5 & \text{elastic spheres} \\ 0.491 & \text{with repulsion} \\ \vdots & \vdots \end{cases}$$

where \bar{c} is the mean thermal speed of gas molecules, $k = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant, T is gas temperature, and m is the mass of a single gas molecule.

The value $\phi = 0.491$ is attributed to Chapman & Enskog for elastic collision of hard spheres with some repulsive force. Compared to collision alone, the effect of repulsion is to slightly lengthen λ .

Note: The expression for mean thermal speed \bar{c} used on the previous page follows from the Maxwell-Boltzmann distribution of gas molecule instantaneous speed:

$$f(c) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} 4\pi c^2 \text{Exp}\left[\frac{-mc^2}{2kT}\right]$$

where f is a probability density function, c is molecular speed (velocity magnitude), m is the mass of a single gas molecule, and we have:

$$\int_0^{\infty} f(c) dc = 1$$

$$\int_0^{\infty} f(c) c dc = \bar{c}$$

Stokes Flow Drag at Low Knudsen Numbers (Continuum Limit)

In the previous sections we expressed the drag on a particle as:

$$\mathbf{F}_D = f \mathbf{u}_{\text{rel}}$$

where f is the Stokes friction coefficient (not dimensionless) and $\mathbf{u}_{\text{rel}} = (\mathbf{u}_f - \mathbf{u}_p)$ is the relative velocity between the particle and surrounding fluid.

We also saw that for a particle in Stokes flow ($\text{Re}_p < 0.1$) we have:

$$f = 3\pi\mu_f d_p$$

This result depends on the continuum hypothesis and is therefore valid as $\text{Kn} \rightarrow 0$.

Stokes Flow Drag at High Knudsen Numbers (Free-Molecular Limit)

By contrast, analysis at the free-molecular limit suggests:

$$f = \frac{4}{3} \rho_f \bar{c} \Omega_{1,1}$$

where \bar{c} is the mean thermal speed of molecules in the surrounding fluid and $\Omega_{1,1}$ is called the collision cross-section or first collision integral:

$$\Omega_{1,1} \approx \frac{\pi}{4} \xi d_p^2$$

where $\xi \approx 1.36$ is a good fit for most data (see Epstein 1924 on Canvas if interested).

In any case, as $\text{Kn} \rightarrow \infty$ we have:

$$f \approx \frac{\pi}{3} \rho_f \bar{c} \xi d_p^2$$

Stokes Flow Drag at Any Knudsen Number

The Stokes friction coefficient depends on Knudsen number.

The ratio between friction coefficients at the continuum and free-molecular limits is:

$$\frac{f_C}{f_{FM}} = \frac{3\pi\mu_f d_p}{\frac{\pi}{3} \rho_f \bar{c} \xi d_p^2} \sim \frac{\mu_f}{\rho_f \bar{c} d_p} \sim \frac{\left(\frac{\mu_f}{\rho_f \bar{c}}\right)}{d_p} \sim \frac{\lambda}{a_p} = \text{Kn}$$

where the \sim operator indicates a scaling relationship (neglecting constants). So besides being a ratio of length scales, Kn can also be thought of as a ratio of friction coefficients at different scales. In fact, keeping constants we get $f_C/f_{FM} \approx 1.625 \text{ Kn}$.

Cunningham (1911) proposed a slip correction factor C_c defined as:

$$C_c = \frac{f_C}{f} = \frac{3\pi\mu_f d_p}{f}$$

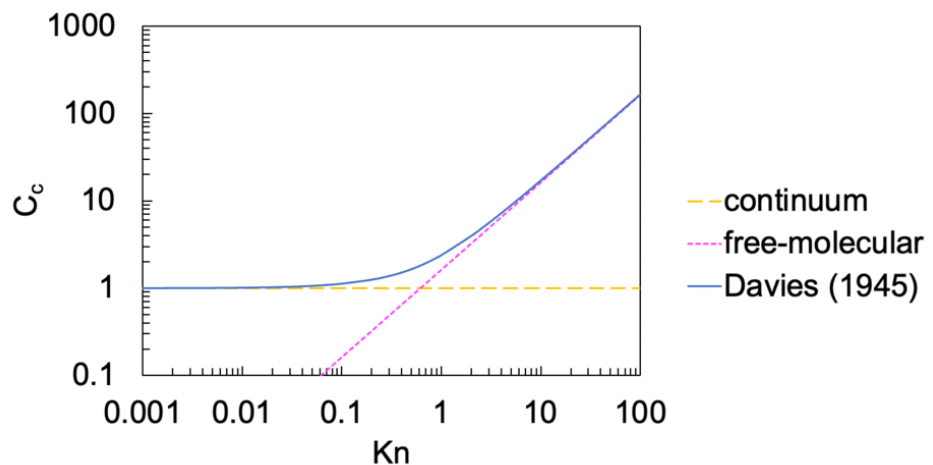
where f is the observed friction coefficient (at arbitrary Kn) and $f_C = 3\pi\mu_f d_p$ is the continuum friction coefficient as seen before. Fitting C_c as a function of Kn would allow accurate prediction of f at any Kn.

$$** \quad \boxed{f = \frac{3\pi\mu_f d_p}{C_c}} \quad **$$

By design, $C_c \rightarrow 1$ as $\text{Kn} \rightarrow 0$, and the above work shows $C_c \rightarrow 1.625 \text{ Kn}$ as $\text{Kn} \rightarrow \infty$. This is the asymptotic behavior of C_c .

For intermediate Kn, observations show that (unsurprisingly) this correction factor smoothly transitions between its two asymptotic scalings.

One empirical fit for C_c (see Davies 1945 on Canvas) is:



$$C_c \approx 1 + \text{Kn} (1.257 + 0.4 \text{Exp}[-1.1/\text{Kn}])$$

Drag at High Reynolds and Knudsen Numbers (Aerospace)

So far we've seen that drag is a strong function of Re_p and Kn .

We spent a lot of time on drag in Stokes flow ($Re_p \rightarrow 0$, with any Kn), and also discussed some continuum drag correlations ($Kn \rightarrow 0$, with any Re_p).

The rest of the (Re_p, Kn) parameter space is large and relatively unexplored, even for drag on a sphere.

Higher Knudsen numbers are commonly encountered in aerospace applications, since outside Earth's atmosphere $Kn \rightarrow \infty$.

Particle Mach number is:

$$Ma_p = \frac{|\mathbf{u}_f - \mathbf{u}_p|}{c_s} = \sqrt{\frac{8}{\pi \gamma}} \left(\frac{|\mathbf{u}_f - \mathbf{u}_p|}{\bar{c}} \right)$$

where c_s is the speed of sound, $\gamma = c_p/c_v$ is the ratio of specific heats, and \bar{c} is the mean thermal speed of molecules in the surrounding fluid.

Particle Mach number is related to the Reynolds and Knudsen numbers as:

$$\frac{Ma_p}{Kn} \sim \left(\frac{|\mathbf{u}_f - \mathbf{u}_p|}{c_s} \right) \left(\frac{\mu_f}{\rho_f \bar{c} d_p} \right)^{-1} = \frac{\rho_f |\mathbf{u}_f - \mathbf{u}_p| d_p}{\mu_f} = Re_p$$

where the \sim operator indicates a scaling relation. So we have:

$$Ma_p \sim Kn Re_p$$

If two of these dimensionless numbers are known, the third is also fully determined.

Basset–Boussinesq–Oseen (BBO) Equation of Particle Motion

The BBO equation (sometimes also Langevin equation if Brownian motion is considered) refers to the equation for Lagrangian particle motion below, or any other form of it that explicitly considers one or more sources for non-drag fluid forces.

$$m_p \frac{d\mathbf{u}_p}{dt} = -f (\mathbf{u}_p - \mathbf{u}_f) + m_p \mathbf{g} + \sum \mathbf{F}_{\text{fluid}} + \sum \mathbf{F}_{\text{field}}$$

$-f (\mathbf{u}_p - \mathbf{u}_f)$ drag force from relative velocity with the surrounding fluid

$m_p \mathbf{g}$ gravity

$\sum \mathbf{F}_{\text{fluid}}$ non-drag interactions with the surrounding fluid (more discussion below)

$\sum \mathbf{F}_{\text{field}}$ non-gravity field forces (electromagnetism, maybe thermophoresis)

$$\sum \mathbf{F}_{\text{fluid}} = \mathbf{F}_B + \mathbf{F}_{VM} + \mathbf{F}_{FK} + \mathbf{F}_{Basset} + \mathbf{F}_{Lift}$$

\mathbf{F}_B Brownian force – nonuniform distribution of collisions on particle surface

\mathbf{F}_{VM} virtual mass – due to incompressible relocation of the surrounding fluid

\mathbf{F}_{FK} Froude–Krylov force – generalized buoyancy

\mathbf{F}_{Basset} (rarely matters) Basset force – time-dependence of particle drag

\mathbf{F}_{Lift} (rarely matters) Saffman lift – large \mathbf{u}_{rel} with strong velocity gradients

Nondimensional BBO Equation for Diffusion-Free Steady Flow Through a Tube

Consider a dispersion subjected to diffusion-free steady flow through a tube. We will non-dimensionalize the following form of the BBO equation:

$$\left(m_p + \frac{1}{2}\rho_f v_p\right) \frac{d\mathbf{u}_p}{dt} = -f(\mathbf{u}_p - \mathbf{u}_f) + m_p \mathbf{g} - v_p \nabla p$$

Here, the virtual mass force $\mathbf{F}_{VM} = \frac{1}{2}\rho_f v_p \left(\frac{d\mathbf{u}_f}{dt} - \frac{d\mathbf{u}_p}{dt}\right)$ becomes $-\frac{1}{2}\rho_f v_p \frac{d\mathbf{u}_p}{dt}$ due to the assumption of steady flow and is moved to the left-hand side (hence the name), and the Froude–Krylov buoyancy force $\mathbf{F}_{FK} = -v_p \nabla p$ is also considered.

One-way coupling is also assumed; that is, the fluid flow influences particle motion, but the particle motion does not significantly influence the fluid flow. This is generally okay for dilute dispersions.

Suppose the tube has diameter L with an average fluid velocity U_0 . Accordingly we will choose the non-dimensional parameters as:

$$\mathbf{u}_f^* = \frac{\mathbf{u}_f}{U_0}$$

$$\mathbf{u}_p^* = \frac{\mathbf{u}_p}{U_0}$$

$$t^* = \frac{t U_0}{L}$$

$$\mathbf{g}^* = \frac{L}{U_0^2} \mathbf{g}$$

$$\nabla^* = L \nabla$$

We will leave m_p and p in dimensional forms for now and see how they turn out later.

Substituting non-dimensional parameters into our original BBO equation, we obtain:

$$\left(m_p + \frac{1}{2}\rho_f v_p\right) \frac{U_0^2}{L} \frac{d\mathbf{u}_p^*}{dt^*} = -U_0 f(\mathbf{u}_p^* - \mathbf{u}_f^*) + \frac{U_0^2}{L} m_p \mathbf{g}^* - \frac{v_p}{L} \nabla^* p$$

We now divide every term by the simplest coefficient, which is $U_0 f$ from the drag term:

$$\left(1 + \frac{1}{2} \frac{\rho_f}{\rho_p}\right) \frac{m_p U_0}{f L} \frac{d\mathbf{u}_p^*}{dt^*} = -(\mathbf{u}_p^* - \mathbf{u}_f^*) + \frac{m_p U_0}{f L} \mathbf{g}^* - \frac{v_p}{f L U_0} \nabla^* p$$

First, it seems that a common term is $\frac{m_p U_0}{f L}$, so using $v_p = \frac{m_p}{\rho_p}$ we can rearrange the Froude–Krylov term to contain this quantity as well:

$$\left(1 + \frac{1}{2} \frac{\rho_f}{\rho_p}\right) \frac{m_p U_0}{f L} \frac{d\mathbf{u}_p^*}{dt^*} = -(\mathbf{u}_p^* - \mathbf{u}_f^*) + \frac{m_p U_0}{f L} \mathbf{g}^* - \frac{m_p U_0}{f L} \left(\frac{1}{\rho_p U_0^2}\right) \nabla^* p$$

Next, it seems that pressure is being non-dimensionalized by $\frac{1}{\rho_p U_0^2}$. It would probably be nicer to use $\rho_f U_0^2$ since it is closely related to kinetic energy in the flow, so we write:

$$\left(1 + \frac{1}{2} \frac{\rho_f}{\rho_p}\right) \frac{m_p U_0}{f L} \frac{d\mathbf{u}_p^*}{dt^*} = -(\mathbf{u}_p^* - \mathbf{u}_f^*) + \frac{m_p U_0}{f L} \mathbf{g}^* - \frac{m_p U_0}{f L} \left(\frac{\rho_f}{\rho_p}\right) \nabla^* \left(\frac{p}{\rho_f U_0^2}\right)$$

Rewriting with $St_k = \frac{m_p U_0}{f L}$ and $p^* = \frac{p}{\rho_f U_0^2}$ we obtain the final dimensionless form:

$$\left(1 + \frac{1}{2} \frac{\rho_f}{\rho_p}\right) \frac{d\mathbf{u}_p^*}{dt^*} = \frac{-1}{St_k} (\mathbf{u}_p^* - \mathbf{u}_f^*) + \mathbf{g}^* - \frac{\rho_f}{\rho_p} \nabla^* p^*$$

The Stokes Number

The dimensionless quantity $\frac{m_p U_0}{f L}$ is known as the Stokes number:

$$** \quad \boxed{St_k = \frac{m_p U_0}{f L}} \quad **$$

The Stokes number compares a particle's inertia to the accelerating influence of fluid velocity (through drag):

$$St_k = \frac{m_p U_0^2}{f U_0 L} = \frac{m_p U_0^2}{F_D L} \sim \frac{\text{maximum possible kinetic energy of the particle}}{\text{ability of drag to keep the particle moving with fluid}}$$

$St_k \rightarrow 0$	particles exactly follow the fluid streamlines
$St_k \rightarrow \infty$	particle trajectories unaffected by fluid streamlines
$St_k \geq 0.7$	particle inertia likely important to its trajectory

Another Look at the Nondimensional BBO Equation

Last time we derived the nondimensional BBO equation:

$$\left(1 + \frac{1}{2} \frac{\rho_f}{\rho_p}\right) \frac{d\mathbf{u}_p^*}{dt^*} = \frac{-1}{St_k} (\mathbf{u}_p^* - \mathbf{u}_f^*) + \mathbf{g}^* - \frac{\rho_f}{\rho_p} \nabla^* p^*$$

where the dimensionless variables are:

$$\begin{aligned} \nabla^* &= L \nabla & \mathbf{u}_f^* &= \frac{\mathbf{u}_f}{U_0} & t^* &= \frac{t U_0}{L} & p^* &= \frac{p}{\rho_f U_0^2} \\ \mathbf{u}_p^* &= \frac{\mathbf{u}_p}{U_0} & \mathbf{g}^* &= \frac{L}{U_0^2} \mathbf{g} & St_k &= \frac{m_p U_0}{f L} \end{aligned}$$

and L and U_0 are the external length and velocity scales of the system.

The particle behavior given by this equation is governed by two dimensionless groupings:

$$\frac{\rho_f}{\rho_p} = \text{density ratio between fluid and particle}$$

$$St_k = \frac{m_p U_0^2}{f U_0 L} = \frac{m_p U_0^2}{F_D L} \sim \frac{\text{maximum possible kinetic energy of the particle}}{\text{ability of drag to keep the particle moving with fluid}}$$

The ratio ρ_f/ρ_p determines the importance of the virtual mass and buoyancy terms.

If $St_k \rightarrow 0$, the BBO equation reduces to $\mathbf{u}_p^* = \mathbf{u}_f^*$ and the particles follow the fluid flow exactly (as “passive tracers”). This is a boring result for analysis, but very useful for experimental methods such as PIV where particles are used to visualize a fluid flow.

If $St_k \rightarrow \infty$, the BBO term containing \mathbf{u}_f^* vanishes and the particles follow “ballistic” trajectories unaffected by fluid velocity (but buoyancy and virtual mass are still present).

The BBO Equation as a Linear Second-Order Differential Equation

Consider the (dimensionless) Lagrangian particle position $\mathbf{x}_p^* = \mathbf{x}_p/L$. Note that \mathbf{x}_p^* is a function of only t^* . Neglecting the Froude–Krylov force, the nondimensional BBO equation can be written:

$$A\mathbf{x}_p^{*''} = \frac{-1}{St_k}(\mathbf{x}_p^{*'} - \mathbf{u}_f^*) + \mathbf{g}^*$$

where $A = 1 + \frac{1}{2} \frac{\rho_f}{\rho_p}$ and the Lagrangian particle velocity $\mathbf{u}_p^* = \mathbf{x}_p^{*'}$ is the derivative of \mathbf{x}_p^* .

This is an ordinary linear second-order nonhomogeneous differential equation for \mathbf{x}_p^* :

$$A\mathbf{x}_p^{*''} + \frac{1}{St_k}\mathbf{x}_p^{*'} = \frac{1}{St_k}\mathbf{u}_f^* + \mathbf{g}^*$$

ordinary: \mathbf{x}_p^* is a function of only one variable (t^*)

linear: \mathbf{x}_p^* and its derivatives are never multiplied together

second-order: the highest derivative of \mathbf{x}_p^* is a second derivative

nonhomogeneous: $\frac{1}{St_k}\mathbf{u}_f^* + \mathbf{g}^*$ is not zero and might be a function of t^*

Solving the BBO Equation as an Initial Value Problem

Suppose \mathbf{u}_f^* is constant in t^* and \mathbf{x}_p^* (\mathbf{g}^* is already a constant) and consider the BBO equation above as an initial value problem where initial particle position and velocity are known at some time $t_0^* = 0$. We seek $\mathbf{x}_p^*(t^*)$ for all $t^* > 0$.

We will follow the typical approach to solving nonhomogeneous linear differential equations to find a solution of the form $\mathbf{x}_p^*(t^*) = \mathbf{x}_{p,H}^*(t^*) + \mathbf{x}_{p,P}^*(t^*)$ where $\mathbf{x}_{p,H}^*(t^*)$ is some linear combination of homogeneous solutions and $\mathbf{x}_{p,P}^*(t^*)$ is a particular solution:

$$A\mathbf{x}_{p,H}^{*''} + \frac{1}{St_k}\mathbf{x}_{p,H}^{*'} = 0$$

$$A\mathbf{x}_{p,P}^{*''} + \frac{1}{St_k}\mathbf{x}_{p,P}^{*'} = \frac{1}{St_k}\mathbf{u}_f^* + \mathbf{g}^*$$

Homogeneous solution

Suppose the form of $\mathbf{x}_{p,H}^*$ is exponential in t^* :

$$\mathbf{x}_{p,H}^* = \text{Exp}[r t^*] \Rightarrow \begin{cases} \mathbf{x}_{p,H}^{*'} = r \text{Exp}[r t^*] \\ \mathbf{x}_{p,H}^{*''} = r^2 \text{Exp}[r t^*] \end{cases}$$

Substituting $\mathbf{x}_{p,H}^* = \text{Exp}[r t^*]$ into the homogenous form of our differential equation and dividing everything by $\text{Exp}[r t^*]$ yields the characteristic polynomial:

$$Ar^2 + \frac{1}{St_k}r = 0 \Rightarrow \begin{cases} r = 0 \\ r = \frac{-1}{ASt_k} \end{cases}$$

This is a second-order differential equation, so we expect to find two solutions or “roots” to the characteristic polynomial (special treatment is needed if roots are repeated). So the homogeneous solution form:

$$\mathbf{x}_{p,H}^* = \sum_i \mathbf{C}_i \text{Exp}[r t^*] = \mathbf{C}_1 \text{Exp}[0] + \mathbf{C}_2 \text{Exp}\left[\frac{-1}{ASt_k} t^*\right] = \mathbf{C}_1 + \mathbf{C}_2 \text{Exp}\left[\frac{-t^*}{ASt_k}\right]$$

will satisfy the homogeneous differential equation:

$$A\mathbf{x}_{p,H}^{*''} + \frac{1}{St_k}\mathbf{x}_{p,H}^{*'} = 0$$

for any constant values of \mathbf{C}_1 and \mathbf{C}_2 (note that \mathbf{C}_1 and \mathbf{C}_2 are vectors here, not scalars).

Particular solution

We can choose any particular solution $\mathbf{x}_{p,p}^*$ that satisfies the nonhomogeneous form of our differential equation:

$$A\mathbf{x}_{p,p}^{*''} + \frac{1}{St_k}\mathbf{x}_{p,p}^{*'} = \frac{1}{St_k}\mathbf{u}_f^* + \mathbf{g}^*$$

There is no universal strategy for finding particular solutions to nonhomogeneous differential equations, but in this case an easy one to choose is:

$$\mathbf{x}_{p,p}^* = (\mathbf{u}_f^* + St_k \mathbf{g}^*) t^*$$

where:

$$\begin{aligned} A\mathbf{x}_{p,p}^{*''} + \frac{1}{St_k}\mathbf{x}_{p,p}^{*'} &= A \frac{d^2}{dt^{*2}} [(\mathbf{u}_f^* + St_k \mathbf{g}^*) t^*] + \frac{1}{St_k} \frac{d}{dt^*} [(\mathbf{u}_f^* + St_k \mathbf{g}^*) t^*] \\ &= 0 + \frac{1}{St_k} [\mathbf{u}_f^* + St_k \mathbf{g}^*] \\ &= \frac{1}{St_k} \mathbf{u}_f^* + \mathbf{g}^* \end{aligned}$$

satisfying the differential equation as desired.

