2.7 Aerosols and coagulation

[Refs]:
Present, Kinetic Theory of Gases
Fuchs, Mechanics of Aerosols
Friedlander, Smoke, Dust and Haze
Seinfeld, Atmospheric Chemistry and Physics of Air Pollution
Levich: Physio-Chemical Hydrodynamics

2.7.1 Brownian diffusion of particles

Particles of sub-micrometer size collide with air molecules randomly and behave collectively as a gas.

Let \( n(z) \) = number of particles per unit volume, i.e., the number density of Brownian particles in air. By the perfect gas law,

\[
p = nkT, \tag{2.7.1}
\]

where \( k \) is Boltzmann’s constant

\[
k = \frac{R}{L},
\]

\[
R = \text{Universal gas constant} = 8.317 \times 10^7 \text{ergs/degree/mole}
\]

and

\[
L = \text{Avogadro’s number} = 6.025 \times 10^{23} \text{molecules/mole} = 2 \text{calories/degree/mole}
\]

When the cloud of particles is in hydrostatic equilibrium,

\[
\frac{dp}{dz} = -\rho g = -nmg \tag{2.7.2}
\]

where \( m \) is the mass per particle. Combining the preceding two equations,

\[
-\frac{dp}{p} = \frac{mg}{kT} dz
\]
hence,
\[ p(z) = p(0) \exp \left( -\frac{mgz}{kT} \right) \]  \hspace{1cm} (2.7.3)

and
\[ n(z) = n(0) \exp \left( -\frac{mgz}{kT} \right) \]  \hspace{1cm} (2.7.4)

which is Boltzmann’s law.

Alternatively, random collisions on the microscale give rise to diffusion on the macroscale. At the equilibrium state, diffusion and gravitational convection must balance each other so that,
\[-D \frac{dn}{dz} - nV = 0 \quad (2.7.5)\]

where \( V \) = fall velocity. Equating Stokes drag with the particle weight \( 6\pi\mu aV = mg \), we get
\[ V = \frac{mg}{6\pi\mu a} \] \hspace{1cm} (2.7.6)

Solving (2.7.5) and using (2.7.6),
\[ n(z) = n(0) \exp \left( -\frac{mgz}{D6\pi\mu a} \right) \] \hspace{1cm} (2.7.7)

Upon comparison with (2.7.4), the Brownian diffusivity can be identified
\[ D = \frac{kT}{6\pi\mu a} \] \hspace{1cm} (2.7.8)

This formula, due to Einstein (1905) and Smoluchowski (1906), is valid if \( 2a \) is smaller than the mean free path \( \ell \) of air molecules. Otherwise Cunningham’s empirical correction is needed,
\[ D = C_c \left( \frac{kT}{6\pi\mu a} \right) \] \hspace{1cm} (2.7.9)

where
\[ C_c = 1 + \frac{\ell}{a} \left[ 1.257 + 0.4 \exp \left( -\frac{1.1a}{\ell} \right) \right] \] \hspace{1cm} (2.7.10)

is the correction factor.

For aerosol particles in air under normal temperature, the diffusivity is
\[ D \approx \frac{1 \times 10^{-3}}{2a} \frac{10^{-2}}{0.15 \times 10^{-3}} = \frac{0.325 \times 10^{-11}}{a} \] \hspace{1cm} (2.7.11)

As a rough order-estimate (Levich), we use Eistein’s formula for water at room temperature, the Brownian diffusivity for colloidal particles is
\[ D \approx \frac{0.55 \times 10^{-13}}{a} \] \hspace{1cm} (2.7.12)
In the following table taken from Seinfeld, p. 325, \( D \) and \( \nu \) are compared. For gases, the mean free path is typically \( \ell = 10^{-5} \sim 10^{-6} \) cm.

<table>
<thead>
<tr>
<th>( 2a (\mu m) )</th>
<th>( D (cm^2/s \quad (T = 20^\circ) )</th>
<th>( V ) (cm/sec) ( (\rho_s = 1g/cm^3) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>( 5.14 \times 10^{-2} )</td>
<td>8.62 ( \times 10^{-5} )</td>
</tr>
<tr>
<td>0.01</td>
<td>( 5.25 \times 10^{-4} )</td>
<td>3.52 ( \times 10^{-3} )</td>
</tr>
<tr>
<td>0.1</td>
<td>( 6.75 \times 10^{-6} )</td>
<td>3.07 ( \times 10^{-3} )</td>
</tr>
<tr>
<td>1</td>
<td>( 2.77 \times 10^{-7} )</td>
<td>30.3</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 2.7.2 Coagulation due to Brownian diffusion

When small particles are bounced around randomly by surrounding fluid molecules, they may come so close to one another that Van der Waals force binds them together. This is coagulation. In a moving fluid additional factors such as fluid shear and Coulomb forces may intervene. A simple model (by Smoluchowski) for a stationary fluid with identical spherical particles of radius \( a \) is as follows.

![Figure 2.7.1: Left: A spherical shell. Right: Two spherical particles in collision.](image)