Combined solution

Above we found a particular solution to the differential equation and the general form of the homogeneous solution. Thus:

$$\mathbf{x}_p^*(t^*) = \mathbf{x}_{p,H}^*(t^*) + \mathbf{x}_{p,p}^*(t^*) = \mathbf{C}_1 + \mathbf{C}_2 \text{Exp} \left[\frac{-t^*}{ASt_k} \right] + (\mathbf{u}_f^* + St_k \mathbf{g}^*) t^*$$

We can now use our initial conditions $\mathbf{x}_p^*(0) = \mathbf{x}_0^*$ (position) and $\mathbf{x}_p^{*'}(0) = \mathbf{x}_0^{*'}(0)$ (velocity) to solve for the constants \mathbf{C}_1 and \mathbf{C}_2 .

$$\begin{aligned} \mathbf{x}_0^* = \mathbf{x}_p^*(0) &= \mathbf{C}_1 + \mathbf{C}_2 \text{Exp} \left[\frac{-0}{ASt_k} \right] + (\mathbf{u}_f^* + St_k \mathbf{g}^*) (0) = \mathbf{C}_1 + \mathbf{C}_2 \\ \Rightarrow \mathbf{C}_1 &= \mathbf{x}_0^* - \mathbf{C}_2 \end{aligned}$$

For velocity, we calculate the first derivative of our solution form:

$$\begin{aligned}\mathbf{x}_p^*(t^*) &= \frac{d}{dt^*} \left(\mathbf{C}_1 + \mathbf{C}_2 \text{Exp} \left[\frac{-t^*}{A \text{St}_k} \right] + (\mathbf{u}_f^* + \text{St}_k \mathbf{g}^*) t^* \right) \\ &= \frac{-\mathbf{C}_2}{A \text{St}_k} \text{Exp} \left[\frac{-t^*}{A \text{St}_k} \right] + \mathbf{u}_f^* + \text{St}_k \mathbf{g}^*\end{aligned}$$

then apply the initial condition:

$$\begin{aligned}\mathbf{x}_0^* &= \mathbf{x}_p^*(0) = \frac{-\mathbf{C}_2}{A \text{St}_k} \text{Exp} \left[\frac{-0}{A \text{St}_k} \right] + \mathbf{u}_f^* + \text{St}_k \mathbf{g}^* = \frac{-\mathbf{C}_2}{A \text{St}_k} + \mathbf{u}_f^* + \text{St}_k \mathbf{g}^* \\ \Rightarrow \mathbf{C}_2 &= A \text{St}_k (-\mathbf{x}_0^* + \mathbf{u}_f^* + \text{St}_k \mathbf{g}^*)\end{aligned}$$

Finally, substituting these expressions for \mathbf{C}_1 and \mathbf{C}_2 into our solution form $\mathbf{x}_p^*(t^*)$ and combining like terms, we obtain the particle position:

$$\mathbf{x}_p^*(t^*) = \mathbf{x}_0^* + A \text{St}_k \left(1 - \text{Exp} \left[\frac{-t^*}{A \text{St}_k} \right] \right) \mathbf{x}_0^* + \left[t^* - A \text{St}_k \left(1 - \text{Exp} \left[\frac{-t^*}{A \text{St}_k} \right] \right) \right] (\mathbf{u}_f^* + \text{St}_k \mathbf{g}^*)$$

and the particle velocity (simply the derivative of \mathbf{x}_p^*):

$$\mathbf{x}_p^{*'}(t^*) = \text{Exp} \left[\frac{-t^*}{A \text{St}_k} \right] \mathbf{x}_0^{*'} + \left(1 - \text{Exp} \left[\frac{-t^*}{A \text{St}_k} \right] \right) (\mathbf{u}_f^* + \text{St}_k \mathbf{g}^*)$$

In dimensional form these are:

$$\begin{aligned}\mathbf{x}_p(t) &= \mathbf{x}_0 + A \tau_R \left(1 - \text{Exp} \left[\frac{-t}{A \tau_R} \right] \right) \mathbf{x}_0' + \left[t - A \tau_R \left(1 - \text{Exp} \left[\frac{-t}{A \tau_R} \right] \right) \right] (\mathbf{u}_f + \tau_R \mathbf{g}) \\ \mathbf{x}_p'(t) &= \text{Exp} \left[\frac{-t}{A \tau_R} \right] \mathbf{x}_0' + \left(1 - \text{Exp} \left[\frac{-t}{A \tau_R} \right] \right) (\mathbf{u}_f + \tau_R \mathbf{g})\end{aligned}$$

where $\tau_R = m_p/f$ is a particle relaxation time characterizing the transition from inertial to drag-induced motion.

Note: Comparing the dimensional and dimensionless equations, we can see that the Stokes number acts like a dimensionless relaxation time.

Scope and limitations of this solution

The preceding work derives a closed-form analytic solution to the given BBO equation, assuming only that \mathbf{u}_f^* is constant in t^* and \mathbf{x}_p^* .

The solution is therefore valid if:

- \mathbf{u}_f^* is constant along any given particle trajectory (*e.g.* in uniform flow); or
- the range of t^* considered is small enough that \mathbf{u}_f^* is *effectively* constant.

Consider a time-advancement scenario where the values $\mathbf{x}_p^*(t_0^*)$ and $\mathbf{x}_p^{*'}(t_0^*)$ are known at some fixed time t_0^* and it is desired to estimate $\mathbf{x}_p^*(t_0^* + \Delta t^*)$ and $\mathbf{x}_p^{*'}(t_0^* + \Delta t^*)$:

- This is equivalent to the initial value problem solved above, where the known values $\mathbf{x}_p^*(t_0^*)$ and $\mathbf{x}_p^{*'}(t_0^*)$ are the initial conditions and Δt^* is the independent variable.
- $\mathbf{x}_p^*(t_0^* + \Delta t^*)$ and $\mathbf{x}_p^{*'}(t_0^* + \Delta t^*)$ can be accurately found if Δt^* is small enough that \mathbf{u}_f^* is approximately constant during the time interval from t_0^* to $t_0^* + \Delta t^*$.
- To continue the time advancement process, the new values $\mathbf{x}_p^*(t_0^* + \Delta t^*)$ and $\mathbf{x}_p^{*'}(t_0^* + \Delta t^*)$ will become the initial conditions for another initial value problem seeking $\mathbf{x}_p^*(t_0^* + \Delta t^* + \Delta t^*)$ and $\mathbf{x}_p^{*'}(t_0^* + \Delta t^* + \Delta t^*)$.

Störmer–Verlet Algorithm for Approximate Time Advancement

The Störmer–Verlet algorithm is a much simpler but less accurate particle tracking method. The discretization method is called Verlet integration.

Consider the BBO equations as expressions for Lagrangian particle acceleration:

$$\mathbf{x}_p^{*''} = \frac{-1}{ASt_k} (\mathbf{x}_p^{*'} - \mathbf{u}_f^*) + \frac{1}{A} \mathbf{g}^* \stackrel{\text{def}}{=} \mathbf{a}_p^*(t^*)$$

$$\mathbf{x}_p'' = \frac{-1}{A \tau_R} (\mathbf{x}_p' - \mathbf{u}_f) + \frac{1}{A} \mathbf{g} \stackrel{\text{def}}{=} \mathbf{a}_p(t)$$

Without loss of generality we will use the dimensional form in the following description.

The time advancement problem is that instantaneous $\mathbf{x}_p(t)$ and $\mathbf{x}_p'(t)$ are known for some particle at time t , and it is desired to estimate $\mathbf{x}_p(t + n\Delta t)$ and $\mathbf{x}_p'(t + n\Delta t)$ for some fixed timestep Δt and all integers $n > 0$.

Abbreviate the particle position, velocity, and acceleration at timestep n as:

$$\begin{aligned} \mathbf{x}_n &\stackrel{\text{def}}{=} \mathbf{x}_p(t + n\Delta t) \\ \mathbf{x}_n' &\stackrel{\text{def}}{=} \mathbf{x}_p'(t + n\Delta t) \\ \mathbf{a}_n &\stackrel{\text{def}}{=} \mathbf{a}_p(t + n\Delta t) \end{aligned}$$

First timestep ($n = 1$):

Estimate \mathbf{x}_1 using a Taylor expansion and the known initial values:

$$\mathbf{x}_1 = \mathbf{x}_0 + \Delta t \mathbf{x}_0' + \frac{\Delta t^2}{2} \mathbf{x}_0'' + \mathcal{O}(\Delta t^3)$$

where $\mathcal{O}(\Delta t^3)$ is the sum of all Taylor expansion terms involving third or higher derivatives of \mathbf{x}_0 . This acts as a residual error term whose order of magnitude scales with Δt^3 (since Δt is small we expect $\Delta t^3 > \Delta t^4 > \dots$).

So our “second-order” approximation is:

$$\mathbf{x}_1 \approx \mathbf{x}_0 + \Delta t \mathbf{x}_0' + \frac{\Delta t^2}{2} \mathbf{a}_0$$

All following timesteps ($n > 1$):

We can now exploit knowledge of particle position and velocity at *two* previous timesteps (steps n and $n - 1$) to reduce our approximation error.

Consider the Taylor expansions around time $t + n\Delta t$:

$$\mathbf{x}_{n-1} = \mathbf{x}_n - \Delta t \mathbf{x}'_n + \frac{\Delta t^2}{2} \mathbf{x}''_n - \frac{\Delta t^3}{6} \mathbf{x}'''_n + \mathcal{O}(\Delta t^4)$$

$$\mathbf{x}_{n+1} = \mathbf{x}_n + \Delta t \mathbf{x}'_n + \frac{\Delta t^2}{2} \mathbf{x}''_n + \frac{\Delta t^3}{6} \mathbf{x}'''_n + \mathcal{O}(\Delta t^4)$$

Adding the above two equations together cancels all odd terms, yielding:

$$\mathbf{x}_{n+1} = 2\mathbf{x}_n - \mathbf{x}_{n-1} + \Delta t^2 \mathbf{x}''_n + \mathcal{O}(\Delta t^4)$$

$$\therefore \mathbf{x}_{n+1} \approx 2\mathbf{x}_n - \mathbf{x}_{n-1} + \Delta t^2 \mathbf{a}_n$$

This equation (which characterizes the Störmer–Verlet method) is a third-order approximation, slightly better than that used for timestep $n = 1$.

Caveats:

The improvements in approximation error discussed above are somewhat compromised when \mathbf{a}_n (acceleration) depends on \mathbf{x}'_n (velocity), which is the case here via drag force:

$$\mathbf{a}_n = \frac{-1}{A \tau_R} (\mathbf{x}'_n - \mathbf{u}_f) + \frac{1}{A} \mathbf{g}$$

Velocity must then be estimated from position estimates using another method, such as backward difference:

$$\mathbf{x}'_n = \frac{\mathbf{x}_n - \mathbf{x}_{n-1}}{\Delta t} + \mathcal{O}(\Delta t)$$

Inertial Impaction

Consider a pure fluid uniformly flowing from a nozzle toward an infinite perpendicular surface some distance away. Let the surface be located on the $x = 0$ plane.

Wall impinging jets are a common topic of study, so we know from any number of methods that the fluid streamlines will bend along the wall away from a central stagnation point.

If particles are present in the jet fluid, their trajectory is determined by Stokes number:

$St_k \rightarrow 0$: fluid drag dominates particle inertia, and the particle follows fluid streamlines, never impacting the surface

$St_k \rightarrow \infty$: particle inertia dominates fluid drag, and the particle impacts the surface at the original jet velocity

These two particle trajectory behaviors are mutually exclusive, with the transition point at some **critical Stokes number**.

$St_k < St_{k,crit}$: no impaction

$St_k > St_{k,crit}$: impaction guaranteed

If all other jet parameters are fixed, impaction is fully determined by particle size. In fact, inertial impaction is exploited as a particle size measurement method.

Critical Stokes Number

The critical Stokes number for inertial impaction can be analytically derived.

In the wall impinging jet from the previous section, a good estimate of the centerline fluid x -velocity between the nozzle and plate is $u_f^*(x^*) \approx -Bx^*$ for some constant B .

Substitute this fluid velocity into the x -momentum BBO equation with $\rho_f/\rho_p \rightarrow 0$:

$$x_p^{*''} = \frac{-1}{St_k} (u_p^* - u_f^*) = \frac{-1}{St_k} (x_p^{*'} - [-Bx_p^*])$$

(Note that x_p^* is simply the particle x -location here, not a vector.) Rearranging we have:

$$x_p^{*''} + \frac{1}{St_k} x_p^{*'} + \frac{B}{St_k} x_p^* = 0$$

This is a homogeneous linear second-order differential equation, so we immediately consider the characteristic polynomial:

$$r^2 + \frac{1}{St_k} r + \frac{B}{St_k} = 0$$

where $x_p^* = \sum C_i \text{Exp}[r_i t^*]$. The roots of this quadratic equation are:

$$r = \frac{1}{2} \left(\frac{-1}{St_k} \pm \sqrt{\frac{1}{St_k^2} - \frac{4B}{St_k}} \right)$$

Now, the qualitative behavior in time of $x_p^* = C_1 \text{Exp}[r_1 t^*] + C_2 \text{Exp}[r_2 t^*]$ depends on whether the roots r_1 and r_2 are real or imaginary.

$St_k < 1/4B$:

- r_1 and r_2 are both real
- particle x -location decreases exponentially in time, but never reaches zero
- $x_p^* > 0$ for all time, so impaction does not occur

$St_k > 1/4B$:

- r_1 and r_2 both have nonzero imaginary parts
- particle x -location follows a sinusoidal curve in time and inevitably reaches zero
- when $x_p^* = 0$, impaction will occur

Note: The identity $e^{i\theta} = \cos \theta + i \sin \theta$ is known as Euler's formula.

Collection Efficiency on an Infinite Surface

Collection efficiency is the fraction of incoming particles that will eventually impact a given surface.

In the previous section, we derived the critical Stokes number for infinite plate impaction from an impinging jet:

$$St_{k,crit} = \frac{1}{4 B}$$

For particles below this critical Stokes number, impaction will *never* occur, and collection efficiency will be $C_E = 0$.

For particles above this critical Stokes number, impaction will *always* occur, and collection efficiency will be $C_E = 1$.

So for a jet impinging on an infinite plate, theoretical collection efficiency is a unit step function increasing exactly at $St_{k,crit}$:

$$C_E = \begin{cases} 0 & St_k < St_{k,crit} \\ 1 & St_k > St_{k,crit} \end{cases}$$

Collection Efficiency on a Finite Surface

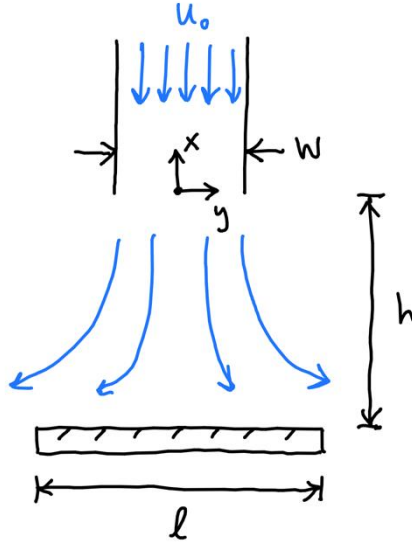
In homework, the average collection efficiency will be estimated for two surfaces with a *finite* projected area.

Impaction depends on particle size and starting location, so tracking of individual particle trajectories is necessary.

You can use the numerical solution methods for the BBO equation introduced in the preceding sections to find the trajectories.

With planar symmetry

Consider a planar jet of width w and velocity U_0 impinging on a plate of length ℓ . The plate and jet are separated by a distance h :



For particles with similar trajectories, impaction may depend on initial location, with particles emerging from the central region of the jet more likely to impact the plate.

Let the initial particle position in the jet be y_0 , with a dimensionless form:

$$y_0^* = \frac{2 y_0}{w}$$

where $0 < y_0^* < 1$ (we will neglect $y_0^* < 0$ by symmetry). Now write:

$$C_E(y_0^*, St_k) = \begin{cases} 0 & \text{particle misses plate} \\ 1 & \text{particle impacts plate} \end{cases}$$

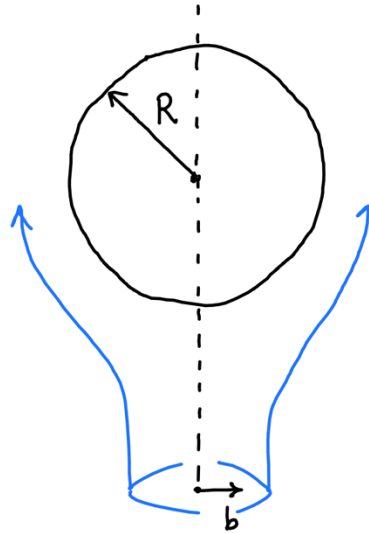
for a particle with initial position y_0^* and Stokes number St_k .

The overall collection efficiency across the entire jet for a given Stokes number is:

$$C_E(St_k) = \frac{\int_0^1 C_E(y_0^*, St_k) dy_0^*}{\int_0^1 dy_0^*} = \frac{y_{0,crit}^*}{1} = y_{0,crit}^*$$

With axisymmetry

Consider Stokes flow of velocity U_0 over a solid sphere of radius R :



Let the initial radial position of a particle from the axis of symmetry be b , with a dimensionless form $b^* = b/R$. This is called the **impact parameter**, and in literature for some reason b is often used instead of the conventional radial coordinate r .

The overall collection efficiency for a given Stokes number is now:

$$C_E(St_k) = \frac{2\pi \int_0^1 C_E(b^*, St_k) b^* db^*}{2\pi \int_0^1 b^* db^*} = \frac{b_{crit}^{*2}}{1^2} = b_{crit}^{*2}$$

This expression integrates collection efficiency over all possible initial radial positions of a particle, with differential ring areas $dA = 2\pi b^* db^*$.

This analysis can be added to the collision rate equations discussed earlier in the course by simply inserting overall collection efficiency as a prefactor. The collision rate of this sphere with species i is:

$$R_i = C_E \pi R^2 U_0 n_i$$

Phoretic Motion and Mechanical Mobility

Phoretic motion is inertialess, diffusionless motion in the presence of an external force.

If particle inertia is insignificant, $St_k \rightarrow 0$ and the BBO equation becomes:

$$-f(\mathbf{u}_p - \mathbf{u}_f) + \sum_{field} \mathbf{F}_{ext} = m_p \frac{d\mathbf{u}_p}{dt} \approx 0$$

Solving for particle velocity we obtain:

$$\begin{aligned} \mathbf{u}_p &= \mathbf{u}_f + \frac{1}{f} \sum_{field} \mathbf{F}_{ext} \\ &= \mathbf{u}_f + B \sum_{field} \mathbf{F}_{ext} \end{aligned}$$

where $B = 1/f$ is called the **mechanical mobility** of the particle.

Recall:

$$St_k = \frac{m_p U_0}{f L}$$

$$f = \frac{6 \pi \mu a_p}{C_c(Kn)}$$

$$C_c(Kn) = 1 + Kn \left(1.257 + 0.4 \exp \left[\frac{-1.1}{Kn} \right] \right)$$

$$Kn = \frac{\lambda}{a_p}$$

Pathline Function for Phoretic Motion of Particles

Even though we supposed particles are effectively inertialess in phoretic motion, they don't exactly follow fluid streamlines due to the external force(s) at work.

In this section we will characterize particle phoretic motion using a pathline function Γ .

Particles will follow pathlines of constant Γ , much like fluid elements follow streamlines of constant ψ . (To simplify the math, a 2-D system will be assumed.)

Recall the stream function (note that these are fluid velocities):

$$d\psi = u_{f,x} dy - u_{f,y} dx$$

Now construct similar parameters Γ and ϕ for the particle trajectory and external force components, respectively (note that these are particle velocities):

$$d\Gamma = u_{p,x} dy - u_{p,y} dx$$

$$d\phi = F_{ext,x} dy - F_{ext,y} dx$$

In the previous section we saw:

$$u_{p,x} = u_{f,x} + B F_{ext,x}$$

$$u_{p,y} = u_{f,y} + B F_{ext,y}$$

So combining the above we see that:

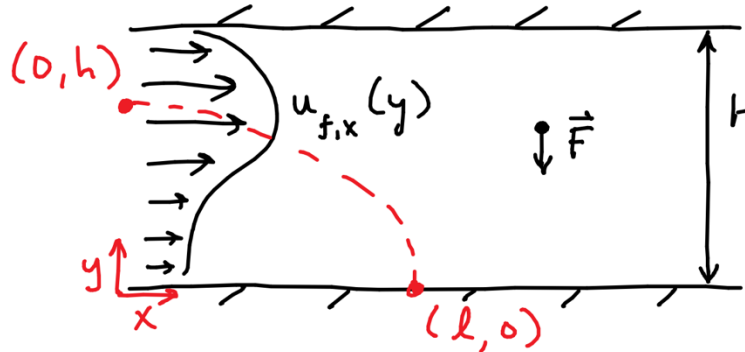
$$\begin{aligned} d\Gamma &= u_{p,x} dy - u_{p,y} dx \\ &= (u_{f,x} + B F_{ext,x}) dy - (u_{f,y} + B F_{ext,y}) dx \\ &= u_{f,x} dy + u_{f,y} dx + B F_{ext,x} dy + B F_{ext,y} dx \\ &= d\psi + B d\phi \end{aligned}$$

$$d\Gamma = d\psi + B d\phi$$

We will make use of this relationship in the next section.

Parallel Plate Precipitator

Consider steady flow of an unknown velocity profile $u_{f,x}(y)$ between infinite parallel plates, with a constant force exerted on particles as $\mathbf{F} = -F\hat{\mathbf{e}}_y$:



Particle pathlines

Let a particle's initial position be $(0, h)$, with an eventual impact location of $(\ell, 0)$ on the bottom plate.

The force \mathbf{F} causes particle $u_{p,y}$ to asymptote toward some terminal settling velocity, but $u_{p,x}$ depends on $u_{f,x}(y)$ and may lead to complicated particle trajectories.

Applying the definitions of Γ , ψ , and ϕ from the previous section, we have:

$$d\psi = u_{f,x}(y) dy$$

$$d\phi = F dx$$

$$d\Gamma = d\psi + B d\phi = u_{f,x}(y) dy + B F dx$$

Now, $d\Gamma = 0$ along a particle trajectory, so:

$$\begin{aligned} 0 &= \int_{(0,h)}^{(\ell,0)} d\Gamma \\ &= \int_{(0,h)}^{(\ell,0)} [u_{f,x}(y) dy + B F dx] \\ &= \int_h^0 u_{f,x}(y) dy + \int_0^\ell B F dx \\ &= - \int_0^h u_{f,x}(y) dy + BF\ell \end{aligned}$$

Thus:

$$\int_0^h u_{f,x}(y) dy = BF\ell$$

$$\ell = \frac{1}{BF} \int_0^h u_{f,x}(y) dy$$

where a particle initially at $(0, h)$ impacts the bottom plate at $(\ell, 0)$.

The farthest impact occurs at:

$$L_{max} = \frac{1}{BF} \int_0^H u_{f,x}(y) dy = \frac{1}{BF} \left(\frac{\dot{Q}}{w} \right) = \frac{\dot{Q}}{BFw}$$

where \dot{Q}/w is the total volumetric fluid flow rate per unit depth. A precipitator with length equal to or greater than L_{max} will have a collection efficiency of 1.

Collection efficiency

Suppose the precipitator has a finite length L , with particles at $(0, h_{crit})$ eventually impacting at $(L, 0)$. The overall collection efficiency of the precipitator is then:

$$C_E = \frac{\dot{Q}_{impact}}{\dot{Q}_{total}} = \frac{\int_0^{h_{crit}} u_{f,x}(y) dy}{\int_0^H u_{f,x}(y) dy} = \frac{BFL}{\dot{Q}/w} = \frac{BFLw}{\dot{Q}}$$

where the third equality follows from the discussion above regarding ℓ and L_{max} .

Different Types of External Forces

Gravity

An “elutriator” precipitates particles using gravitational settling.

$$\mathbf{F} = m_p \mathbf{g}$$

$$C_E = \frac{L w m_p g}{f \dot{Q}}$$

Electromagnetism

For electrostatic forces in gases:

$$\mathbf{F} = ze\mathbf{E}$$

$$\mathbf{E} = -\nabla\Phi$$

where z is integer charge level (surplus number of electrons), $e = 1.6 \times 10^{-19}$ C is the charge of a single electron, \mathbf{E} is the (static) electric field, and Φ is electric potential.

We have $\mathbf{u}_p = \mathbf{u}_f + B \mathbf{F} = \mathbf{u}_f + zeB \mathbf{E}$, and zeB is called the “electrical mobility” or “ion mobility” of the particle.

A precipitator using this force is an “electrostatic precipitator.”

Thermophoresis (Soret diffusion)

When a finite-sized particle encounters a temperature gradient, it experiences more collisions with molecules from the surrounding fluid on its warmer side, where the molecules have a higher translational energy compared to those on the colder side.

This imbalance of collisions with the surrounding fluid leads to a net momentum transfer to the particle, characterized by the thermophoretic force:

$$\mathbf{F}_{th} = \begin{cases} -v_{gas} \frac{\nabla T}{T} \rho_{gas} \bar{c}_{gas} \pi a_p^2 & \text{Kn} \rightarrow \infty \text{ (free molecular)} \\ -6\pi C_s \frac{\nabla T}{T} \mu_{gas} v_{gas} \eta a_p & \text{Kn} \rightarrow 0 \text{ (continuum)} \end{cases}$$

where:

$$\eta = \frac{2 \left(\frac{k_{cond,f}}{k_{cond,p}} \right)}{1 + 2 \left(\frac{k_{cond,f}}{k_{cond,p}} \right)}$$

and $0.75 \leq C_s \leq 1.17$ is an active area of research.

Note: \mathbf{F}_{th} does not depend on pressure as $\text{Kn} \rightarrow \infty$, so this force becomes very significant at very low pressures.

Also of interest, the ratio of thermophoretic forces at the continuum and free molecular limits is:

$$\frac{\mathbf{F}_{th,c}}{\mathbf{F}_{th,FM}} = \frac{-6\pi C_s \frac{\nabla T}{T} \mu_{gas} v_{gas} \eta a_p}{-v_{gas} \frac{\nabla T}{T} \rho_{gas} \bar{c}_{gas} \pi a_p^2} \sim \frac{\mu_{gas}}{\rho_{gas} \bar{c}_{gas} a_p} \sim \frac{\lambda}{a_p} = \text{Kn}$$

More About Thermophoresis

Terminal velocity

We apply $\mathbf{U}_{th,term} = \frac{1}{f} \mathbf{F}_{th}$ with the appropriate definitions of \mathbf{F}_{th} and f , then combine like terms to obtain the terminal velocities:

$Kn \rightarrow 0$:

$$\mathbf{U}_{th,term} = C_s \eta v_{gas} \left(\frac{-\nabla T}{T} \right)$$

$Kn \rightarrow \infty$:

$$\mathbf{U}_{th,term} = \frac{3}{4\xi} v_{gas} \left(\frac{-\nabla T}{T} \right)$$

Nondimensional thermophoretic force

The thermophoretic force can be nondimensionalized as:

$$\mathbf{F}_{th}^* = \frac{\mathbf{F}_{th}}{-k_B \nabla T a_p^3 n_{gas}} = \left(\frac{-T}{\nabla T} \right) \frac{F_{th}}{a_p^3 p}$$

where the second equality follows from $p = nk_B T$.

At the continuum and free molecular limits of Kn we get:

$$F_{th}^* = \begin{cases} 11.95 C_s \eta Kn^2 & Kn \rightarrow 0 \\ 3.99 Kn & Kn \rightarrow \infty \end{cases}$$

In between these limits the scaling dependence of F_{th}^* is between Kn and Kn^2 , as in the semi-analytical result from Talbot et al. (1980):

$$F_{th}^* = \left[\frac{1 + \left(\frac{1-\eta}{\eta} \right) 2 C_t Kn}{(1 + 3 C_m Kn)(1 + [1 - \eta] 2 C_t Kn)} \right] 11.95 C_s \eta Kn^2$$

$$C_m = 1.14$$

$$C_s = 1.17$$

$$C_t = 2.18$$

Van der Waals Forces

The van der Waals force is an attractive force that only becomes significant at extremely close distances.

Several physical mechanisms may contribute to the van der Waals force, including but not limited to induced dipoles and phase-locked electrons as neighboring materials begin to interact on a submolecular scale.

Suppose D is the shortest distance from a flat surface to the edge (not center) of a nearby particle of radius a_p . Then the energy of van der Waals interaction is:

$$W = \frac{-A a_p}{6 D}$$

where A is the Hamaker constant (a negative energy indicates attraction), and the associated van der Waals force is:

$$F_{vdw} = \frac{-\partial W}{\partial D} = \frac{-A a_p}{6 D^2}$$

Note: The Hamaker constant is a material-dependent constant on the order of 10^{-19} J.

Brownian Motion

Even in an isothermal system, particle motions may appear erratic at small scales due to random collisions with molecules in the surrounding fluid.

The effect of these collisions on the trajectory of a single particle can be represented as a Brownian force \mathbf{F}_B . For example:

$$m_p \frac{d\mathbf{u}_p}{dt} = -f(\mathbf{u}_p - \mathbf{u}_f) + \Sigma \mathbf{F}_{\text{ext}} + \mathbf{F}_B$$

Averaged over many particles at one instant in time, the net Brownian force is zero due to its random nature. This type of average is called an ensemble mean (written $\langle \mathbf{F}_B \rangle$):

$$\langle \mathbf{F}_B \rangle \stackrel{\text{def}}{=} \frac{1}{N} \sum_{i=1}^N (\mathbf{F}_B)_i = 0$$

Additionally, the Brownian force is uncorrelated with other system parameters like particle position or velocity. This can be expressed in terms of a correlation function C_{xy} defined using ensemble mean values:

$$C_{x,y} \stackrel{\text{def}}{=} \langle xy \rangle - \langle x \rangle \langle y \rangle$$

The parameters x and y are strongly correlated if $C_{x,y}$ is large and positive, uncorrelated if it is zero, and strongly anti-correlated if it is large and negative. So we observe:

$$C_{\mathbf{F}_B, \mathbf{X}} = 0$$

for all $\mathbf{X} \neq \mathbf{F}_B$.

Particle Diffusion Coefficient

Fick's Law observations

If a small droplet of dye is placed in the center of a quiescent liquid film, the dye will slowly spread outward over time.

In this two-dimensional example, the mean squared radial displacement of the dye in time has been experimentally observed to follow:

$$\langle r^2 \rangle = 4Dt$$

where the diffusion coefficient D is some system-specific constant with units of m^2/s . In three dimensions, mean squared displacement of the dye follows:

$$\langle \mathbf{x}^2 \rangle = 6Dt$$

These early observations of diffusion led to some interest in characterizing D .

Stokes–Einstein Equation derivation

The analytical form of the diffusion coefficient for a particle was independently discovered by William Sutherland (1904), Albert Einstein (1905), and Marian Smoluchowski (1906).

The derivation below combines the Langevin equation with results from kinetic theory and the above experimental observations (numbered here consistently with the lecture).

1. Consider a particle in quiescent isothermal fluid, and neglect gravity. The Langevin equation reduces to:

$$m_p \frac{d\mathbf{u}_p}{dt} = -f\mathbf{u}_p + \mathbf{F}_B$$

2. Write $\Gamma = f/m_p = 1/\tau_R$ and $\mathbf{A} = \mathbf{F}_B/m_p$. Keep in mind that \mathbf{A} , \mathbf{F}_B , \mathbf{u}_p , and \mathbf{x}_p are all functions of time, which we will be integrating over later.
3. After substituting definitions from (2), equation (1) becomes:

$$\frac{d\mathbf{u}_p}{dt} = -\Gamma\mathbf{u}_p + \mathbf{A}$$

4. Observe that in general:

$$\begin{aligned}\frac{d(\mathbf{x}_p \cdot \mathbf{u}_p)}{dt} &= \mathbf{x}_p \cdot \frac{d\mathbf{u}_p}{dt} + \mathbf{u}_p \cdot \frac{d\mathbf{x}_p}{dt} \\ &= \mathbf{x}_p \cdot \frac{d\mathbf{u}_p}{dt} + \mathbf{u}_p^2\end{aligned}$$

5. Combining (3) and (4) we obtain:

$$\begin{aligned}\frac{d(\mathbf{x}_p \cdot \mathbf{u}_p)}{dt} - \mathbf{u}_p^2 &= \mathbf{x}_p \cdot \frac{d\mathbf{u}_p}{dt} \\ &= \mathbf{x}_p \cdot (-\Gamma \mathbf{u}_p + \mathbf{A}) \\ &= -\Gamma \mathbf{x}_p \cdot \mathbf{u}_p + \mathbf{x}_p \cdot \mathbf{A}\end{aligned}$$

6. Rearrange (5) as:

$$\frac{d(\mathbf{x}_p \cdot \mathbf{u}_p)}{dt} + \Gamma(\mathbf{x}_p \cdot \mathbf{u}_p) = \mathbf{x}_p \cdot \mathbf{A} + \mathbf{u}_p^2$$

7. Prepare for integration by multiplying (6) by $e^{\Gamma t}$ (the integrating factor technique):

$$e^{\Gamma t} \frac{d(\mathbf{x}_p \cdot \mathbf{u}_p)}{dt} + \Gamma e^{\Gamma t} (\mathbf{x}_p \cdot \mathbf{u}_p) = (\mathbf{x}_p \cdot \mathbf{A} + \mathbf{u}_p^2) e^{\Gamma t}$$

By the chain rule the left-hand side now simplifies:

$$\frac{d(e^{\Gamma t} \mathbf{x}_p \cdot \mathbf{u}_p)}{dt} = (\mathbf{x}_p \cdot \mathbf{A} + \mathbf{u}_p^2) e^{\Gamma t}$$

And so:

$$d(e^{\Gamma t} \mathbf{x}_p \cdot \mathbf{u}_p) = (\mathbf{x}_p \cdot \mathbf{A} + \mathbf{u}_p^2) e^{\Gamma t} dt$$

8. Integrate (7c) directly:

$$\begin{aligned}
 e^{\Gamma t} \mathbf{x}_p \cdot \mathbf{u}_p &= \int_0^t d\xi = \int_0^t (\mathbf{x}_p \cdot \mathbf{A} + \mathbf{u}_p^2) e^{\Gamma \tau} d\tau \\
 &= \int_0^t e^{\Gamma \tau} \mathbf{x}_p \cdot \mathbf{A} d\tau + \int_0^t e^{\Gamma \tau} \mathbf{u}_p^2 d\tau
 \end{aligned}$$

9. The left-hand side of (8) is easy, but the right-hand side will need more work:

$$e^{\Gamma t} \mathbf{x}_p \cdot \mathbf{u}_p = \int_0^t e^{\Gamma \tau} \mathbf{x}_p \cdot \mathbf{A} d\tau + \int_0^t e^{\Gamma \tau} \mathbf{u}_p^2 d\tau$$

Recall that this is still an equation describing the trajectory of a single particle.

10. Now, average equation (9) across many particles of uniform $\Gamma = f/m_p$:

$$\langle e^{\Gamma t} \mathbf{x}_p \cdot \mathbf{u}_p \rangle = \left\langle \int_0^t e^{\Gamma \tau} \mathbf{x}_p \cdot \mathbf{A} d\tau + \int_0^t e^{\Gamma \tau} \mathbf{u}_p^2 d\tau \right\rangle$$

Since particle identity and time are independent, we can move the ensemble averaging inside the integrals:

$$\langle e^{\Gamma t} \mathbf{x}_p \cdot \mathbf{u}_p \rangle = \int_0^t \langle e^{\Gamma \tau} \mathbf{x}_p \cdot \mathbf{A} \rangle d\tau + \int_0^t \langle e^{\Gamma \tau} \mathbf{u}_p^2 \rangle d\tau$$

Furthermore, at any given time all considered particles share the same value of $e^{\Gamma t}$, so this can be factored out of any ensemble averages as a constant:

$$e^{\Gamma t} \langle \mathbf{x}_p \cdot \mathbf{u}_p \rangle = \int_0^t e^{\Gamma \tau} \langle \mathbf{x}_p \cdot \mathbf{A} \rangle d\tau + \int_0^t e^{\Gamma \tau} \langle \mathbf{u}_p^2 \rangle d\tau$$

And finally, since $\langle \mathbf{x}_p \cdot \mathbf{A} \rangle - \langle \mathbf{x}_p \rangle \cdot \langle \mathbf{A} \rangle = C_{\mathbf{x}_p, \mathbf{A}} = C_{\mathbf{x}_p, \mathbf{F}_B} = 0$ (*Brownian force is uncorrelated with particle position*) and $\langle \mathbf{A} \rangle = \langle \mathbf{F}_B \rangle = 0$ (*Brownian motion is isotropic*):

$$\int_0^t e^{\Gamma \tau} \langle \mathbf{x}_p \cdot \mathbf{A} \rangle d\tau = \int_0^t e^{\Gamma \tau} \langle \mathbf{x}_p \rangle \cdot \langle \mathbf{A} \rangle d\tau = 0$$

11. Steps in (10) obtained:

$$e^{\Gamma t} \langle \mathbf{x}_p \cdot \mathbf{u}_p \rangle = \int_0^t e^{\Gamma \tau} \langle \mathbf{u}_p^2 \rangle d\tau$$

From kinetic theory, we know $\langle \mathbf{u}_p^2 \rangle$ is constant in time for a given particle mass and temperature. Therefore:

$$e^{\Gamma t} \langle \mathbf{x}_p \cdot \mathbf{u}_p \rangle = \langle \mathbf{u}_p^2 \rangle \int_0^t e^{\Gamma \tau} d\tau = \langle \mathbf{u}_p^2 \rangle \left(\frac{e^{\Gamma t} - 1}{\Gamma} \right)$$

12. Rearrange (11b) as:

$$\begin{aligned} \langle \mathbf{x}_p \cdot \mathbf{u}_p \rangle &= e^{-\Gamma t} \langle \mathbf{u}_p^2 \rangle \left(\frac{e^{\Gamma t} - 1}{\Gamma} \right) \\ &= \frac{\langle \mathbf{u}_p^2 \rangle}{\Gamma} (1 - e^{-\Gamma t}) \end{aligned}$$

13. Prepare for another integration by manipulating the left-hand side of (12):

$$\begin{aligned} \frac{\langle \mathbf{u}_p^2 \rangle}{\Gamma} (1 - e^{-\Gamma t}) &= \langle \mathbf{x}_p \cdot \mathbf{u}_p \rangle \\ &= \langle \mathbf{x}_p \cdot \frac{d\mathbf{x}_p}{dt} \rangle \\ &= \frac{1}{2} \left\langle \frac{d(\mathbf{x}_p^2)}{dt} \right\rangle \\ &= \frac{1}{2} \frac{d\langle \mathbf{x}_p^2 \rangle}{dt} \end{aligned}$$

where the last equality is possible because ensemble averaging and time are independent.

Separating variables, we have:

$$\frac{1}{2} d\langle \mathbf{x}_p^2 \rangle = \frac{\langle \mathbf{u}_p^2 \rangle}{\Gamma} (1 - e^{-\Gamma t}) dt$$

14. Integrate (13b), recalling that $\langle \mathbf{u}_p^2 \rangle$ is constant in time:

$$\frac{1}{2} \int_0^{\langle \mathbf{x}_p^2 \rangle} d\xi = \frac{\langle \mathbf{u}_p^2 \rangle}{\Gamma} \int_0^t (1 - e^{-\Gamma \tau}) d\tau$$

15. Solve both integrals in (14):

$$\begin{aligned} \frac{1}{2} \langle \mathbf{x}_p^2 \rangle &= \frac{\langle \mathbf{u}_p^2 \rangle}{\Gamma} \left(t + \frac{e^{-\Gamma t} - 1}{\Gamma} \right) \\ &= \frac{\langle \mathbf{u}_p^2 \rangle}{\Gamma} t \left(1 + \frac{e^{-\Gamma t} - 1}{\Gamma t} \right) \end{aligned}$$

Diffusion is a slow process compared to convection, so if diffusion is significant at some time t it seems reasonable that $t \gg \tau_R$ or equivalently $\Gamma t = t/\tau_R \rightarrow \infty$:

$$\lim_{\Gamma t \rightarrow \infty} \frac{e^{-\Gamma t} - 1}{\Gamma t} = \frac{0 - 1}{\infty} = 0$$

Accordingly we make the approximation:

$$\frac{1}{2} \langle \mathbf{x}_p^2 \rangle = \frac{\langle \mathbf{u}_p^2 \rangle}{\Gamma} t \left(1 + \frac{e^{-\Gamma t} - 1}{\Gamma t} \right) \approx \frac{\langle \mathbf{u}_p^2 \rangle}{\Gamma} t$$

at diffusion timescales.

16. In (15c), we are left with $\langle \mathbf{x}_p^2 \rangle$ and $\langle \mathbf{u}_p^2 \rangle$. From experimental observations of diffusion:

$$\langle \mathbf{x}_p^2 \rangle = 6Dt \quad (\text{or } 2Dt \text{ per dimension})$$

So we have:

$$6Dt = \langle \mathbf{x}_p^2 \rangle = 2 \frac{\langle \mathbf{u}_p^2 \rangle}{\Gamma} t$$

17. Rearrange (16b) and expand $\Gamma = f/m_p$:

$$D = \frac{1}{3} \frac{\langle \mathbf{u}_p^2 \rangle}{\Gamma} = \frac{m_p \langle \mathbf{u}_p^2 \rangle}{3f}$$

18. Next, from kinetic theory the average particle kinetic energy is:

$$\frac{1}{2} m_p \langle \mathbf{u}_p^2 \rangle = \frac{3}{2} k_B T \quad (\text{or } \frac{1}{2} k_B T \text{ per dimension})$$

19. Combining (17) and (18) we obtain:

$$D = \frac{m_p \langle \mathbf{u}_p^2 \rangle}{3 f} = \frac{(3 k_B T)}{3 f} = \frac{k_B T}{f}$$

This is known as the Stokes–Einstein Equation:

$$D = \frac{k_B T}{f}$$

Notes:

- Recall that $f = 3\pi\mu d_p/C_c$
- $St_k = m_p/f t = 1/\Gamma t$ where $t = L/U_0$, so $\Gamma t \rightarrow \infty$ assumes $St_k \rightarrow 0$
- Diffusion increases with temperature (note approx. $f \sim \mu \sim T^{1/2}$ for gases)
- Diffusion coefficient $D \sim f^{-1} \sim d_p^{-1}$ is very sensitive to particle size

Other forms of this equation include:

$$B = \frac{D}{k_B T} \quad \text{where mobility } B = 1/f$$

$$Z_p = \frac{zeD}{k_B T} \quad \text{in charged gases}$$

Brownian Dynamics (Lagrangian Perspective)

Brownian dynamics: phoretic motion with diffusion (no particle inertia)

As recently introduced, mean-squared displacement during diffusive motion scales as:

$$\langle \mathbf{x}_p^2 \rangle = 6Dt \quad \text{and} \quad \langle x_p^2 \rangle = \langle y_p^2 \rangle = \langle z_p^2 \rangle = 2Dt$$

for a particle in a quiescent fluid, where the diffusion coefficient D is characterized by the Stokes–Einstein equation:

$$D = \frac{k_B T}{f} = \frac{k_B T C_c}{3\pi\mu d_p}$$

A numerical particle tracking algorithm can incorporate this random diffusive behavior of $\langle \mathbf{x}_p^2 \rangle$ using a Gaussian distributed random variable (GRV), here written as θ_i , where:

$$\begin{array}{ll} \langle \theta_i \rangle = 0 & \text{and} \quad \sigma_{\theta_i} = 1 \\ \text{zero mean} & \text{unit standard deviation} \end{array}$$

Under phoretic motion with diffusion, particle x -location is advanced as:

$$x_p(t + \Delta t) = x_p(t) + \Delta t u_f + \Delta t B \Sigma F_x + (2D\Delta t)^{1/2} \theta_x$$

where:

Δt	is small enough that u_f is effectively constant
u_f	is local fluid velocity
B	is mechanical mobility
ΣF_x	includes all external forces
$(2D\Delta t)^{1/2}$	is root-mean-square displacement by diffusion after Δt
θ_x	is a GRV with zero mean and unit standard deviation

Particle displacement in the y and z directions would be estimated with identical but independent equations.

Notes:

- All θ_i are independent, *i.e.* for a given timestep in general $\theta_x \neq \theta_y \neq \theta_z$ and between timesteps $\theta_{x,t} \neq \theta_{x,t+\Delta t}$
- Particle trajectories are not necessarily linear between consecutive timesteps, *i.e.* one should not connect estimated particle positions with a straight line

Gaussian random variables

All θ_i used in the preceding section have a **standard normal distribution** (zero mean and unit standard deviation).

Most modern programming languages directly support normally distributed random variables, *e.g.* **randn** in Matlab.

If only *uniformly* distributed random variables are available (such as **rand**), a standard normal distribution may be approximated as:

$$\theta_i = \text{randn} \approx \left(\sum_{i=1}^{12} \text{rand}_i \right) - 6$$

This approximation makes use of the Central Limit Theorem, which states that large enough samples from *any* underlying distribution will have normally distributed mean values.

Notes on the above approximation:

- Values more extreme than $\pm 6\sigma$ have zero probability (a potential issue).
- The numbers 12 and 6 cannot in general be replaced by N and $N/2$. Doing so for $N \neq 12$ would violate $\sigma_\theta = 1$. The true form is:

$$\text{randn} \approx \frac{1}{\sigma_N} \left[\frac{1}{N} \left(\sum_{i=1}^N \text{rand}_i \right) - \mu_N \right]$$

where μ_N and σ_N are the expected mean and standard deviation of many sample averages $\frac{1}{N} (\sum_{i=1}^N \text{rand}_i)$. The case $N = 12$ is suggested simply because $\sigma_{N=12} \approx N^{-1/2}$ and the only surviving coefficient is $N\mu_N = 6$.

Mass Transfer with Diffusion (Eulerian Perspective)

Brownian motion has the macroscopic appearance of a net particle flux being driven by a concentration gradient:

$$J''_{diff} = -D \frac{\partial n}{\partial x}$$

$$\mathbf{J}''_{diff} = -D \nabla n$$

where J'' is particle flux with units of $\text{m}^{-2}\text{s}^{-1}$. This relationship is known as Fick's Law, and has a form identical to Fourier's Law for conduction: $\mathbf{q}''_{cond} = -k_{cond} \nabla T$.

Monodisperse diffusion

Consider the movement of particles of size k in the x -direction through a stationary control volume of differential dimensions $\delta x \delta y \delta z$. Neglecting particle inertia, we have:

$$\delta x \delta y \delta z \frac{\partial n_k}{\partial t} + \delta y \delta z (J''_{k,out} - J''_{k,in}) = \delta x \delta y \delta z \sum n_k'''$$

where J''_k is total flux and n_k''' is volumetric production of particles (source/sink term). Dividing by $\delta x \delta y \delta z$ and letting $\delta x \rightarrow 0$, we obtain the differential mass balance:

$(1\text{-D}) \quad \frac{\partial n_k}{\partial t} + \frac{\partial J''_k}{\partial x} = \sum n_k'''$ $(3\text{-D}) \quad \frac{\partial n_k}{\partial t} + \nabla \cdot \mathbf{J}''_k = \sum n_k'''$

Considering particle diffusion, advection, and phoretic motion, we can expand:

$$\begin{aligned} \mathbf{J}''_k &= \mathbf{J}''_{k,diff} + \mathbf{J}''_{k,fluid} + \mathbf{J}''_{k,forces} \\ &= -D \nabla n_k + n_k \mathbf{u}_f + B n_k \Sigma \mathbf{F}_{ext} \end{aligned}$$

where $B = 1/f = D/k_B T$ is particle mobility.

Expanding \mathbf{J}'' in the 3-D mass balance, we obtain:

$$\frac{\partial n_k}{\partial t} + \nabla \cdot (-D \nabla n_k + n_k \mathbf{u}_f + B n_k \Sigma \mathbf{F}_{\text{ext}}) = \sum n_k'''$$

$$\frac{\partial n_k}{\partial t} + \mathbf{u}_f \cdot \nabla n_k + \frac{D}{k_B T} (\Sigma \mathbf{F}_{\text{ext}} \cdot \nabla n_k + n_k \nabla \cdot \Sigma \mathbf{F}_{\text{ext}}) = D \nabla^2 n_k + \sum n_k'''$$

assuming the surrounding fluid is incompressible ($\nabla \cdot \mathbf{u}_f = 0$).

The term here multiplied by $D/k_B T$ differentiates this equation from the heat transfer equation, since external forces can drive mass transfer, but not heat transfer.

If the external forces can be represented as the gradient of a potential energy ($\mathbf{F} = -\nabla \Phi$), we obtain the form:

$$\frac{\partial n_k}{\partial t} + \mathbf{u}_f \cdot \nabla n_k - \frac{D}{k_B T} (\nabla \Phi \cdot \nabla n_k + n_k \nabla^2 \Phi) = D \nabla^2 n_k + \sum n_k'''$$

where the term $\nabla^2 \Phi$ is often zero or negligible, depending on the type of force field.

Boundary and initial conditions are needed in order to solve this partial differential equation for $n_k(\mathbf{x}, t)$.

If particles impacting a solid surface always adhere, the appropriate boundary condition for the surface is $n_k = 0$, and boundary layer solutions similar to those for heat or momentum diffusion can be obtained.

Polydisperse diffusion

It would be nice to extend the analysis for particles of a single size ($\partial n_k / \partial t$) to include size distribution moments ($\partial M_k / \partial t$). Then we could handle polydisperse particles.

Starting from the above analysis, neglect phoretic forces. Then:

$$\frac{\partial n}{\partial t} + \mathbf{u}_f \cdot \nabla n = D \nabla^2 n + \sum \frac{\partial n}{\partial t}_{reaction}$$

where n is now the concentration of particles with volume v_p , and n''' from each reaction type contributes $\partial n / \partial t_{reaction}$. Multiplying everything by the constant v_p^k we get:

$$\begin{aligned} v_p^k \left(\frac{\partial n}{\partial t} + \mathbf{u}_f \cdot \nabla n \right) &= v_p^k \left(D \nabla^2 n + \sum \frac{\partial n}{\partial t}_{react} \right) \\ \Rightarrow \frac{\partial (v_p^k n)}{\partial t} + \mathbf{u}_f \cdot \nabla (v_p^k n) &= \nabla^2 (D v_p^k n) + \sum \left[\frac{\partial (v_p^k n)}{\partial t} \right]_{react} \end{aligned}$$

Note that this is still an equation for a single particle size. Summing this equation across all possible particle sizes in our size distribution, we obtain:

$$\begin{aligned} \frac{\partial}{\partial t} \left(\int v_p^k \partial n \right) + \mathbf{u}_f \cdot \nabla \left(\int v_p^k \partial n \right) &= \nabla^2 \left(\int D v_p^k \partial n \right) + \sum \frac{\partial}{\partial t} \left(\int v_p^k \partial n \right)_{react} \\ \Rightarrow \frac{\partial}{\partial t} \left(\int_0^\infty v_p^k \frac{\partial n}{\partial v_p} \partial v_p \right) + \mathbf{u}_f \cdot \nabla \left(\int_0^\infty v_p^k \frac{\partial n}{\partial v_p} \partial v_p \right) \\ &= \nabla^2 \left(\int_0^\infty D v_p^k \frac{\partial n}{\partial v_p} \partial v_p \right) + \sum \frac{\partial}{\partial t} \left(\int_0^\infty v_p^k \frac{\partial n}{\partial v_p} \partial v_p \right)_{react} \\ \Rightarrow \frac{\partial M_k}{\partial t} + \mathbf{u}_f \cdot \nabla M_k &= \nabla^2 \left(\int_0^\infty D v_p^k \frac{\partial n}{\partial v_p} \partial v_p \right) + \sum \left[\frac{\partial M_k}{\partial t} \right]_{react} \end{aligned}$$

Note that D must stay inside the particle size integral since it depends on v_p .

Also note that possible $(\partial M_k / \partial t)_{react}$ include volumetric moment change rates due to coagulation, deposition, fragmentation, *etc.* exactly as discussed earlier in the course.

The integral $\int_0^\infty D v_p^k \frac{\partial n}{\partial v_p} \partial v_p$ is our only remaining challenge. We know that:

$$v_p = \frac{4\pi}{3} a_p^3$$

$$D = \frac{k_B T}{f} = \frac{k_B T}{6\pi\mu} a_p^{-1} C_c = \frac{k_B T}{6\pi\mu} \left(\frac{4\pi}{3}\right)^{\frac{1}{3}} v_p^{-\frac{1}{3}} C_c$$

$$C_c = 1 + \frac{\lambda}{a_p} \left(1.257 + 0.4 \exp\left[\frac{-1.1 a_p}{\lambda}\right] \right)$$

At low pressures, $\text{Kn} \rightarrow \infty$ and we approximate:

$$C_c \approx 1 + 1.657 \frac{\lambda}{a_p} = 1 + 1.657 \lambda \left(\frac{4\pi}{3}\right)^{\frac{1}{3}} v_p^{-\frac{1}{3}}$$

$$D \approx \frac{k_B T}{6\pi\mu} \left(\frac{4\pi}{3}\right)^{\frac{1}{3}} \left[v_p^{-\frac{1}{3}} + 1.657 \lambda \left(\frac{4\pi}{3}\right)^{\frac{1}{3}} v_p^{-\frac{2}{3}} \right]$$

Therefore:

$$\begin{aligned} \int_0^\infty D v_p^k \frac{\partial n}{\partial v_p} \partial v_p &\approx \frac{k_B T}{6\pi\mu} \left(\frac{4\pi}{3}\right)^{\frac{1}{3}} \left[\int_0^\infty v_p^{k-\frac{1}{3}} \frac{\partial n}{\partial v_p} \partial v_p + 1.657 \lambda \left(\frac{4\pi}{3}\right)^{\frac{1}{3}} \int_0^\infty v_p^{k-\frac{2}{3}} \frac{\partial n}{\partial v_p} \partial v_p \right] \\ &= \frac{k_B T}{6\pi\mu} \left(\frac{4\pi}{3}\right)^{\frac{1}{3}} \left[M_{k-\frac{1}{3}} + 1.657 \lambda \left(\frac{4\pi}{3}\right)^{\frac{1}{3}} M_{k-\frac{2}{3}} \right] \end{aligned}$$

And:

$$\frac{\partial M_k}{\partial t} + \mathbf{u}_f \cdot \nabla M_k = \frac{k_B T}{6\pi\mu} \left(\frac{4\pi}{3}\right)^{\frac{1}{3}} \nabla^2 \left(M_{k-\frac{1}{3}} + 1.657 \lambda \left(\frac{4\pi}{3}\right)^{\frac{1}{3}} M_{k-\frac{2}{3}} \right) + \sum \left[\frac{\partial M_k}{\partial t} \right]_{react}$$

Finite Difference Methods

Finite difference methods are used to numerically approximate the derivatives of an unknown function. The general idea comes from Taylor series, which can (exactly) express any function's value with respect to its value and derivatives at a second point:

$$\begin{aligned} f(x + \Delta x) &= \sum_{n=0}^{\infty} \frac{f^{(n)}(x)}{n!} \Delta x^n \\ &= f(x) + \frac{f'(x)}{1!} \Delta x + \frac{f''(x)}{2!} \Delta x^2 + \dots \end{aligned}$$

where $f^{(n)}$ is the n -th derivative of f . If some error is acceptable, then the infinite series can be truncated and rearranged, leaving an approximation for f' :

$$f(x + \Delta x) \approx f(x) + \frac{f'(x)}{1!} \Delta x$$

$$\Rightarrow f'(x) \approx \frac{f(x + \Delta x) - f(x)}{\Delta x}$$

This is known as a **forward-differencing** scheme, since $f'(x)$ is approximated by looking ahead to $f(x + \Delta x)$.

The analogous *backward-differencing* scheme can be obtained from the truncated Taylor expansion $f(x - \Delta x) \approx f(x) - f'(x) \Delta x$.

Note the similarity of forward-differencing to the fundamental definition of a derivative:

$$f'(x) \stackrel{\text{def}}{=} \lim_{\Delta x \rightarrow 0} \frac{f(x + \Delta x) - f(x)}{\Delta x}$$

In the finite difference method, Δx remains finite in size (not vanishingly small). This gives rise to what is called local truncation error, referring to the Taylor series truncations above. (An important question is how the order of truncation error scales with Δx , which is discussed in detail in AEM 8253 – Computational Methods in Fluid Mechanics.)

Similarly, for a second derivative f'' :

$$f(x + \Delta x) \approx f(x) + \frac{f'(x)}{1!} \Delta x + \frac{f''(x)}{2!} \Delta x^2$$

and

$$f(x - \Delta x) \approx f(x) + \frac{f'(x)}{1!} (-\Delta x) + \frac{f''(x)}{2!} (-\Delta x)^2$$

$$\Rightarrow f(x + \Delta x) + f(x - \Delta x) \approx 2f(x) + f''(x) \Delta x^2$$

$$\Rightarrow f''(x) \approx \frac{f(x - \Delta x) - 2f(x) + f(x + \Delta x)}{\Delta x^2}$$

This would be called a central differencing scheme, since it approximates f'' using values of f spread uniformly around x .

There are many other finite differencing schemes, including some that are more complex but more accurate than those shown above. In general, having more points of information on the right-hand side of the equation can reduce the overall approximation error.

Solving PDEs with Finite Difference Methods

Finite difference methods can convert any ordinary or partial differential equation into a system of algebraic equations, but only with reduced solution accuracy and resolution.

Each derivative in the equation is replaced by finite difference approximations like those shown above, with Δx and Δy step sizes chosen as some finite grid of points.

After determining appropriate boundary conditions at the grid edges, solving the resulting system of algebraic equations for the entire grid will yield the approximate values of all unknown functions in the PDE at each grid point.

If the PDE is linear, obtaining a solution on an $M \times N$ size grid will be no worse than inverting an $M \times N$ matrix. (In the example below, the solution is much easier.)

To illustrate, consider a spatially developing thermal boundary layer:

$$u \frac{\partial T}{\partial x} = \alpha \frac{\partial^2 T}{\partial y^2}$$

where α is assumed constant and conduction in the x -direction is neglected. For simplicity suppose the grid space is rectangular with $x_{min} = 0$.

Replacing the two derivatives with finite-difference approximations, we have:

$$u(x, y) \left[\frac{T(x + \Delta x, y) - T(x, y)}{\Delta x} \right] = \alpha \left[\frac{T(x, y - \Delta y) - 2 T(x, y) + T(x, y + \Delta y)}{\Delta y^2} \right]$$

And rearranging we obtain:

$$T(x + \Delta x, y) = T(x, y) + \frac{\alpha \Delta x}{u(x, y) \Delta y^2} [T(x, y - \Delta y) - 2 T(x, y) + T(x, y + \Delta y)]$$

Note that the entire right-hand side can be calculated using only knowledge of the temperature and velocity values at x , not $x + \Delta x$. If temperature profiles are known at the grid boundaries, the solution temperature field $T(x, y)$ can be immediately calculated column by column, moving in the positive x -direction from the $x = 0$ boundary.

In this case, for numerical stability we need:

$$\frac{\alpha \Delta x}{u(x, y) \Delta y^2} < \frac{1}{2}$$

This criteria comes from von Neumann or Fourier stability analysis.

Dimensionless Groupings in Mass Transfer

A generic non-dimensional species mass balance is:

$$\frac{\partial n^*}{\partial t^*} + \mathbf{u}^* \cdot \nabla^* n^* = \frac{D}{U_0 L} \nabla^{*2} n^* + \frac{L}{U_0 n_0} \sum R$$

where n_0 is some reference concentration and $\sum R$ are reaction source/sink rates.

The two dimensionless groupings left over are the Peclet and Damköhler numbers:

$$\frac{\partial n^*}{\partial t^*} + \mathbf{u}^* \cdot \nabla^* n^* = \frac{1}{\text{Pe}} \nabla^{*2} n^* + \text{Da}$$

Peclet number compares the species transport by advection and diffusion:

$$\text{Pe} = \frac{U_0 L}{D} = \text{Re}_L \text{Sc}$$

where Schmidt number is the diffusivity ratio $\text{Sc} = \nu_f / D$. Note that D is size-dependent, so the qualitative behavior of a given flow may actually depend on particle size!

Damköhler number compares the reaction rates to advection:

$$\text{Da} = \frac{L}{U_0 n_0} \sum R$$

**Note: Damköhler number is not standardized and multiple definitions exist.

Collisions Caused by Brownian Motion

If particles have Brownian motion, it could lead to more collisions.

The following rate coefficient for collisions arising from Brownian motion was derived by Smoluchowski in 1917.

Consider particles of two sizes, a_i and a_j , colliding due to Brownian motion.

Since the Brownian trajectories of particles i and j are uncorrelated, suppose we solve the i - j collision problem for a stationary spherical collector of radius $a_i + a_j$ impacted by wandering point masses of diffusivity $D_{ij} = D_i + D_j$.

We seek the steady-state radial concentration profile $n(r)$ of wandering particles around this spherical collector. Thus:

$$\begin{aligned} 0 &= \frac{\partial n}{\partial t} \\ &= D \nabla^2 n \\ &= \frac{D}{r^2} \left[\frac{d}{dr} \left(r^2 \frac{dn}{dr} \right) \right] \end{aligned}$$

Integrating twice we obtain:

$$n(r) = C_2 - \frac{C_1}{r}$$

Adding boundary conditions:

$$\begin{aligned} n(\infty) = n_\infty &\quad \Rightarrow \quad C_2 = n_\infty \\ n(a_i + a_j) = 0 &\quad \Rightarrow \quad C_1 = n_\infty (a_i + a_j) \end{aligned}$$

$$\therefore n(r) = n_\infty \left(1 - \frac{a_i + a_j}{r} \right)$$

Now, the rate of particles depositing on the surface of the single collector is:

$$\begin{aligned}
 R_{dep} &= A_{surf} D_{ij} \left(\frac{\partial n}{\partial r} \right)_{r=a_i+a_j} \\
 &= 4\pi(a_i + a_j)^2 D_{ij} \left(\frac{n_\infty}{a_i + a_j} \right) \\
 &= 4\pi D_{ij} (a_i + a_j) n_\infty
 \end{aligned}$$

So the total collision rate is:

$$\begin{aligned}
 R_{ij} &= R_{dep} n_{collector} \\
 &= 4\pi D_{ij} (a_i + a_j) n_\infty n_{collector} \\
 &= 4\pi D_{ij} (a_i + a_j) n_i n_j
 \end{aligned}$$

Hence we see that:

$$\beta_{ij} = \frac{R_{ij}}{n_i n_j} = 4\pi(D_i + D_j)(a_i + a_j)$$

And using $D_i = k_B T / f_i = k_B T / 6\pi\mu a_i$ ($C_c = 1$ continuum Stokes flow) we obtain:

$$\beta_{ij} = \frac{2k_B T}{3\mu} \left(\frac{1}{a_i} + \frac{1}{a_j} \right) (a_i + a_j)$$

In spite of the strange assumptions made above, this result is actually very accurate.

Moment Methods for Brownian Coagulation

In terms of particle volume:

$$\begin{aligned}\beta_{ij} &= \frac{2k_B T}{3\mu} \left(\frac{1}{a_i} + \frac{1}{a_j} \right) (a_i + a_j) \\ &= \frac{2k_B T}{3\mu} \left(v_i^{-\frac{1}{3}} + v_j^{-\frac{1}{3}} \right) \left(v_i^{\frac{1}{3}} + v_j^{\frac{1}{3}} \right) \\ &= \frac{2k_B T}{3\mu} \left(2 + v_i^{-\frac{1}{3}} v_j^{\frac{1}{3}} + v_i^{\frac{1}{3}} v_j^{-\frac{1}{3}} \right)\end{aligned}$$

Substituting into the familiar equations for $\partial M_k / \partial t$, we have:

$$\partial R_{ij} = \frac{2k_B T}{3\mu} \left(2 + v_i^{-\frac{1}{3}} v_j^{\frac{1}{3}} + v_i^{\frac{1}{3}} v_j^{-\frac{1}{3}} \right) \frac{\partial n}{\partial v_i} \frac{\partial n}{\partial v_j} \partial v_i \partial v_j$$

And:

$$\begin{aligned}\frac{\partial M_0}{\partial t} &= \frac{1}{2} \iint_0^\infty \partial R_{ij} \frac{\partial(\partial M_0 / \partial t)}{\partial R_{ij}} \\ &= \frac{1}{2} \iint_0^\infty \left[\frac{2k_B T}{3\mu} \left(2 + v_i^{-\frac{1}{3}} v_j^{\frac{1}{3}} + v_i^{\frac{1}{3}} v_j^{-\frac{1}{3}} \right) \frac{\partial n}{\partial v_i} \frac{\partial n}{\partial v_j} \partial v_i \partial v_j \right] [-1] \\ &= \frac{-k_B T}{3\mu} \iint_0^\infty \left(2 + v_i^{-\frac{1}{3}} v_j^{\frac{1}{3}} + v_i^{\frac{1}{3}} v_j^{-\frac{1}{3}} \right) \frac{\partial n}{\partial v_i} \frac{\partial n}{\partial v_j} \partial v_i \partial v_j \\ &= \frac{-2k_B T}{3\mu} \left[M_0^2 + M_{\frac{1}{3}} M_{-\frac{1}{3}} \right]\end{aligned}$$

$$\frac{\partial M_1}{\partial t} = 0$$

(still zero)

$$\begin{aligned}
\frac{\partial M_2}{\partial t} &= \frac{1}{2} \iint_0^\infty \partial R_{ij} \frac{\partial \left(\frac{\partial M_2}{\partial t} \right)}{\partial R_{ij}} \\
&= \frac{1}{2} \iint_0^\infty \left[\frac{2k_B T}{3\mu} \left(2 + v_i^{-\frac{1}{3}} v_j^{\frac{1}{3}} + v_i^{\frac{1}{3}} v_j^{-\frac{1}{3}} \right) \frac{\partial n}{\partial v_i} \frac{\partial n}{\partial v_j} \partial v_i \partial v_j \right] [2v_i v_j] \\
&= \frac{2k_B T}{3\mu} \iint_0^\infty \left(2v_i v_j + v_i^{\frac{2}{3}} v_j^{\frac{4}{3}} + v_i^{\frac{4}{3}} v_j^{\frac{2}{3}} \right) \frac{\partial n}{\partial v_i} \frac{\partial n}{\partial v_j} \partial v_i \partial v_j \\
&= \frac{4k_B T}{3\mu} \left[M_1^2 + M_{\frac{2}{3}} M_{\frac{4}{3}} \right]
\end{aligned}$$

Compare the rate coefficients $\beta_{ij,Br} = \frac{2k_B T}{3\mu} \left(\frac{1}{a_i} + \frac{1}{a_j} \right) (a_i + a_j)$ for Brownian coagulation and $\beta_{ij,Sh} = \frac{4}{3} G(a_i + a_j)^3$ for coagulation due by laminar shear.

As particle radius vanishes, $\beta_{ij,Br}$ dominates $\beta_{ij,Sh}$ and we see that Brownian coagulation becomes more significant for smaller particles.

As particle size increases, $\beta_{ij,Sh}$ dominates $\beta_{ij,Br}$ and we see that orthokinetic coagulation becomes more significant for larger particles.

Colloids and Aggregation

Let's revisit the problem of diffusion-driven collisions from an earlier section.

Considering Brownian motion, Smoluchowski found the collision rate:

$$R_{ij} = \beta_{ij} n_i n_j \quad \text{where} \quad \beta_{ij} = 4\pi(D_i + D_j)(a_i + a_j)$$

While this model is considered to be accurate, some suspensions are much more stable over time than this aggregation rate would suggest, while others coagulate more readily.

So what else is happening here in addition to diffusive motion?

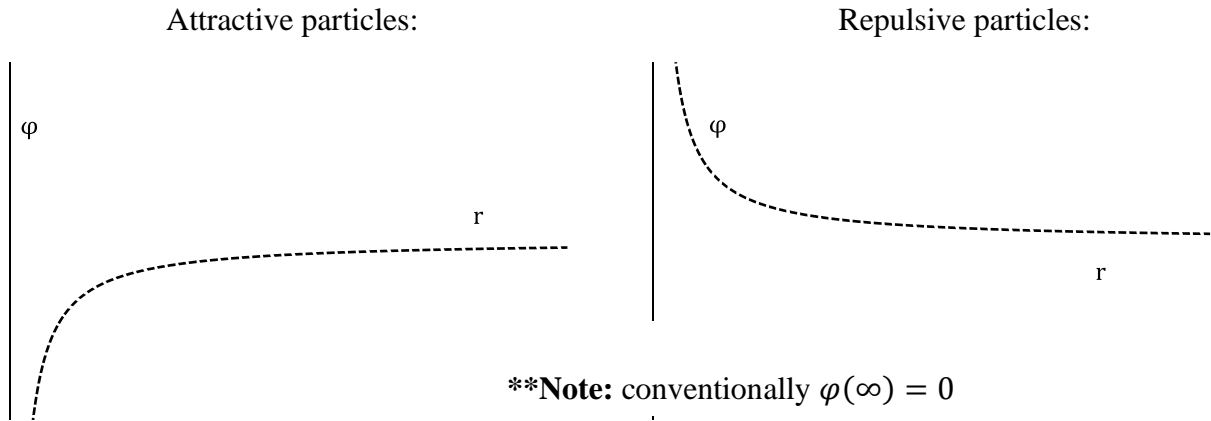
The answer is interparticle forces: some particles are attracted to each other, while others avoid making contact.

Interparticle Potential

Interparticle force can be represented with a potential energy of interaction $\varphi(r)$ in units of Joules, where the distance between the particles is r :

$$F_{ij}(r) = \frac{-\partial\varphi(r)}{\partial r} \quad \text{or in 3-D} \quad \mathbf{F}_{ij} = -\nabla\varphi$$

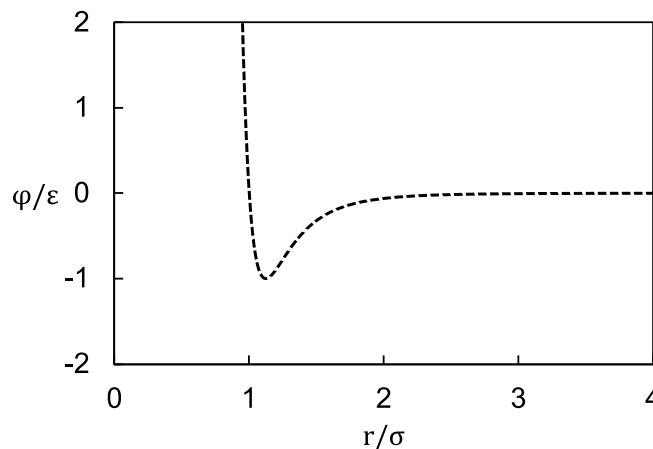
On a plot of φ as a function of r , particle spacing will tend toward minima of φ :



More complicated with a minimum energy spacing:

Lennard-Jones potential (popular for neutral atoms or molecules)

$$\varphi_{LJ} = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$



Diffusion can cause particle behavior to deviate from strictly following the energy curve.

Diffusion is driven by thermal energy of order $k_B T$, so the normalized value $\varphi/k_B T$ can indicate the strength of potential wells (whether or not particles can be trapped there).

Collision Rate Coefficient with Interparticle Potential and Diffusion

Repeating the Smoluchowski analysis with the addition of interparticle forces, reconsider a spherical collector of radius $a_i + a_j$ surrounded by wandering point mass particles with diffusivity $D = D_i + D_j$.

With the addition of interparticle potential φ we now have:

$$\frac{\partial n}{\partial t} - B \frac{\partial \varphi}{\partial r} = D \nabla^2 n$$

where the mechanical mobility of wandering particles is $B = B_i + B_j$.

We seek an expression for the collision rate coefficient β_{ij} which includes interparticle potential (numbering below follows whiteboard in lecture).

1. At any radial distance from the collector, the total inward particle flux is:

$$\beta_{ij} n_\infty = -4\pi r^2 J''(r)$$

2. Total outward particle flux $J''(r)$ at any radial distance from the collector is:

$$J''(r) = -D \frac{\partial n(r)}{\partial r} - B \frac{\partial \varphi(r)}{\partial r} n(r)$$

where $n(r)$ is the local particle concentration.

3. Combining (1) and (2) with $D = Bk_B T$ we obtain:

$$\begin{aligned} \beta_{ij} n_\infty &= 4\pi r^2 \left(D \frac{\partial n(r)}{\partial r} + B \frac{\partial \varphi(r)}{\partial r} n(r) \right) \\ &= 4\pi r^2 D \left(\frac{\partial n(r)}{\partial r} + \frac{1}{k_B T} \frac{\partial \varphi(r)}{\partial r} n(r) \right) \end{aligned}$$

4. Rearranging (3) as an ordinary differential equation for $n(r)$ we have:

$$n' + \frac{1}{k_B T} \frac{\partial \varphi(r)}{\partial r} n = \frac{\beta_{ij} n_\infty}{4\pi D} r^{-2}$$

Note that n , φ , and the right-hand side are each functions of r .

5. (4) is of the form $dn/dr + P(r) n = Q(r)$; so try the integrating factor method:

$$P(r) = \frac{1}{k_B T} \frac{\partial \varphi(r)}{\partial r}$$

$$\Rightarrow \int P(r) dr = \int \frac{1}{k_B T} \frac{\partial \varphi(r)}{\partial r} dr = \frac{\varphi(r)}{k_B T}$$

$$\therefore \text{multiply (4) throughout by: } \text{Exp}\left[\int P(r) dr\right] = \text{Exp}\left[\frac{\varphi(r)}{k_B T}\right]$$

Now (4) becomes: (left-hand side by the design of the integrating factor method)

$$\frac{d}{dr} \left(n(r) \text{Exp}\left[\frac{\varphi(r)}{k_B T}\right] \right) = \frac{\beta_{ij} n_\infty}{4\pi D} r^{-2} \text{Exp}\left[\frac{\varphi(r)}{k_B T}\right]$$

Integrating both sides from r to ∞ we get:

$$\int_r^\infty \frac{d}{dX} \left(n(X) \text{Exp}\left[\frac{\varphi(X)}{k_B T}\right] \right) dX = \int_r^\infty \frac{\beta_{ij} n_\infty}{4\pi D} X^{-2} \text{Exp}\left[\frac{\varphi(X)}{k_B T}\right] dX$$

$$n_\infty \text{Exp}\left[\frac{\varphi(\infty)}{k_B T}\right] - n(r) \text{Exp}\left[\frac{\varphi(r)}{k_B T}\right] = \frac{\beta_{ij} n_\infty}{4\pi D} \int_r^\infty X^{-2} \text{Exp}\left[\frac{\varphi(X)}{k_B T}\right] dX$$

By convention $\varphi(\infty) = 0$, so we simplify:

$$n_\infty - n(r) \text{Exp}\left[\frac{\varphi(r)}{k_B T}\right] = \frac{\beta_{ij} n_\infty}{4\pi D} \int_r^\infty X^{-2} \text{Exp}\left[\frac{\varphi(X)}{k_B T}\right] dX$$

$$\boxed{n(r) = \text{Exp}\left[\frac{-\varphi(r)}{k_B T}\right] \left(n_\infty - \frac{\beta_{ij} n_\infty}{4\pi D} \int_r^\infty X^{-2} \text{Exp}\left[\frac{\varphi(X)}{k_B T}\right] dX \right)}$$

6. Now we apply the absorbing boundary condition $n(a_i + a_j) = 0$:

$$0 = n(a_i + a_j)$$

$$= \text{Exp}\left[\frac{-\varphi(a_i + a_j)}{k_B T}\right] \left(n_\infty - \frac{\beta_{ij} n_\infty}{4\pi D} \int_{a_i + a_j}^\infty X^{-2} \text{Exp}\left[\frac{\varphi(X)}{k_B T}\right] dX \right)$$

$$\Rightarrow n_{\infty} = \frac{\beta_{ij} n_{\infty}}{4\pi D} \int_{a_i+a_j}^{\infty} X^{-2} \text{Exp} \left[\frac{\varphi(X)}{k_B T} \right] dX$$

$$\Rightarrow \beta_{ij} = \frac{4\pi D}{\int_{a_i+a_j}^{\infty} X^{-2} \text{Exp} \left[\frac{\varphi(X)}{k_B T} \right] dX}$$

Replacing $D = D_i + D_j$ we finally obtain:

$$\boxed{\beta_{ij} = \frac{4\pi(D_i + D_j)}{\int_{a_i+a_j}^{\infty} X^{-2} \text{Exp} \left[\frac{\varphi(X)}{k_B T} \right] dX}}$$

Stability Ratio and Enhancement Factor

7. Recalling the Smoluchowski result, we can rewrite (6) above as:

$$\beta_{ij} = \frac{4\pi(D_i + D_j)(a_i + a_j)}{W} \quad \text{where} \quad W \stackrel{\text{def}}{=} (a_i + a_j) \int_{a_i+a_j}^{\infty} X^{-2} \text{Exp} \left[\frac{\varphi(X)}{k_B T} \right] dX$$

Here W is called the **stability ratio**, a popular metric in colloids where aggregation is often *undesirable* (large W is good).

In the real world W can vary by orders of magnitude, significantly reducing aggregation.

In aerosol science, aggregation is sometimes *desirable*. In this case **enhancement factor** might be used instead (large η_c is good):

$$\beta_{ij} = 4\pi \eta_c (D_i + D_j)(a_i + a_j) \quad \text{where} \quad \eta_c \stackrel{\text{def}}{=} \frac{1}{W}$$

Coulomb Interactions

For electrically charged particles, interparticle potential is given by:

$$\varphi(r) = \frac{z_i z_j e^2}{4\pi\epsilon_0 r}$$

where z_i and z_j are the numbers of excess electrons on the two particles, elementary (electron) charge $e = 1.6 \times 10^{-19}$ C, and vacuum permittivity $\epsilon_0 = 8.85 \times 10^{-12}$ F/m.

In this case, the enhancement factor is:

$$\eta_c = \frac{-\psi_E}{1 - \text{Exp}[\psi_E]} \quad \text{where} \quad \psi_E \stackrel{\text{def}}{=} \frac{z_i z_j e^2}{4\pi\epsilon_0 (a_i + a_j) k_B T}$$

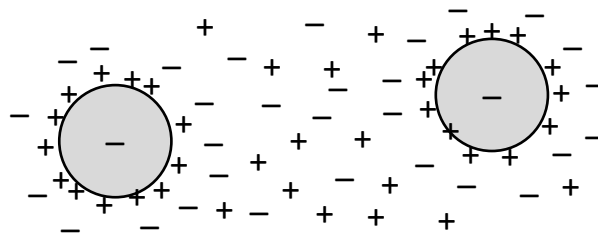
Ion Double Layers and Screening

Consider two identical particles in a liquid with (much smaller) ions.

Several forces are present in this example:

- van der Waals attraction between the two particles
- electrostatic repulsion between the two particles
- electrostatic attraction between each particle and the ions around it
- electrostatic attraction between the ions

On average, the ions associate into shells of alternating charge around the two particles, with shell strength decreasing with distance from the particle surface.



Double layer models consider the first layer of ions attached to the particle surface and the adjacent layer of ions of opposite charge.

At high enough ion concentrations, the effect of these ion layers is to electrostatically shield the two particles from each other – this is known as **screening**.

Screening enhances particle aggregation by reducing the effect of electrostatic repulsion between like particles.

This idea is commonly used in water treatment, where salt ions are added to facilitate the aggregation and sedimentation of contaminants (called **flocculation**).

DLVO Theory

(named after Derjaguin, Landau, Verwey, and Overbeek)

DLVO Theory models interparticle potential as the sum of van der Waals potential and electrostatic potential using a double layer model.

$$\varphi(r) = \varphi_{VDW}(r) + \varphi_{DL}(r)$$

For identical particles of radius a_p in a solution of small ions of symmetric integer charge $\pm z$ and solute (ion pair) concentration n_s :

$$\varphi_{VDW}(r) = \frac{-A_H}{6} \left[\frac{1}{2(r^{*2} - 1)} + \frac{1}{2r^{*2}} + \ln \left(\frac{r^{*2} - 1}{r^{*2}} \right) \right]$$

A_H : Hamaker constant (in joules)

$$r^* = r/2a_p$$

r : center-to-center particle separation (in meters)

$$\varphi_{DL}(r) = 64\pi \frac{n_s k_B T a_p^2 \gamma^2}{\kappa^2 r} \text{Exp}[-\kappa(r - 2a_p)]$$

$\gamma = \tanh(ze\psi_0/4k_B T)$ ("reduced surface potential")

e : electron charge (in coulombs)

ψ_0 : particle surface potential (in volts)

$$\kappa = (2n_s e^2 z^2 / \epsilon_r \epsilon_0 k_B T)^{1/2}$$

$1/\kappa$: Debye screening length

ϵ_r : dielectric constant of the liquid (dimensionless)

ϵ_0 : vacuum permittivity (in farads per meter)

Debye screening length $1/\kappa$ characterizes the penetration depth of electrostatic interparticle forces into the ion suspension.

Note: Even if $r < 1/\kappa$, the effect of electrostatic forces can still be dominated by diffusion (characterized by $k_B T$).

Recombination Rates after Ionization

Suppose a particle with initially neutral charge splits into one cation (positive charge) and one anion (negative).

We can use our results with enhancement factor from a previous section to find a recombination rate for the two ion species after ionization:

$$R_{\oplus\ominus} = \beta_{\oplus\ominus} n_{\oplus} n_{\ominus}$$

$$\beta_{\oplus\ominus} = 4\pi \eta_c (D_{\oplus} + D_{\ominus})(a_{\oplus} + a_{\ominus})$$

where the enhancement factor for charged particles was given as:

$$\eta_c = \frac{-\psi_E}{1 - \text{Exp}[\psi_E]} \quad \text{where} \quad \psi_E \stackrel{\text{def}}{=} \frac{z_{\oplus} z_{\ominus} e^2}{4\pi\epsilon_0(a_{\oplus} + a_{\ominus})k_B T}$$

Combining these expressions we obtain:

$$\beta_{\oplus\ominus} = \frac{D_{\oplus} + D_{\ominus}}{\epsilon_0 k_B T} \left(\frac{-z_{\oplus} z_{\ominus} e^2}{1 - \text{Exp}[\psi_E]} \right)$$

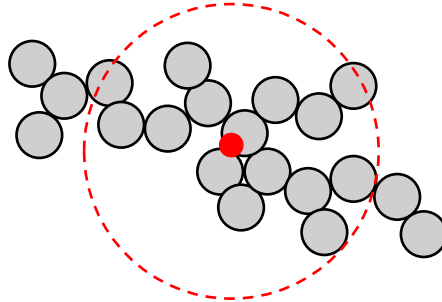
Since ψ_E here is large and negative ($z_{\oplus} z_{\ominus} < 0$), we approximate $\text{Exp}[\psi_E] \approx 0$ and so:

$$\begin{aligned} \beta_{\oplus\ominus} &\approx \frac{D_{\oplus} + D_{\ominus}}{\epsilon_0 k_B T} (-z_{\oplus} z_{\ominus} e^2) \\ &= \frac{B_{\oplus} + B_{\ominus}}{\epsilon_0} (-z_{\oplus} z_{\ominus} e^2) \\ &= \frac{-e}{\epsilon_0} (Z_{\oplus} z_{\ominus} + z_{\oplus} Z_{\ominus}) \end{aligned}$$

where $B = D/k_B T$ is the mechanical mobility and $Z = zeB$ is the electrical mobility.

Cluster Aggregates

So far we have assumed that two colliding particles fuse into a single larger sphere, but in the real world particles often coagulate into non-spherical clusters. For example:



Center of mass and radius of gyration

The shape of these clusters can be statistically characterized by center of mass (\mathbf{x}_{CM}) and radius of gyration (R_g).

Center of mass is the average location of the cluster weighted by mass:

$$\mathbf{x}_{\text{CM}} = \frac{\sum_i m_i \mathbf{x}_i}{\sum_i m_i}$$

Radius of gyration characterizes the rotational inertia of the cluster (expressed here for rotation about the center of mass):

$$R_g^2 = \frac{\sum_i m_i (\mathbf{x}_i - \mathbf{x}_{\text{CM}})^2}{\sum_i m_i}$$

(Note the square on R_g^2 in the equation above.) A point mass $\sum_i m_i$ located a distance of R_g from \mathbf{x}_{CM} has the same rotational inertia as the given cluster.

If a cluster consists of N identical spheres, then these expressions can be simplified:

$$\mathbf{x}_{\text{CM}} = \frac{1}{N} \sum_{i=1}^N \mathbf{x}_i$$

$$R_g^2 = \frac{1}{N} \sum_{i=1}^N (\mathbf{x}_i - \mathbf{x}_{\text{CM}})^2$$

Fractal dimension

The shape of an aggregate cluster can also be described by its **fractal dimension**, which characterizes how tightly the component monomers are packed.

For a cluster consisting of N identical spheres, fractal dimension D_f is given by:

$$N = k_f \left(\frac{R_g}{a_p} \right)^{D_f}$$

where a_p is the sphere radius and k_f is an empirical fit coefficient of order 1.

In general, $1 \leq D_f \leq 3$, where $D_f = 1$ for minimal packing (linear polymer shape) and $D_f = 3$ for maximal packing (round polymer shape).

Types of collisions

Early in a coagulation process, clusters mostly collide with single monomers since there are many more monomers than clusters.

Later in a coagulation process, few single monomers remain, so clusters mostly collide with other clusters.

The average fractal dimensions of clusters formed by these different collision types are summarized in the table below:

Coagulation type	Cluster-monomer collisions	Cluster-cluster collisions
Diffusion-limited <ul style="list-style-type: none"> Continuum mechanics With diffusion Every collision binds 	$D_f \rightarrow 2.5$	** $D_f \rightarrow 1.78$ **
Ballistic <ul style="list-style-type: none"> Free molecular mechanics No diffusion Every collision binds 	$D_f \rightarrow 3$	$D_f \rightarrow 1.91$
Reaction-limited <ul style="list-style-type: none"> Continuum mechanics With diffusion Probabilistic chance of binding for each collision 	$D_f \rightarrow 3$	$D_f \rightarrow 2.1$

**** $D_f \rightarrow 1.78$ is the most common case for aerosols.**

Friction coefficient

$\text{Kn} \rightarrow 0$: At the continuum limit, hydrodynamic radius R_H is defined such that:

$$f_c = 6\pi\mu R_H$$

where R_H must be determined by measurement of the actual friction coefficient f_c or predicted by some correlation. If $D_f \approx 1.78$ for a cluster of N identical spheres of radius a_p , an empirical fit for hydrodynamic radius is $R_H \approx 0.9772 a_p N^{0.492}$.

$\text{Kn} \rightarrow \infty$: At the free molecular limit, friction coefficient follows:

$$f_{FM} = \frac{4}{3} \rho_{gas} \bar{c}_{gas} \xi A_P$$

where A_P is the average projected area of the cluster (it is assumed that the cluster tumbles randomly in its trajectory). Compared to the spherical free-molecular friction coefficient seen earlier, the projected area A_P here simply replaces $\pi d_p^2/4$.

If $D_f \approx 1.78$ for a cluster of N identical spheres of radius a_p , an empirical fit for average projected area is $A_P \approx 3.085 a_p^2 N^{0.9016}$.

$0 < \text{Kn} < \infty$: For intermediate Kn , do we even know Kn for a cluster?

Knudsen number depends on particle length scale, but clusters have multiple length scales to choose from because in general $\pi R_H^2 \neq A_P$.

Solution: Earlier (for spheres) we obtained $\text{Kn} = \lambda/a_p$ as a ratio of friction coefficients. Repeating now for cluster friction coefficients:

$$\text{Kn} \sim \frac{f_c}{f_{FM}} = \frac{6\pi\mu R_H}{\frac{4}{3} \rho_{gas} \bar{c}_{gas} \xi A_P} \sim \frac{\mu}{\rho_{gas} \bar{c}_{gas}} \cdot \frac{R_H}{A_P} \sim \lambda \frac{R_H}{A_P}$$

So we adopt the length scale $A_P/\pi R_H$:

$$\text{Kn} = \frac{\lambda \pi R_H}{A_P}$$

where the factor of π allows agreement with our earlier result for spherical particles $\text{Kn}_{\text{sphere}} = \lambda/a_p$.

**Note: Once f is known, we can also find $D = k_B T/f$, terminal settling velocity, etc.

Finally, it turns out that this more general expression for Kn allows aspherical particles to use the same slip correction correlation presented earlier for spheres:

$$f = \frac{6\pi\mu R_H}{C_c}$$

$$C_c = 1 + \text{Kn} \left(1.257 + 0.4 \text{Exp} \left[\frac{-1.1}{\text{Kn}} \right] \right)$$

for Stokes flow around any particle at any Knudsen number.

Cluster–Monomer Collision Rates

For the diffusion-driven collision of spheres, we found:

$$\beta_{ij,spheres} = 4\pi(D_i + D_j)(a_i + a_j)$$

For diffusion-driven cluster–monomer collisions, a Monte Carlo algorithm is suggested:

$$\beta_{ij,cluster} = 4\pi(D_i + D_j)R_0\mathcal{P}_c$$

where \mathcal{P}_c is the average probability of eventual collision* when two particles are initially separated by some arbitrary radial distance R_0 .

Many such particle trajectories are simulated from these initial conditions, after which \mathcal{P}_c is equal to the fraction of trajectories leading to collision (*or binding, if binding is not guaranteed by collision).

Trajectory algorithm:

1. Fix a coordinate system to the center of the cluster (particle i) and consider the monomer (particle j) to have diffusivity $D_i + D_j$. Choose an arbitrary initial particle separation R_0 (to be constant throughout).
2. Place the monomer at a random initial location on the spherical shell $x_0^2 + y_0^2 + z_0^2 = R_0^2$. Be careful that this initial location is chosen with a uniform distribution (<https://mathworld.wolfram.com/SpherePointPicking.html>).
3. Simulate monomer diffusion for a single timestep (refer to the Brownian Dynamics section for details):

$$\mathbf{x}_j(t + \Delta t) = \mathbf{x}_j(t) + \sqrt{2D\Delta t} \boldsymbol{\theta}(t + \Delta t)$$

where \mathbf{x}_j is the monomer position vector and each element of $\boldsymbol{\theta}$ is an independent Gaussian random variable.

- a. If the monomer is now located outside the R_0 shell (if $|\mathbf{x}_j| > R_0$), it can be shown that the escape probability (never returning) is:

$$\mathcal{P}_{esc} = 1 - \frac{R_0}{|\mathbf{x}_j|}$$

Choose a uniform random number between 0 and 1. If it is greater than \mathcal{P}_{esc} reset \mathbf{x}_j to a random location on the R_0 shell and continue to step 4. If it is less than \mathcal{P}_{esc} the monomer escapes and the trajectory ends unsuccessfully.

- b. Check if collision has occurred (expression depends on the cluster shape). If conditional or probabilistic outcomes are considered, also choose a result of collision, either binding or bouncing. If bouncing, reset $\mathbf{x}_j(t + \Delta t) = \mathbf{x}_j(t)$ and continue to step 4. If binding, the trajectory ends successfully.

4. The monomer is still within a distance of R_0 , so repeat step 3 to advance its trajectory farther in time.

This algorithm is repeated from step 2 to obtain a large sample size of monomer trajectories.

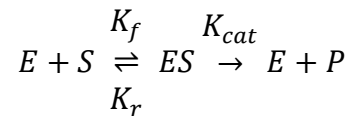
If the monomer (particle j above) is treated as a point mass, the Hubbard & Douglas approximation indicates:

$$R_H \approx R_0 \mathcal{P}_c$$

so the method can be used to obtain the **hydrodynamic radius** of a given cluster geometry.

Biophysical Reactions: Enzyme-Substrate Kinetics

Consider a simple enzyme-substrate reaction:



where E is an enzyme, S is substrate, ES is an intermediate stage activated substrate, P is product, and the double arrow \rightleftharpoons indicates a two-way reaction. The enzyme facilitates the reaction but is not consumed by it.

Rather than β , chemical kinetics conventionally uses K for reaction rate coefficients, where we have for the above reaction:

$$\frac{\partial[P]}{\partial t} = K_{cat}[ES]$$

$$\frac{\partial[S]}{\partial t} = -K_f[E][S] + K_r[ES]$$

$$\frac{\partial[E]}{\partial t} = -K_f[E][S] + K_r[ES] + K_{cat}[ES]$$

$$\frac{\partial[ES]}{\partial t} = K_f[E][S] - K_r[ES] - K_{cat}[ES]$$

where the notation $[X]$ indicates a volumetric molar concentration. Like β , the dimensions of each K depend on the number of reactants.

The reaction rate coefficients K are often known from experimental data, so the time concentrations of each species in a reacting system like this can be obtained by solving the associated system of differential equations.

(It is worth mentioning that in a system like this the concentration $[ES]$, important to product creation, is likely to be very small and difficult to measure.)

The above equations are nonlinear, complicating the solution process. In practice several simplifying assumptions are popular:

- **Quasi-steady-state** ($\partial[X]/\partial t \approx 0$) for species of lowest concentration; and/or
- **Quasi-equilibrium** for the fastest sub-reaction(s).

Here we might assume quasi-equilibrium of the $E + S \rightleftharpoons ES$ reaction, if the product reaction is much slower. In other words, any temporary surplus of ES will likely decompose back into $E + S$ before becoming a product. So:

$$K_f [E][S] \approx K_r [ES] \quad \Rightarrow \quad [E] = \frac{K_r [ES]}{K_f [S]}$$

Combining this result with a mass balance of E :

$$[E]_0 = [E] + [ES]$$

where $[E]_0$ is the initial concentration of E , we obtain:

$$[ES] = \frac{[E]_0 [S]}{\frac{K_r}{K_f} + [S]}$$

Substituting this result into the product reaction rate:

$$\frac{\partial [P]}{\partial t} = K_{cat} [ES] = K_{cat} [E]_0 \frac{[S]}{\frac{K_r}{K_f} + [S]}$$

The first term here $K_{cat} [E]_0$ functions as a speed limit for this product reaction, limiting the amount of product that can be created even as $[S] \rightarrow \infty$:

$$\lim_{[S] \rightarrow \infty} \frac{\partial [P]}{\partial t} = \lim_{[S] \rightarrow \infty} K_{cat} [E]_0 \frac{[S]}{\frac{K_r}{K_f} + [S]} = K_{cat} [E]_0$$

Low-Pressure Systems

All discussion so far has focused on dispersion behaviors at large timescales, $t \gg \tau_R = \frac{m_p}{f}$.

The opposite condition, $t \ll \tau_R$, occurs at small timescales, across small distances, or at low ambient pressures.

Dividing the basic equation of particle motion by m_p we obtain:

$$\frac{d\mathbf{u}_p}{dt} = \frac{-1}{\tau_R}(\mathbf{u}_p - \mathbf{u}_f) + \frac{1}{m_p} \sum \mathbf{F}_{\text{ext}}$$

For large relaxation time ($\tau_R \rightarrow \infty$) the drag term vanishes:

$$\frac{d\mathbf{u}_p}{dt} \approx \frac{1}{m_p} \sum \mathbf{F}_{\text{ext}}$$

This limit is called the free molecular, ballistic, or (in plasma sciences) collisionless regime of particle motion.

Free molecular velocity distributions

Particles in free molecular motion are not subject to collisions with a surrounding continuous phase (*drag*), but they may still collide with other dispersed phase particles.

Momentum transfer from these collisions can maintain an equilibrium particle speed distribution, represented by a speed distribution function (*cf.* size distribution function).

If no external forces are present, and the system is in thermal equilibrium, free molecular particles within it will exhibit the **Maxwell–Boltzmann speed distribution**:

$$f_{eq}(u_p) = 4\pi \left(\frac{m_p}{2\pi k_B T} \right)^{\frac{3}{2}} u_p^2 \text{Exp} \left[\frac{-m_p u_p^2}{2k_B T} \right]$$

where f_{eq} is a speed distribution function and $f_{eq}(u_p) \delta u_p$ is the probability of a given particle having a speed between $u_p - \delta u_p$ and $u_p + \delta u_p$.

(Note: f_{eq} is a PDF and $\int_0^\infty f_{eq}(u_p) du_p = 1$.)

Mean thermal speed of a gas is related to the Maxwell–Boltzmann speed distribution:

$$\bar{c}_{gas} = \frac{M_1}{M_0} = \frac{\int_0^\infty f_{eq}(u_p) u_p du_p}{\int_0^\infty f_{eq}(u_p) du_p} = \frac{\int_0^\infty f_{eq}(u_p) u_p du_p}{1} = \sqrt{\frac{8k_B T}{\pi m}}$$

It can also be shown that the *relative speed* u_{ij} between two randomly chosen particles from a Maxwell–Boltzmann distribution is:

$$f_{eq}(u_{ij}) = 4\pi \left(\frac{m_{ij}}{2\pi k_B T} \right)^{\frac{3}{2}} u_{ij}^2 \text{Exp} \left[\frac{-m_{ij} u_{ij}^2}{2k_B T} \right]$$

where:

$$m_{ij} = \left(\frac{1}{m_i} + \frac{1}{m_j} \right)^{-1} = \frac{m_i m_j}{m_i + m_j}$$

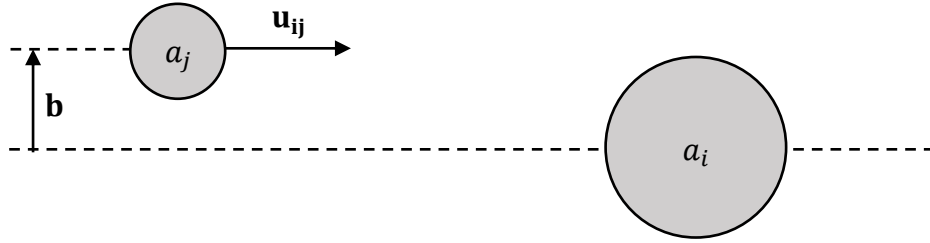
is called the **reduced mass**.

Ballistic Collision Rates

We will derive another expression for the collision rate coefficient β_{ij} , now for $t \ll \tau_R$:

$$R_{ij} = \beta_{ij} n_i n_j$$

Consider free molecular i - j collision using the impact parameter method as before:



Without loss of generality, align the coordinate system as shown, so that $\mathbf{b} \perp \mathbf{u}_{ij}$ and all collisions occur in the same coordinate direction. If no forces are present (external or potential), the trajectory of j is a straight line toward i , and $b_{crit} = a_i + a_j$ always.

The collision rate coefficient for the above diagram is simply the swept volume:

$$\beta_{ij} = \pi b_{crit}^2 u_{ij} = \pi (a_i + a_j)^2 u_{ij}$$

As an added complication, the relative speed u_{ij} is probabilistic, not a universal value. As introduced earlier each speed has a probability given by $f_{eq}(u_{ij}) du_{ij}$. So we sum over all expected contributions from each possible relative speed:

$$\begin{aligned} d\beta_{ij} &= \pi (a_i + a_j)^2 u_{ij} f_{eq}(u_{ij}) du_{ij} \\ \beta_{ij} &= \int d\beta_{ij} \\ &= \int_0^{\infty} \pi (a_i + a_j)^2 u_{ij} f_{eq}(u_{ij}) du_{ij} \\ &= \pi (a_i + a_j)^2 \int_0^{\infty} u_{ij} f_{eq}(u_{ij}) du_{ij} \end{aligned}$$

Re-using the same integral result shown earlier for mean thermal speed, we obtain:

$$\boxed{\beta_{ij} = \pi (a_i + a_j)^2 \sqrt{\frac{8k_B T}{\pi m_{ij}}}}$$

Ballistic Collisions with Attractive Potentials

Let's revisit the i - j collision from the previous section, adding an attractive potential φ .

Now the particle trajectories can curve toward collision and the critical impact parameter $b_{crit} > a_i + a_j$ depends on both the speed and potential:

$$d\beta_{ij} = \pi b_{crit}^2(u_{ij}, \varphi) u_{ij} f_{eq}(u_{ij}) du_{ij}$$

$$\beta_{ij} = \pi \int_0^\infty b_{crit}^2(u_{ij}, \varphi) u_{ij} f_{eq}(u_{ij}) du_{ij}$$

We will now seek an expression for b_{crit} that allows us to compute this integral.

Consider a colliding trajectory starting from b_{crit} with relative speed u_{ij} .

1. Energy is conserved along any trajectory since there is no interference from fluid drag or non-potential forces: $E(r) = \frac{1}{2}m_{ij}u_{rel}^2(r) + \varphi(r) = \text{const.}$

$$\text{Initial condition when } r \rightarrow \infty: \quad E(\infty) = \frac{1}{2}m_{ij}u_{ij}^2 + \varphi(\infty) = \frac{1}{2}m_{ij}u_{ij}^2$$

$$\text{Before collision when } r = a_i + a_j: \quad E(a_i + a_j) = \frac{1}{2}m_{ij}u_f^2 + \varphi(a_i + a_j)$$

where u_f is the unknown final velocity after collision. Equating the initial and final energies we obtain:

$$\frac{1}{2}m_{ij}(u_{ij}^2 - u_f^2) = \varphi_0$$

where $\varphi_0 = \varphi(a_i + a_j) < 0$ is the interparticle potential energy at contact.

2. It can be shown that a b_{crit} collision must occur *tangentially*. Consider conservation of angular momentum at the same initial and final states as in step (1):

$$\text{Initial condition when } r \rightarrow \infty: \quad L(\infty) = b_{crit}m_{ij}u_{ij}$$

$$\text{Before collision when } r = a_i + a_j: \quad L(a_i + a_j) = (a_i + a_j)m_{ij}u_f$$

Equating the initial and final angular momentums we obtain:

$$u_f = \frac{b_{crit}u_{ij}}{a_i + a_j}$$

3. Substituting (2) into (1) we obtain:

$$b_{crit}^2 = (a_i + a_j)^2 \left(1 - \frac{2\varphi_0}{m_{ij}} u_{ij}^{-2} \right)$$

4. Substitute b_{crit}^2 from (3) into the earlier β_{ij} integral and proceed:

$$\begin{aligned} \beta_{ij} &= \pi \int_0^\infty b_{crit}^2(u_{ij}, \varphi) u_{ij} f_{eq}(u_{ij}) du_{ij} \\ &= \pi \int_0^\infty \left[(a_i + a_j)^2 \left(1 - \frac{2\varphi_0}{m_{ij}} u_{ij}^{-2} \right) \right] u_{ij} f_{eq}(u_{ij}) du_{ij} \\ &= \pi (a_i + a_j)^2 \int_0^\infty \left(1 - \frac{2\varphi_0}{m_{ij}} u_{ij}^{-2} \right) u_{ij} f_{eq}(u_{ij}) du_{ij} \\ &= \pi (a_i + a_j)^2 \left(M_1 - \frac{2\varphi_0}{m_{ij}} M_{-1} \right) \end{aligned}$$

where M_1 and M_{-1} are moments of the relative speed distribution $f_{eq}(u_{ij})$.

5. For the Maxwell–Boltzmann relative speed distribution $f_{eq}(u_{ij})$, it has already been noted that $M_1 = \sqrt{8k_B T / \pi m_{ij}}$ in relation to the mean thermal speed of a gas, and $M_{-1} = \sqrt{2m_{ij} / \pi k_B T}$ can be obtained by direct integration. Thus:

$$\beta_{ij} = \pi (a_i + a_j)^2 \left(\sqrt{\frac{8k_B T}{\pi m_{ij}}} - \frac{2\varphi_0}{m_{ij}} \sqrt{\frac{2m_{ij}}{\pi k_B T}} \right)$$

6. Rearranging (5) we have:

$$\beta_{ij} = \pi (a_i + a_j)^2 \sqrt{\frac{8k_B T}{\pi m_{ij}}} \left(1 - \frac{\varphi_0}{k_B T} \right)$$

7. For Coulomb potential:

$$\phi(r) = \frac{z_i z_j e^2}{4\pi \epsilon_0 r}$$

$$\beta_{ij} = \pi (a_i + a_j)^2 \sqrt{\frac{8k_B T}{\pi m_{ij}}} \left(1 - \frac{z_i z_j e^2}{4\pi \epsilon_0 k_B T (a_i + a_j)} \right) = \pi (a_i + a_j)^2 \sqrt{\frac{8k_B T}{\pi m_{ij}}} (1 - \psi_E)$$

Note: We have seen $\psi_E = \varphi_0 / k_B T$ from step (7) before, in the Coulomb Interactions section.

For neutral potential we found the free molecular collision rate coefficient:

$$\beta_{ij} = \pi(a_i + a_j)^2 \sqrt{\frac{8k_B T}{\pi m_{ij}}}$$

For attractive Coulomb potential, $\psi_E < 0$ and we found:

$$\beta_{ij} = \pi(a_i + a_j)^2 \sqrt{\frac{8k_B T}{\pi m_{ij}}} (1 - \psi_E)$$

As expected, the addition of attractive potential increases the collision rate with an enhancement factor of:

$$\eta_{FM} = 1 - \psi_E$$

This can be compared to the enhancement factor for continuum collision rates with Coulomb potential and diffusion:

$$\eta_c = \frac{-\psi_E}{1 - \text{Exp}[\psi_E]}$$

Comment: For repulsive potentials $\psi_E > 0$. However, this could allow $\eta_{FM} < 0$ with the above expression for free molecular β_{ij} , which is physically impossible (negative collision rate?). Next we will derive an expression for β_{ij} valid for repulsive potentials.

Ballistic Collisions with Repulsive Potentials

Last time we derived a collision rate coefficient for neutral or attractive interparticle potentials, where particle collisions were driven by relative thermal speed u_{ij} :

$$R_{ij} = \beta_{ij} n_i n_j$$

$$\beta_{ij, \varphi_0 \leq 0} = \pi \int_0^{\infty} b_{crit}^2(u_{ij}, \varphi) u_{ij} f_{eq}(u_{ij}) du_{ij}$$

$$= \pi (a_i + a_j)^2 \sqrt{\frac{8k_B T}{\pi m_{ij}}} \left(1 - \frac{\varphi_0}{k_B T}\right)$$

Interparticle potential review:

By convention:	$\varphi(\infty) = 0$
For neutral potential:	$\varphi(r) = 0$
For attractive potential:	$\frac{d\varphi}{dr} > 0 \Rightarrow \varphi_0 < 0$

We applied conservation of energy and angular momentum to a colliding trajectory starting from $b = b_{crit}$ and ending tangentially at $r = a_i + a_j$ with some final approach velocity u_f . Using these two conservation equations we eliminated u_f and obtained an expression for b_{crit} for substitution into the above β_{ij} integral:

$$b_{crit}^2 = (a_i + a_j)^2 \left(1 - \frac{2\varphi_0}{m_{ij}} u_{ij}^{-2}\right)$$

This expression for b_{crit} doesn't depend on any assumptions about the potential energy at contact $\varphi_0 = \varphi(a_i + a_j)$, so it can also be used for repulsive potential—with one caveat.

As the potential strength becomes increasingly repulsive ($\varphi_0 \rightarrow \infty$), we have the new possibility of $1 - \frac{2\varphi_0}{m_{ij}} u_{ij}^{-2} < 0$, leading to the physically meaningless result $b_{crit}^2 < 0$.

In truth, a negative b_{crit}^2 (imaginary b_{crit}) indicates a situation where the initial kinetic energy ($m_{ij}u_{ij}^2/2$) is insufficient to overcome the repulsive potential (φ_0), and collision is impossible for any impact parameter. This occurs below some critical velocity:

$$1 - \frac{2\varphi_0}{m_{ij}} u_{crit}^{-2} = 0 \quad \Rightarrow \quad u_{crit} = \sqrt{\frac{2\varphi_0}{m_{ij}}}$$

Therefore we adjust the earlier β_{ij} integration limits to include only those relative speeds where collision is possible, then proceed with substitution and direct integration:

$$\begin{aligned}
 \beta_{ij, \varphi_0 > 0} &= \pi \int_{u_{crit}}^{\infty} b_{crit}^2(u_{ij}, \varphi) u_{ij} f_{eq}(u_{ij}) du_{ij} \\
 &= \pi \int_{\sqrt{\frac{2\varphi_0}{m_{ij}}}}^{\infty} (a_i + a_j)^2 \left(1 - \frac{2\varphi_0}{m_{ij}} u_{ij}^{-2}\right) u_{ij} f_{eq}(u_{ij}) du_{ij} \\
 &= 4\pi^2 (a_i + a_j)^2 \left(\frac{m_{ij}}{2\pi k_B T}\right)^{\frac{3}{2}} \int_{\sqrt{\frac{2\varphi_0}{m_{ij}}}}^{\infty} \left(1 - \frac{2\varphi_0}{m_{ij}} u_{ij}^{-2}\right) u_{ij}^3 \text{Exp}\left[\frac{-m_{ij} u_{ij}^2}{2k_B T}\right] du_{ij} \\
 &= \pi (a_i + a_j)^2 \sqrt{\frac{8k_B T}{\pi m_{ij}}} \text{Exp}\left[\frac{-\varphi_0}{k_B T}\right]
 \end{aligned}$$

In conclusion, for free-molecular particle collisions driven by relative thermal speed, with simple interparticle potentials where $d\varphi/dr$ does not change sign, we found:

$$\beta_{ij} = \begin{cases} \pi (a_i + a_j)^2 \sqrt{\frac{8k_B T}{\pi m_{ij}}} \left(1 - \frac{\varphi_0}{k_B T}\right) & \varphi_0 \leq 0 \\ \pi (a_i + a_j)^2 \sqrt{\frac{8k_B T}{\pi m_{ij}}} \text{Exp}\left[\frac{-\varphi_0}{k_B T}\right] & \varphi_0 > 0 \end{cases}$$

where $\varphi_0 = \varphi(a_i + a_j)$ is the interparticle potential energy at contact, and the physical significance of $\frac{\varphi_0}{k_B T} = \psi_E$ is a ratio of potential and thermal energy magnitudes.

This collision rate analysis is attributed to Langmuir.

Dusty Plasmas

A **plasma** is a fundamental state of matter where a significant fraction of atoms have been ionized. For example, in an argon plasma Ar, Ar⁺, and e⁻ (free electrons) all exist in significant concentration.

Free electrons in a plasma have very high thermal energy, conventionally measured in electronvolts (1 eV = 1.6 × 10⁻¹⁹ J). This energy level can be converted to an electron temperature (T_e) as 1 eV/ k_B = 1.16 × 10⁴ K.

In **thermal plasmas**, the cations (T_{ion}) and neutral atoms (T) are also hot, reaching temperatures similar to $T_e \sim 10^4$ K. Thermal plasma is present in stars such as the sun.

In **nonthermal plasmas** (or “cold plasmas”), T_{ion} and T remain much lower than T_e . Nonthermal plasma is present inside a fluorescent lamp operating near room temperature.

A plasma containing additional nano- or micro-scale particles is called a **dusty plasma**.

Consider the collision and accumulation of cations and free electrons ($n_{ion} \approx n_e$) onto an initially neutral particle in a cold dusty plasma. In the preceding section we derived:

$$\beta_{ij} \sim T^{\frac{1}{2}} m_{ij}^{-\frac{1}{2}}$$

If the particle is large compared to a cation, then $m_{ij} \rightarrow m_e$ for incoming electrons and $m_{ij} \rightarrow m_{ion}$ for incoming cations. Since $T_e \gg T_{ion}$ and $m_e \ll m_{ion}$ we see that:

$$\beta_e \sim T_e^{\frac{1}{2}} m_e^{-\frac{1}{2}} \gg T_{ion}^{\frac{1}{2}} m_{ion}^{-\frac{1}{2}} \sim \beta_{ion}$$

So large particles collide far more readily with the free electrons and must build up a net negative charge over time. In fact, we can derive an expression to quantify this charge.

When a particle is at an equilibrium net charge, its collision rates with electrons and cations must be equal if all collisions lead to binding:

$$\beta_e n_e = R_e = R_{ion} = \beta_{ion} n_{ion}$$

If $n_{ion} \approx n_e$ then the rate coefficients are also equal. Substituting the appropriate definitions from the preceding section for a particle of negative net charge, we get:

$$\pi a_p^2 \sqrt{\frac{8k_B T_e}{\pi m_e}} \text{Exp}[-\psi_e] \approx \beta_e \approx \beta_{ion} \approx \pi a_p^2 \sqrt{\frac{8k_B T_{ion}}{\pi m_{ion}}} (1 - \psi_{ion})$$

Canceling like terms, we obtain the relationship:

$$\sqrt{\frac{T_e}{m_e}} \text{Exp}[-\psi_e] \approx \sqrt{\frac{T_{ion}}{m_{ion}}} (1 - \psi_{ion})$$

Write the (Coulomb) surface potential of the particle as $\Phi_p = z_p e / 4\pi\epsilon_0 a_p$. (Note that $z_p < 0$ and $\Phi_p < 0$ here, and knowledge of either determines the net particle charge.)

Expanding ψ yields an implicit equation for z_p or Φ_p :

$$\begin{aligned} \sqrt{\frac{T_e}{m_e}} \text{Exp}\left[\frac{z_p e^2}{4\pi\epsilon_0 k_B T_e a_p}\right] &\approx \sqrt{\frac{T_{ion}}{m_{ion}}} \left(1 - \frac{z_p e^2}{4\pi\epsilon_0 k_B T_{ion} a_p}\right) \\ \sqrt{\frac{T_e}{m_e}} \text{Exp}\left[\frac{e\Phi_p}{k_B T_e}\right] &\approx \sqrt{\frac{T_{ion}}{m_{ion}}} \left(1 - \frac{e\Phi_p}{k_B T_{ion}}\right) \end{aligned}$$

These can be solved numerically to obtain the equilibrium particle charge.

Screening in Plasmas

Particles in a plasma become negatively charged, but n_e and n_{ion} may be sufficiently large to cause screening effects between particles.

The Yukawa potential or “screened Coulomb potential” is given by:

$$\varphi(r) = \frac{z_i z_j e^2}{4\pi\epsilon_0 r} \text{Exp}\left[\frac{-r}{\lambda_D}\right]$$

where $\lambda_D = 1/\kappa$ is the Debye length:

$$\lambda_D = \sqrt{\frac{\epsilon_0 k_B T}{\sum n_i z_i^2 e^2}}$$

Ion Drag

By the same argument as that for particles, any surface in a plasma will acquire a net negative charge. So particles should be repelled from walls as well as each other.

However, particles in a plasma can be observed to hover some distance away from walls, with the repulsive electrostatic force apparently balanced by some other force.

This mysterious force is caused by a net flux of cations toward the negatively charged wall: the **ion drag** force. Passing cations transfer momentum to the particle directly by collision or indirectly by the electrostatic force (as the particle bends their trajectories).

It turns out that the particles are more significantly affected by the electrostatic forces from passing ions, rather than by direct collision.

The ion drag force can be approximated as:

$$F_{ion\ drag} = K_{mt} n_{ion} m_{ion} u_{rel}$$

where u_{rel} is the relative speed between the particle and cation far from the particle (often $u_{rel} = Z_{ion} E$ for electric mobility $Z = ze/f$ and electric field strength E) and:

$$K_{mt} = \frac{2C_1 B^2}{\sqrt{\pi} u_{th}^3} \left[\ln \left(1 + \frac{1}{\alpha} \right) \right]^2$$

$$B = \frac{z_p e^2}{2\pi \epsilon_0 m_{ion}}$$

$$\alpha = \frac{B}{\lambda_D u_{th}^2 \sqrt{C_2}}$$

$$u_{th} = \sqrt{\frac{2k_B T}{m_{ion}}}$$

$$C_1 \approx 0.9369$$

$$C_2 \approx 61.32$$

Langevin Dynamics

When inertia, fluid drag, and diffusion all significantly affect particle motion and cannot be neglected, the resulting BBO equation is usually called the **Langevin equation**, especially in the context of Stokes flow:

$$m_p \frac{d\mathbf{u}_p}{dt} = -f(\mathbf{u}_p - \mathbf{u}_f) + \mathbf{F}_B + \sum \mathbf{F}_{\text{ext}}$$

where:

$$f = \frac{6\pi\mu a_p}{C_c} \quad C_c = 1 + \text{Kn} \left(1.257 + 0.4 \text{Exp} \left[\frac{-1.1}{\text{Kn}} \right] \right)$$

Some properties of the Brownian force:

$$\langle \mathbf{F}_B(t) \rangle = 0 \quad \langle \mathbf{F}_B(t) \cdot \mathbf{F}_B(t') \rangle = 6k_B T f \delta(t - t')$$

where the delta function is given by:

$$\delta(t) = \begin{cases} 1 \text{ s}^{-1} & t = 0 \\ 0 \text{ s}^{-1} & t \neq 0 \end{cases}$$

Ermak & Buckholtz Algorithm (1980)

This is a two-part algorithm for stepwise time advancement of the velocity $\mathbf{u}_p(t)$ and position $\mathbf{x}_p(t)$ of a single particle. For a Δt timestep beginning at time t :

1. Calculate the particle velocity at time $t + \Delta t$:

$$\mathbf{u}_p(t + \Delta t) = \text{Exp}\left[\frac{-\Delta t}{\tau_R}\right] \mathbf{u}_p(t) + \left(\frac{1 - \text{Exp}\left[\frac{-\Delta t}{\tau_R}\right]}{f}\right) \sum \mathbf{F}_{\text{ext}} + \mathbf{B}_1(t)$$

$$\mathbf{B}_1(t) = \sqrt{\frac{k_B T}{m_p}} \sqrt{1 - \text{Exp}\left[\frac{-2\Delta t}{\tau_R}\right]} \boldsymbol{\theta}(t)$$

$$\boldsymbol{\theta}(t) = (\text{randn}, \text{randn}, \text{randn})$$

2. Calculate the particle position at time $t + \Delta t$:

$$\mathbf{x}_p(t + \Delta t) = \mathbf{x}_p(t) + \tau_R \left(\frac{1 - \text{Exp}\left[\frac{-\Delta t}{\tau_R}\right]}{1 + \text{Exp}\left[\frac{-\Delta t}{\tau_R}\right]} \right) \left(\mathbf{u}_p(t + \Delta t) + \mathbf{u}_p(t) - \frac{2}{f} \sum \mathbf{F}_{\text{ext}} \right) + \mathbf{B}_2(t)$$

$$\mathbf{B}_2(t) = \sqrt{\frac{2k_B T m_p}{f^2}} \sqrt{\frac{\Delta t}{\tau_R} - 2 \left(\frac{1 - \text{Exp}\left[\frac{-\Delta t}{\tau_R}\right]}{1 + \text{Exp}\left[\frac{-\Delta t}{\tau_R}\right]} \right)} \boldsymbol{\theta}(t)$$

**Notes:

- $\mathbf{x}_p(t + \Delta t)$ depends on $\mathbf{u}_p(t + \Delta t)$ (must calculate in given order).
- \mathbf{F}_{ext} here includes the fluid drag force.
- The Gaussian random variables \mathbf{B}_1 and \mathbf{B}_2 have zero mean and variances of:

$$\langle \mathbf{B}_1(t) \cdot \mathbf{B}_1(t') \rangle = \left(\frac{3k_B T}{m_p} \right) \left(1 - \text{Exp}\left[\frac{-2\Delta t}{\tau_R}\right] \right)$$

$$\langle \mathbf{B}_2(t) \cdot \mathbf{B}_2(t') \rangle = \left(\frac{6k_B T m_p}{f^2} \right) \left(\frac{\Delta t}{\tau_R} - 2 \left(\frac{1 - \text{Exp}\left[\frac{-\Delta t}{\tau_R}\right]}{1 + \text{Exp}\left[\frac{-\Delta t}{\tau_R}\right]} \right) \right)$$

Diffusive Knudsen Number

Non-dimensionalize the Ermak & Buckholtz solutions above, neglecting $\sum \mathbf{F}_{\text{ext}}$ and \mathbf{u}_f :

$$\tau = \frac{t}{\tau_R} \quad \mathbf{x}_p^* = \frac{1}{L} \mathbf{x}_p \quad \mathbf{u}_p^* = \frac{\tau_R}{L} \mathbf{u}_p$$

We obtain:

$$\mathbf{u}_p^*(\tau + \Delta\tau) = \text{Exp}[-\Delta\tau] \mathbf{u}_p^*(\tau) + \mathbf{B}_1^*(\tau)$$

$$\mathbf{x}_p^*(\tau + \Delta\tau) = \mathbf{x}_p^*(\tau) + \left(\frac{1 - \text{Exp}[-\Delta\tau]}{1 + \text{Exp}[-\Delta\tau]} \right) (\mathbf{u}_p^*(\tau + \Delta\tau) + \mathbf{u}_p^*(\tau)) + \mathbf{B}_2^*(\tau)$$

$$\langle \mathbf{B}_1^*(\tau) \cdot \mathbf{B}_1^*(\tau') \rangle = 3 \left(\frac{k_B T m_p}{f^2 L^2} \right) (1 - \text{Exp}[-2\Delta\tau])$$

$$\langle \mathbf{B}_2^*(\tau) \cdot \mathbf{B}_2^*(\tau') \rangle = 6 \left(\frac{k_B T m_p}{f^2 L^2} \right) \left(\Delta\tau - 2 \left(\frac{1 - \text{Exp}[-\Delta\tau]}{1 + \text{Exp}[-\Delta\tau]} \right) \right)$$

Note that the same dimensionless grouping characterizes the variance of both \mathbf{B}_1^* and \mathbf{B}_2^* , the terms that contribute Brownian motion to the particle trajectory in this equation. This dimensionless grouping is called the diffusive Knudsen number:

$$\text{Kn}_D \stackrel{\text{def}}{=} \frac{\sqrt{k_B T m_p}}{f L} = \left(\frac{k_B T}{f} \right) \left(\sqrt{\frac{m_p}{k_B T}} \right) \left(\frac{1}{L} \right) \sim \frac{D}{\bar{c} L} = \frac{D/L^2}{\bar{c}/L} \sim \frac{\text{diffusive timescale}}{\text{thermal speed timescale}}$$

$\text{Kn} = \lambda/a_p$ (**Knudsen number**): characterizes continuum ($\text{Kn} \rightarrow 0$) vs. free molecular ($\text{Kn} \rightarrow \infty$) *momentum transfer* between a particle and its environment.

$\text{Kn}_D = \sqrt{k_B T m_p} / f L$ (**diffusive Knudsen number**): characterizes continuum ($\text{Kn}_D \rightarrow 0$) vs. free molecular ($\text{Kn}_D \rightarrow \infty$) *particle movement* through the environment.

Interestingly the ratio of continuum and free molecular collision rate coefficients is:

$$\frac{\beta_c}{\beta_{FM}} = \frac{4\pi(D_i + D_j)(a_i + a_j)}{\pi(a_i + a_j)^2 \sqrt{8k_B T / \pi m_{ij}}} \sim \frac{\sqrt{k_B T m_{ij}}}{(a_i + a_j) f_{ij}} = \text{Kn}_D$$

where the reduced friction coefficient is given by $f_{ij}^{-1} = f_i^{-1} + f_j^{-1}$.

Recall from previous discussion that the (regular) Knudsen number characterizes the ratio of continuum and free-molecular friction coefficients ($\text{Kn} \sim f_c / f_{FM}$).

Collision Rates at Intermediate Diffusive Knudsen Numbers

Recall: The slip correction factor $C_c(\text{Kn})$ was introduced to express the Stokes friction coefficient for any Knudsen number as $f = 6\pi\mu a_p/C_c$.

So how about collision rate coefficient β_{ij} for any diffusive Knudsen number? Write the dimensionless form of β_{ij} as:

$$H = \frac{\beta_{ij} m_{ij}}{(a_i + a_j)^3 f_{ij}}$$

Then we have:

$$\beta_{ij} = \begin{cases} 4\pi \left(\frac{k_B T}{f_{ij}} \right) (a_i + a_j) & \text{Kn}_D \rightarrow 0 \\ \sqrt{\frac{8\pi k_B T}{m_{ij}}} (a_i + a_j)^2 & \text{Kn}_D \rightarrow \infty \end{cases}$$

$$H = \begin{cases} 4\pi \text{Kn}_D^2 & \text{Kn}_D \rightarrow 0 \\ \sqrt{8\pi} \text{Kn}_D & \text{Kn}_D \rightarrow \infty \end{cases}$$

The behavior of H at intermediate Kn_D is experimentally observed to follow:
(from Gopalakrishnan & Hogan, 2011)

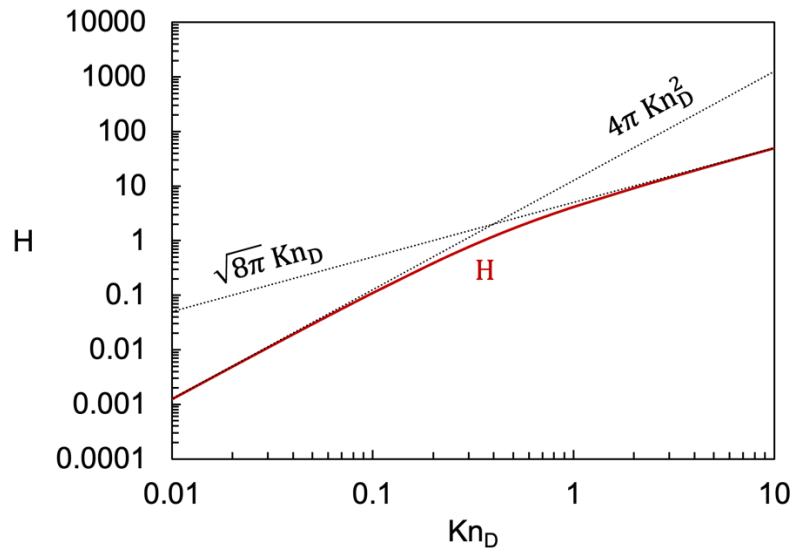
$$H \approx \frac{4\pi \text{Kn}_D^2 + C_1 \text{Kn}_D^3 + \sqrt{8\pi} C_2 \text{Kn}_D^4}{1 + C_3 \text{Kn}_D + C_4 \text{Kn}_D^2 + C_2 \text{Kn}_D^3}$$

$$C_1 \approx 25.886$$

$$C_2 \approx 11.211$$

$$C_3 \approx 3.502$$

$$C_4 \approx 7.211$$



Mean First Passage Time Calculation

Consider i - j particle collision using the (by now) familiar construct of a stationary collector of radius $a_i + a_j$ surrounded by wandering point masses m_{ij} with diffusivity $D_i + D_j$ and reduced drag coefficient f_{ij} .

Locate the collector in the center of a rectangular domain of volume V_{box} , and let a wandering particle explore the box (using *e.g.* the Ermak & Buckholtz algorithm).

If the wandering particle would leave the box, apply periodic boundary conditions.

Eventually the wandering particle collides with the collector. At this point the trajectory ends and the time of impact is recorded (the “first passage time”).

Over the simulation of many such trajectories, a large sample set of first passage times is accumulated $\{t_1, t_2, t_3, \dots, t_N\}$. (These times happen to be exponentially distributed.)

For sufficiently large N the collision rate coefficient is approximated by the box volume divided by mean first passage time:

$$\beta_{ij} \approx \frac{V_{box}}{\frac{1}{N} \sum_{i=1}^N t_i}$$

This general approach is valid for any Kn_D (when using a valid trajectory algorithm).

Multiphase Thermodynamics

The Gibbs free energy of a multicomponent system is:

$$G = H - TS = \sum_i N_i \mu_i$$

where H is enthalpy, S is entropy, and N_i and μ_i are the number of molecules and molecular chemical potential of each species.

In multiphase systems, energy may also be stored at interfaces (σ has units of J/m²). The total free energy of a system containing a single liquid droplet and its vapor is therefore:

$$G_{tot} = N_p \mu_p + N_v \mu_v + 4\pi\sigma a_p^2$$

where N_p is the number of molecules in liquid form in the droplet, N_v is the number of molecules in vapor form, and a_p is droplet radius.

The free energy in a system is minimized at thermodynamic equilibrium; that is, any partial derivative of G_{tot} is zero. Notably, this fact allows some simplified theoretical analysis of multiphase systems, which are otherwise rather complicated.

Droplet-Vapor Equilibrium (Kelvin Effect)

Consider a single liquid droplet and its vapor in thermodynamic equilibrium.

1. As already introduced in the previous section, the total free energy of this system is:

$$G_{tot} = N_p \mu_p + N_v \mu_v + 4\pi\sigma a_p^2$$

2. Molecules of a single species make up both the droplet and the vapor, so mass conservation requires that:

$$\partial N_p = -\partial N_v$$

3. Also mentioned in the previous section, at equilibrium we have (for example):

$$\frac{\partial G_{tot}}{\partial N_p} = 0$$

4. Combining (1), (2), and (3) we obtain:

$$\mu_p - \mu_v + 4\pi\sigma \frac{\partial(a_p^2)}{\partial N_p} = 0$$

5. Writing molecular volume in the liquid state as $v_m = \frac{4}{3}\pi a_p^3 / N_p$, we calculate:

$$a_p^2 = \left(\frac{3v_m}{4\pi} \right)^{\frac{2}{3}} N_p^{\frac{2}{3}}$$

$$\frac{\partial(a_p^2)}{\partial N_p} = \frac{2}{3} \left(\frac{3v_m}{4\pi} \right)^{\frac{2}{3}} N_p^{-\frac{1}{3}} = \frac{v_m}{2\pi a_p}$$

$$\therefore \mu_p - \mu_v + \frac{2\sigma v_m}{a_p} = 0$$

6. The total derivative of (5) is:

$$\partial\mu_p - \partial\mu_v + 2\sigma v_m \partial\left(\frac{1}{a_p}\right) = 0$$

7. It can be shown that:

$$\begin{aligned} \partial\mu_p &= v_m \partial p_{surf} \\ \partial\mu_v &= v_v \partial p_{surf} \end{aligned}$$

where v_v is the molecular volume in vapor form and p_{surf} is the vapor pressure at the droplet surface.

8. Combining (6) and (7) we obtain:

$$2\sigma v_m \partial\left(\frac{1}{a_p}\right) = (v_v - v_m) \partial p_{surf} \approx v_v \partial p_{surf}$$

where the approximation is made assuming that $v_v \gg v_m$.

9. The ideal gas law gives the molecular volume in vapor form (single molecule) as $p_{surf} v_v = k_B T$. So we have:

$$2\sigma v_m \partial\left(\frac{1}{a_p}\right) = \frac{k_B T}{p_{surf}} \partial p_{surf}$$

10. Integrate (9) over droplet radius, from infinity to a_p :

$$2\sigma v_m \int_0^{1/a_p} \partial \left(\frac{1}{a} \right) = k_B T \int_{p_{sat}}^{p_{surf}} \frac{1}{p} \partial p$$

(A droplet of infinite radius has an effectively planar surface, so p_{surf} in that case must be equal to p_{sat} by the definition of saturation pressure.)

11. The result of (10) is:

$$\frac{2\sigma v_m}{a_p} = k_B T [\ln(p_{surf}) - \ln(p_{sat})] = k_B T \ln \left(\frac{p_{surf}}{p_{sat}} \right)$$

12. Rearrange (11) to obtain the **Kelvin equation**:

$$\frac{p_{surf}}{p_{sat}} = \text{Exp} \left[\frac{2\sigma v_m}{k_B T a_p} \right]$$

The Kelvin equation demonstrates that the actual vapor pressure over a curved droplet surface is higher than saturation pressure over a flat surface. This pressure ratio increases exponentially with surface tension, liquid form molecular volume, or interface curvature.

Particles in a liquid

Similarly, for the precipitation of particles from a solute in a liquid, the actual solute concentration at the particle surface is:

$$\frac{c_{surf}}{c_{sat}} = \text{Exp} \left[\frac{2\sigma_{SL} v_m}{k_B T a_p} \right]$$

where c_{sat} is the saturation concentration, σ_{SL} is the solid-liquid interfacial tension, and v_m is now the molecular volume in solid form.

Dissolved species in a droplet

For a liquid droplet containing a solute of mole fraction χ_s and activity coefficient γ_s :

$$\frac{p_{surf}}{p_{sat}} = (1 - \chi_s \gamma_s) \text{Exp} \left[\frac{2\sigma v_m}{k_B T a_p} \right] = \text{Exp} \left[\frac{2\sigma v_m}{k_B T a_p} + \ln(1 - \chi_s \gamma_s) \right]$$

where p_{surf} and p_{sat} are still vapor pressures.

Condensation and Evaporation Rates

The rate of change of a single droplet volume during condensation or evaporation is:

$$\frac{dv_p}{dt} = (R_{cond} - R_{evap}) v_m$$

where R_{cond} and R_{evap} are time rates of condensation and evaporation on the droplet and v_m is still the molecular volume in liquid form.

For vapor pressure p_{vap} and saturation $S = p_{vap}/p_{sat}$, the condensation rate is:

$$R_{cond} = \beta_{cond} n_{vap} = \beta_{cond} \frac{p_{vap}}{k_B T} = \beta_{cond} \frac{p_{sat}}{k_B T} S$$

where the form of β_{cond} depends on Kn_D :

$$\beta_{cond} = \frac{H a_p^3 k_B T}{D_{vap} m_{vap}} = \begin{cases} 4\pi D_{vap} a_p & \text{Kn}_D \rightarrow 0 \\ a_p^2 \sqrt{\frac{8\pi k_B T}{m_{vap}}} & \text{Kn}_D \rightarrow \infty \end{cases}$$

It can be shown that $\beta_{cond} = \beta_{evap} = \beta$ (the same analysis is valid for either condensation or evaporation). So the evaporation rate is:

$$R_{evap} = \beta_{evap} n_{surf} = \beta \frac{p_{surf}}{k_B T} = \beta \frac{p_{sat}}{k_B T} \text{Exp} \left[\frac{2\sigma v_m}{k_B T a_p} \right]$$

Substituting these expressions for R_{cond} and R_{evap} we obtain:

$$\frac{dv_p}{dt} = \beta \frac{p_{sat} v_m}{k_B T} \left(S - \text{Exp} \left[\frac{2\sigma v_m}{k_B T a_p} \right] \right)$$

For particles in a liquid, $\text{Kn}_D \rightarrow 0$ and we have:

$$\frac{dv_p}{dt} = 4\pi D_{sol} a_p c_{sat} \left(S - \text{Exp} \left[\frac{2\sigma_{SL} v_m}{k_B T a_p} \right] \right)$$

with $dv_p/dt = 0$ at the critical particle radius:

$$a_{p,crit} = 2\sigma_{SL} v_m / k_B T \ln S$$

Particles smaller than $a_{p,crit}$ shrink ($dv_p/dt < 0$), while larger particles grow. This behavior is known as **Ostwald ripening**.

Heat Transfer to a Small Droplet

Heat transfer to a droplet of uniform temperature (*e.g.* small Biot number) in a simple environment can be characterized by:

$$\begin{aligned} m_{drop} c_{p,drop} \frac{dT_{drop}}{dt} &= \dot{Q}_{cond/conv} + \dot{Q}_{rad} + \dot{Q}_{cond/evap} \\ &= \dot{Q}_{cond/conv} + 4\pi a_p^2 \sigma_{SB} (T_{env}^4 - T_{drop}^4) + \Delta H_v \beta \frac{p_{sat}}{k_B T} \left(S - \text{Exp} \left[\frac{2\sigma v_m}{k_B T a_p} \right] \right) \end{aligned}$$

where $\sigma_{SB} = 5.67 \times 10^{-8} \text{ W/m}^2 \text{K}^4$ is the Stefan–Boltzmann constant, ΔH_v is the enthalpy or “latent heat” of vaporization for one molecule, and $\dot{Q}_{cond/conv}$ is the heat transfer due to conduction or convection with the surrounding fluid (depending on its relative velocity to the droplet).

For a droplet in stagnant fluid:

$$\dot{Q}_{cond} = \begin{cases} 4\pi a_p^2 k_f \frac{T_{env} - T_{drop}}{a_p} & \text{Kn} \rightarrow 0 \\ 2\alpha_T \sqrt{\frac{8k_B T_{env}}{\pi m_{gas}}} \left(\frac{p_{gas}}{k_B T_{env}} \right) \pi a_p^2 (T_{env} - T_{drop}) & \text{Kn} \rightarrow \infty \end{cases}$$

where k_f is thermal conductivity and $0 < \alpha_T < 1$ is a thermal accommodation coefficient characterizing the transfer of thermal energy by free molecular collisions.

Note: Heat transfer is very slow in the free molecular regime.

Macroscopic Heat Transfer and Vapor Concentration

Macroscopic heat transfer in a system of evaporating and condensing (polydisperse) particles is given by:

$$\rho c_p \left(\frac{\partial T}{\partial t} + \mathbf{u} \cdot \nabla T \right) = \nabla \cdot (k \nabla T) + q'''$$

where q''' is volumetric heat generation from the latent heat of net condensation. The net condensation rate onto a single particle was previously derived as:

$$R_{cond,net} = \beta \frac{p_{sat}}{k_B T} \left(S - \text{Exp} \left[\frac{2\sigma v_m}{k_B T a_p} \right] \right)$$

where β is chosen appropriately depending on Kn_D . For large particles, $a_p \rightarrow \infty$ until $k_B T a_p \gg 2\sigma v_m$. So we approximate:

$$R_{cond,net} \approx \beta \frac{p_{sat}}{k_B T} (S - 1)$$

(Note: If the particles are not sufficiently large for this approximation, a finite Taylor expansion of the Exp term would still allow the application of moment methods.)

The total contribution to q''' from a single particle size is then:

$$\partial q''' = \Delta H_v R_{cond,net} \partial n = \Delta H_v \beta \frac{p_{sat}}{k_B T} (S - 1) \partial n$$

where ∂n is the concentration of the given particle size. Integrating over all particles:

$$\begin{aligned} q''' &= \int \partial q''' \\ &= \int \Delta H_v \beta \frac{p_{sat}}{k_B T} (S - 1) \partial n \\ &= \int_0^\infty \Delta H_v \beta \frac{p_{sat}}{k_B T} (S - 1) \frac{\partial n}{\partial v_p} \partial v_p \end{aligned}$$

If $\text{Kn}_D \rightarrow 0$ (continuum mechanics), then:

$$\beta = 4\pi(D_{vap} + D_p)(a_{vap} + a_p) \approx 4\pi D_{vap} a_p = 4\pi \left(\frac{3}{4\pi}\right)^{1/3} D_{vap} v_p^{1/3}$$

$$\therefore q''' = 48^{1/3} \pi^{2/3} \Delta H_v D_{vap} \left(\frac{p_{sat}}{k_B T}\right) (S - 1) M_{1/3}$$

The time rate of change in vapor concentration is obtained through similar analysis:

$$\frac{\partial n_{vap}}{\partial t} = -48^{1/3} \pi^{2/3} D_{vap} \left(\frac{p_{sat}}{k_B T}\right) (S - 1) M_{1/3}$$

And the change in individual droplet sizes:

$$\begin{aligned} \frac{\partial v_p}{\partial t} &= R_{cond,net} v_m \\ &\approx 4\pi D_{vap} a_p \left(\frac{p_{sat}}{k_B T}\right) (S - 1) v_m \\ &= 48^{1/3} \pi^{2/3} D_{vap} \left(\frac{p_{sat}}{k_B T}\right) (S - 1) v_m v_p^{1/3} \end{aligned}$$

using $4\pi a_p^3 = 3v_p$. The change with respect to droplet radius immediately follows:

$$\begin{aligned} \Rightarrow 12\pi a_p^2 \frac{\partial a_p}{\partial t} &= 3 \frac{\partial v_p}{\partial t} \\ \therefore \frac{\partial a_p}{\partial t} &= \frac{D_{vap}}{a_p} \left(\frac{p_{sat}}{k_B T}\right) (S - 1) v_m \end{aligned}$$

Moment Methods for Condensation

Also from the same analysis, the change in the k -th moment of the volumetric droplet size distribution due to net condensation with $\text{Kn}_D \rightarrow 0$ is given by:

$$\frac{\partial M_k}{\partial t} = 48^{1/3} \pi^{2/3} \Delta H_v D_{vap} \left(\frac{p_{sat}}{k_B T} \right) (S - 1) \int_0^\infty v_p^{1/3} \left[(v_p + v_m)^k - v_p^k \right] \frac{\partial n}{\partial v_p} \partial v_p$$

Note: This is a unary reaction, so we aren't double-counting during integration and don't need to add a $1/2$ factor in front as for coagulation.

In the following equations, abbreviate the integral prefactor for convenience:

$$X = 48^{1/3} \pi^{2/3} \Delta H_v D_{vap} \left(\frac{p_{sat}}{k_B T} \right) (S - 1)$$

For $k = 1, 2, 3$ we get:

$$\frac{\partial M_0}{\partial t} = X \int_0^\infty v_p^{1/3} (0) \frac{\partial n}{\partial v_p} \partial v_p = 0$$

$$\frac{\partial M_1}{\partial t} = X \int_0^\infty v_p^{1/3} (v_m) \frac{\partial n}{\partial v_p} \partial v_p = X v_m M_{1/3}$$

$$\frac{\partial M_2}{\partial t} = X \int_0^\infty v_p^{1/3} (2v_p v_m + v_m^2) \frac{\partial n}{\partial v_p} \partial v_p = X (2 v_m M_{4/3} + v_m^2 M_{1/3})$$

Equilibrium Distribution of Droplet Sizes

Consider a system of condensing and evaporating particles at some equilibrium size distribution, held at a constant vapor pressure. Let $n_{g,eq}$ be the volumetric concentration of particles containing exactly g molecules.

The (forward) rate of condensation onto g particles is:

$$R_{f,g} = \beta_g n_1 n_{g,eq} = \beta_g S n_{sat} n_{g,eq}$$

The (backward) rate of evaporation from $g + 1$ particles is:

$$R_{b,g+1} = \alpha_{g+1} n_{1,surf,g+1} n_{g+1,eq}$$

At equilibrium we have:

$$\begin{aligned} R_{f,g} &= R_{b,g+1} \\ \Rightarrow \frac{n_{g+1,eq}}{n_{g,eq}} &= \frac{\beta_g}{\alpha_{g+1}} S \frac{n_{sat}}{n_{1,surf,g+1}} \end{aligned}$$

Now consider the concentration ratio:

$$\begin{aligned} \frac{n_{g,eq}}{n_1} &= \frac{n_{2,eq}}{n_1} \cdot \frac{n_{3,eq}}{n_{2,eq}} \cdot \frac{n_{4,eq}}{n_{3,eq}} \cdot \dots \cdot \frac{n_{g,eq}}{n_{g-1,eq}} \\ &= \prod_{i=1}^{g-1} \frac{n_{i+1,eq}}{n_{i,eq}} \\ &= \prod_{i=1}^{g-1} \left(\frac{\beta_i}{\alpha_{i+1}} S \frac{n_{sat}}{n_{1,surf,i+1}} \right) \\ &= S^{g-1} \prod_{i=1}^{g-1} \left(\frac{\beta_i}{\alpha_{i+1}} \cdot \frac{n_{sat}}{n_{1,surf,i+1}} \right) \end{aligned}$$

Moving $n_1 = S n_{sat}$ to the right-hand side:

$$n_{g,eq} = S^g n_{sat} \prod_{i=1}^{g-1} \left(\frac{\beta_i}{\alpha_{i+1}} \cdot \frac{n_{sat}}{n_{1,surf,i+1}} \right)$$

Considering $n_{1,surf,i+1}$, recall from the Kelvin effect that:

$$\frac{n_{1,surf}}{n_{sat}} = \text{Exp} \left[\frac{2\sigma v_m}{k_B T a_p} \right]$$

Therefore we can write:

$$n_{g,eq} = S^g n_{sat} \prod_{i=1}^{g-1} \left(\frac{\beta_i}{\alpha_{i+1}} \text{Exp} \left[\frac{-2\sigma v_m}{k_B T a_{i+1}} \right] \right)$$

Now, suppose g is large such that $i \pm 1 \approx i$ and $\beta_i/\alpha_{i+1} \approx 1$ for the majority of all i :

$$\begin{aligned} n_{g,eq} &\approx S^g n_{sat} \prod_{i=1}^{g-1} \text{Exp} \left[\frac{-2\sigma v_m}{k_B T a_i} \right] \\ &= S^g n_{sat} \prod_{i=1}^{g-1} \text{Exp} \left[\frac{-2\sigma v_m}{k_B T} \left(\frac{4\pi}{3v_m} \right)^{1/3} i^{-1/3} \right] \\ &= S^g n_{sat} \text{Exp} \left[\frac{-2\sigma v_m}{k_B T} \left(\frac{4\pi}{3v_m} \right)^{1/3} \sum_{i=1}^{g-1} i^{-1/3} \right] \end{aligned}$$

Approximating the discrete sum as an integral:

$$\begin{aligned} n_{g,eq} &\approx S^g n_{sat} \text{Exp} \left[\frac{-2\sigma v_m}{k_B T} \left(\frac{4\pi}{3v_m} \right)^{1/3} \int_{i=1}^{g-1} i^{-1/3} di \right] \\ &= S^g n_{sat} \text{Exp} \left[\frac{-2\sigma v_m}{k_B T} \left(\frac{4\pi}{3v_m} \right)^{1/3} \left(\frac{3}{2} [(g-1)^{2/3} - 1] \right) \right] \\ &\approx S^g n_{sat} \text{Exp} \left[\frac{-2\sigma v_m}{k_B T} \left(\frac{4\pi}{3v_m} \right)^{1/3} \left(\frac{3}{2} [g^{2/3} - 1] \right) \right] \\ &= S^g n_{sat} \text{Exp} \left[\frac{(36\pi)^{1/3} \sigma v_m^{2/3} (1 - g^{2/3})}{k_B T} \right] \end{aligned}$$

Moving S inside the exponential term, we obtain the equilibrium concentration:

$$\boxed{\begin{aligned} \frac{n_{g,eq}}{n_{sat}} &\approx \text{Exp} \left[\frac{\theta(1 - g^{2/3}) + g k_B T \ln S}{k_B T} \right] \\ \theta &= (36\pi)^{1/3} \sigma v_m^{2/3} \end{aligned}}$$

Critical Cluster Size at Equilibrium

Using the Kelvin equation and several approximations for large cluster sizes, we found the equilibrium concentration of clusters containing g molecules:

$$\frac{n_{g,eq}}{n_{sat}} \approx \text{Exp} \left[\frac{\theta(1 - g^{2/3}) + g k_B T \ln S_{sat}}{k_B T} \right] = \text{Exp} \left[\frac{-\Delta_f G_g}{k_B T} \right]$$

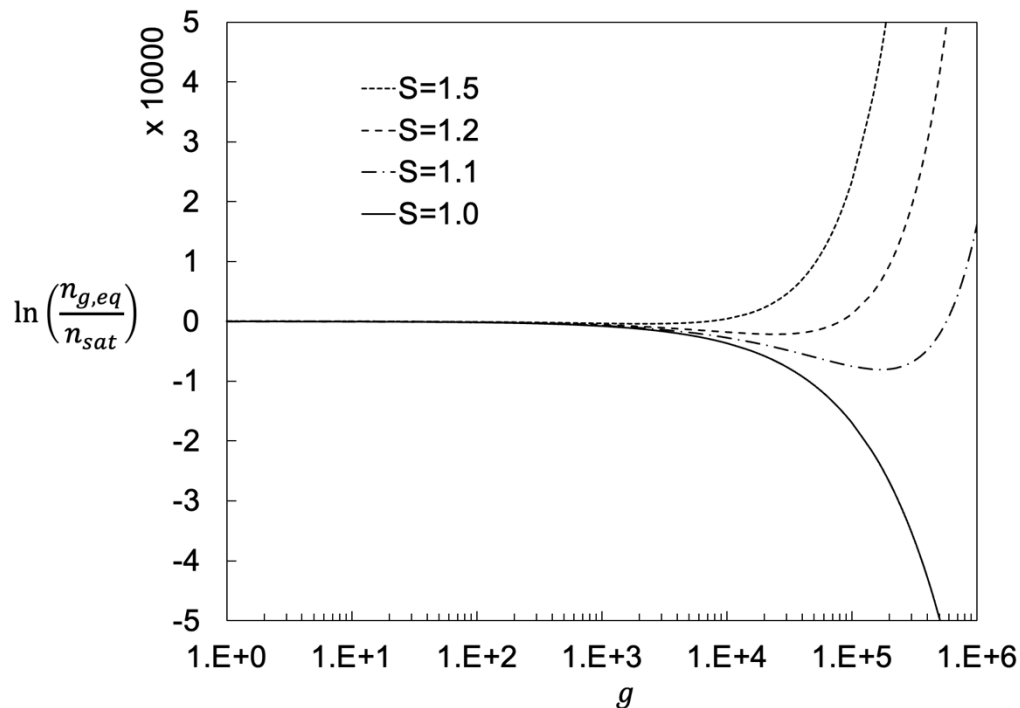
$$\theta = (36\pi)^{1/3} \sigma v_m^{2/3}$$

where $\Delta_f G_g = \Delta_f H - T \Delta_f S_{ent}$ is the Gibbs free energy change of forming a single cluster of g molecules: $g A_1 \rightarrow A_g$.

The term $\Delta_f H = \theta(g^{2/3} - 1)$ is positive for $g > 1$ and represents an *enthalpic barrier* to the formation of clusters.

The term $-T \Delta_f S_{ent} = -g k_B T \ln S_{sat}$ may be positive or negative, and clustering is *entropically favorable* ($-T \Delta_f S_{ent} < 0$) for supersaturated systems ($S_{sat} > 1$).

Equilibrium concentration curves are shown below for water at 300 K. For supersaturated conditions ($S_{sat} > 1$), the equilibrium concentration decreases monotonically from an initial value of $n_1 = S_{sat} n_{sat}$, then (theoretically) diverges exponentially toward infinity at some critical cluster size g_{crit} where $T \Delta_f S_{ent}$ first overwhelms $\Delta_f H$.



At the critical cluster size:

$$0 = \frac{\partial \left(\frac{n_{g,eq}}{n_{sat}} \right)}{\partial g} = \left(\frac{-\Delta_f G_g}{k_B T} \right) \left(\frac{\partial \Delta_f G_g}{\partial g} \right) \text{Exp} \left[\frac{-\Delta_f G_g}{k_B T} \right]$$

This implies:

$$0 = \frac{\partial \Delta_f G_g}{\partial g} = \frac{2}{3} \theta g_{crit}^{-1/3} - k_B T \ln S_{sat}$$

Therefore we have:

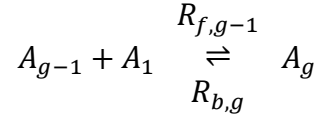
$$g_{crit} = \frac{36\pi \sigma^3 v_m^2}{(k_B T \ln S_{sat})^3}$$

And since $3 g_{crit} v_m = 4\pi a_{crit}^3$, also:

$$a_{crit} = \frac{3 \sigma v_m}{k_B T \ln S_{sat}}$$

Steady State Nucleation

Let J_g be the net forward reaction rate for condensational growth to a cluster of size g :



$$J_g = R_{f,g-1} - R_{b,g} = \beta_{g-1} n_1 n_{g-1} - \alpha_g n_{1,surf,g} n_g$$

$$\frac{\partial n_g}{\partial t} = J_g - J_{g+1}$$

At equilibrium, $J_g = 0$ for all g .

At steady state, $J_g = J_{g+1}$ for all g .

In either equilibrium or steady state, $\partial n_g / \partial t = 0$.

Consider a nucleating system at steady state ($J_g = J_{g+1}$ for all g , and $S > 1$). We will derive an expression for the (universal) steady state nucleation rate J_{ss} .

Noting that $n_1 = S n_{sat}$, we start with:

$$J_g = \beta_{g-1} S n_{sat} n_{g-1} - \alpha_g n_{1,surf,g} n_g$$

We can replace $\alpha_g n_{1,surf,g}$ in terms of the equilibrium conditions:

$$\frac{n_{g,eq}}{n_{g-1,eq}} = \frac{\beta_{g-1}}{\alpha_g} S \frac{n_{sat}}{n_{1,surf,g}} \quad \Rightarrow \quad \alpha_g n_{1,surf,g} = \beta_{g-1} S n_{sat} \frac{n_{g,eq}}{n_{g-1,eq}}$$

$$\therefore J_g = \beta_{g-1} S n_{sat} \left(n_{g-1} - n_g \left[\frac{n_{g,eq}}{n_{g-1,eq}} \right] \right)$$

$$\Rightarrow \frac{J_g}{S n_{sat}} \left[\frac{1}{\beta_{g-1} n_{g-1,eq}} \right] = \frac{n_{g-1}}{n_{g-1,eq}} - \frac{n_g}{n_{g,eq}}$$

Add this expression over all $g > 1$ up to some arbitrarily large G :

$$\begin{aligned}
 \frac{J_{ss}}{Sn_{sat}} \sum_{g=2}^G \left[\frac{1}{\beta_{g-1} n_{g-1,eq}} \right] &= \sum_{g=2}^G \left[\frac{n_{g-1}}{n_{g-1,eq}} - \frac{n_g}{n_{g,eq}} \right] \\
 &= \frac{n_1}{n_{1,eq}} + \sum_{g=2}^{G-1} \left[\frac{n_g}{n_{g,eq}} - \frac{n_g}{n_{g,eq}} \right] - \frac{n_G}{n_{G,eq}} \\
 &= 1 + 0 - \frac{n_G}{n_{G,eq}}
 \end{aligned}$$

To factor out J_{ss} on the left-hand side, recall that $J_g = J_{g+1}$ for all g at steady state.

For large enough G we know $n_{G,eq} \rightarrow \infty$, but realistically also $n_G \rightarrow 0$ since clusters larger than the system itself are impossible. Hence $n_G/n_{G,eq} \approx 0$ and we get:

$$\frac{J_{ss}}{Sn_{sat}} \sum_{g=2}^G \left[\frac{1}{\beta_{g-1} n_{g-1,eq}} \right] \approx 1$$

Since $n_{G,eq} \rightarrow \infty$ we can also re-index the left-hand side as:

$$\frac{J_{ss}}{Sn_{sat}} \sum_{g=2}^G \left[\frac{1}{\beta_{g-1} n_{g-1,eq}} \right] \approx \frac{J_{ss}}{Sn_{sat}} \sum_{g=1}^G \left[\frac{1}{\beta_g n_{g,eq}} \right]$$

Finally we obtain:

$$J_{ss} \approx \frac{Sn_{sat}}{\sum_{g=1}^G \left[\frac{1}{\beta_g n_{g,eq}} \right]} = \frac{Sn_{sat}^2}{\sum_{g=1}^G \left[\beta_g^{-1} \left(\frac{n_{g,eq}}{n_{sat}} \right)^{-1} \right]}$$

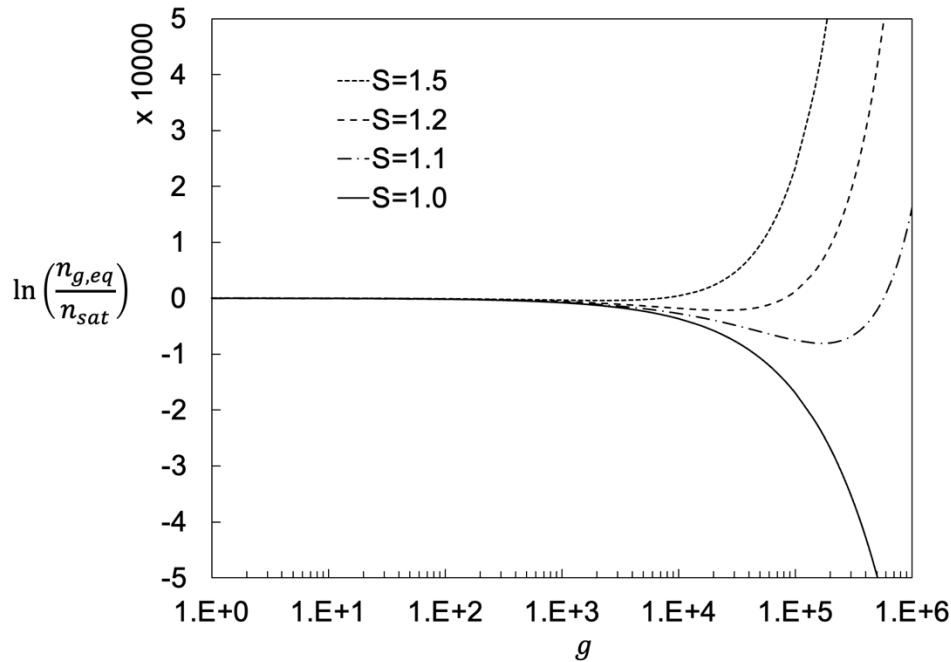
Inserting our earlier exponential result for $n_{g,eq}/n_{sat}$ and approximating the discrete sum as a continuous integral:

$$J_{ss} \approx \frac{Sn_{sat}^2}{\int_1^\infty \beta_g^{-1} \text{Exp} \left[\frac{\Delta_f G_g}{k_B T} \right] dg}$$

Nucleation Moment Methods

For supersaturated conditions, we've seen that the theoretical equilibrium concentration increases exponentially for clusters larger than g_{crit} :

$$\lim_{g \rightarrow \infty} n_{g,eq} = \infty$$



Clearly

arrangement is not physically attainable.

this

- It is unrealistic to anticipate arbitrarily large droplets in a finite system.
- The maximum volumetric concentration of a non-overlapped droplet is $1/v_p$.

One typical solution is to assume the exact steady-state results for cluster concentration $n_{g,eq}$ and nucleation rate J_{ss} for all $g < g_{crit}$, but monitor larger $g \geq g_{crit}$ cluster size distributions using moments or other methods.

If using moment methods to monitor only $g \geq g_{crit}$ clusters, the effect of steady state nucleation is that clusters of volume $g_{crit}v_m$ appear at the rate J_{ss} , in addition to any coagulation, evaporation, etc:

$$\begin{aligned} \left(\frac{\partial M_0}{\partial t}\right)_{nucleation} &= \frac{\partial n_{tot}}{\partial t} = J_{ss} \\ \left(\frac{\partial M_1}{\partial t}\right)_{nucleation} &= \frac{\partial v_{tot}}{\partial t} = J_{ss} g_{crit} v_m \\ \left(\frac{\partial M_2}{\partial t}\right)_{nucleation} &= J_{ss} (g_{crit} v_m)^2 \end{aligned}$$

Total Phase Change

All the phase change analysis so far has assumed the presence of some passive continuous phase ($p_{vap} \ll p_{tot}$). So what if the entire system changes phase?

Consider a certain amount of pure water freezing solid.

Supersaturation ($S > 1$) drives condensation; supercooling ($T < T_{melt}$) drives freezing.

Like other dispersions, the size of crystals growing through phase change can be tracked as a size distribution. **The symbol ρ is typically used instead of $\partial n / \partial a_p$.**

*Here “crystal” refers to any solid, not necessarily crystalline.

For crystal growth velocity $u_g = \partial a_p / \partial t$ (often assumed to be size-independent), the conservation of mass with no other processes besides crystal growth requires that:

$$\frac{\partial \rho}{\partial t} + \frac{\partial (u_g \rho)}{\partial a_p} = 0$$

To solve for $\rho(a_p, t)$, we need one initial condition and one boundary condition.

In the case of pure water that later freezes, the initial crystal size distribution is zero:

$$\rho(a_p, 0) = \rho_0(a_p) = 0$$

The **population balance model** uses the boundary condition:

$$\rho(a_{crit}, t) = \frac{J(t)}{u_g}$$

where a_{crit} is the minimum crystal size, $J(t)$ is (time-dependent) nucleation rate, and u_g is a constant crystal growth velocity. The concentration of minimum-size crystals varies directly with nucleation rate, and inversely with crystal growth velocity.

Justification: the number of nucleated particles during a small time interval δt must be:

$$J(t) \delta t = \int_{a_{crit}}^{a_{crit} + u_g \delta t} \rho(a_p, t) \partial a_p \approx \rho(a_{crit}, t) \int_{a_{crit}}^{a_{crit} + u_g \delta t} \partial a_p = \rho(a_{crit}, t) u_g \delta t$$

(Particles $a_p \leq a_{crit} + u_g \delta t$ must have nucleated during δt , or they would be larger.)

To handle total freezing of water, let f be the fraction that has already frozen.

The fraction of water that is still liquid is a product over all crystals. For N crystals:

$$1 - f = \prod_{i=1}^N \left(1 - \frac{V_i}{V_{tot}}\right)$$

where V_i is the volume of each crystal and V_{tot} is the total system volume.

Taking the natural log:

$$\begin{aligned} \ln(1 - f) &= \sum_{i=1}^N \ln\left(1 - \frac{V_i}{V_{tot}}\right) \\ &\approx \sum_{i=1}^N \frac{-V_i}{V_{tot}} \\ &= \frac{-1}{V_{tot}} \sum_{i=1}^N V_i \\ &= \frac{-V_e}{V_{tot}} \end{aligned}$$

where the approximation comes from a first-order Taylor expansion for small V_i/V_{tot} and the **extended volume** is $V_e = \sum V_i$.

If crystals are allowed to overlap as they grow, some phase change is double-counted and the extended volume V_e will exceed V_{tot} after sufficient time has passed. We are left with:

$$f = 1 - \text{Exp}\left[\frac{-V_e}{V_{tot}}\right]$$

$$\frac{V_e}{V_{tot}} = \frac{4\pi}{3} \int_0^{\infty} a_p^3 \rho \partial a_p$$

where $f \rightarrow 1$ as $V_e \rightarrow \infty$.

Avrami Equation

For an isothermal system with a constant nucleation rate J , constant and size-independent crystal growth velocity u_g , and spherical crystal shape, the extended volume at any time t can be expressed as an integral over crystal nucleation times $0 < t_0 < t$:

$$V_e = \int_0^t \frac{4\pi}{3} (u_g[t - t_0])^3 J V_{tot} dt_0 = \frac{\pi}{3} J V_{tot} u_g^3 t^4$$

Substituting this expression for V_e into the result from the previous page:

$$f = 1 - \text{Exp} \left[\frac{-\pi}{3} J u_g^3 t^4 \right]$$

This general form is known as the **Avrami equation** for isothermal phase change.

In practice, crystals aren't spherical and observations are fit by:

$$f = 1 - \text{Exp}[-kt^n]$$

for some constant k and Avrami exponent $n \leq 4$.

Porous Media

Porous media include:

- rocks and soil
- packed bed reactors
- fibrous filters

In these systems the volume fractions of continuous and dispersed components have similar orders of magnitude so that the fibers or particles remain in close contact with other fibers or particles.

Porous media can be characterized by a size distribution function describing the size of either the solid particles or the pores between them.

Another common descriptor is **specific surface area (SSA)**:

$$SSA = \frac{A_{total}}{m_{total}} = \frac{\int_0^\infty A_p \frac{\partial n}{\partial v_p} \partial v_p}{\int_0^\infty m_p \frac{\partial n}{\partial v_p} \partial v_p}$$

where A is surface area and m is mass. For spherical particles with moments M_k :

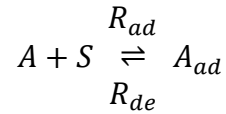
$$SSA_{spheres} = \frac{3^{2/3}(4\pi)^{1/3} M_{2/3}}{\rho_p M_1}$$

Adsorption

Adsorption: a particle attaching to the surface of a collector, perhaps temporarily

Absorption: a particle penetrating into a collector

Consider a chemical A attaching and detaching from an open site S on a collector:



where R_{ad} is adsorption rate:

$$R_{ad} = k_{ad} p_A [S]$$

R_{de} is desorption rate:

$$R_{de} = k_{de} [A_{ad}]$$

and A_{ad} is adsorbed A . The partial vapor pressure of A is p_A , and would be replaced by concentration c_A if in liquid solution. The site densities $[S]$ and $[A_{ad}]$ are usually expressed in units of $\#/m^2$ (sites per unit surface area).

A conservation balance on adsorption sites requires that:

$$[S]_0 = [S] + [A_{ad}]$$

where $[S]_0$ is the initial site density before adsorption begins.

Write the fraction of sites occupied by adsorbed A as $\theta_A = [A_{ad}]/[S]_0$ (it follows that also $1 - \theta_A = [S]/[S]_0$), and let a dimensional equilibrium coefficient be:

$$K_{eq} = \frac{k_{ad}}{k_{de}} = \frac{[A_{ad}]}{p_A [S]}$$

(The form of this coefficient comes from $R_{ad} = R_{de}$ at equilibrium.)

Rewriting adsorption site conservation, we obtain the **Langmuir Adsorption Isotherm**:

$$\theta_A = \frac{p_A K_{eq}}{1 + p_A K_{eq}}$$

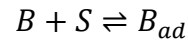
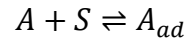
The total chemical A adsorbed per porous media mass is (sites per unit mass):

$$\Xi_A = \theta_A [S]_0 SSA$$

Competitive Adsorption

Often other chemicals are present that may compete for adsorption sites.

Consider a system with independently competing chemicals A and B :



Site conservation is now:

$$[S]_0 = [S] + [A_{ad}] + [B_{ad}]$$

We define:

$$K_{eq}^A = \frac{[A_{ad}]}{p_A[S]}$$

$$K_{eq}^B = \frac{[B_{ad}]}{p_B[S]}$$

$$\theta_A = \frac{[A_{ad}]}{[S]_0}$$

$$\theta_B = \frac{[B_{ad}]}{[S]_0}$$

After substitution we obtain:

$$\theta_A = \frac{p_A K_{eq}^A}{1 + p_A K_{eq}^A + p_B K_{eq}^B}$$

$$\theta_B = \frac{p_B K_{eq}^B}{1 + p_A K_{eq}^A + p_B K_{eq}^B}$$

The pattern for extrapolation is self-evident if more than two chemicals are present.

Other Types of Adsorption

Multilayer adsorption:

- BET theory (Brunauer–Emmett–Teller theory)
- not just a single layer of sites on the surface, but adsorption builds up layers

Freundlich isotherm:

- an empirical fit of the Langmuir isotherm: $\theta_A = \alpha_F p_A^{C_F}$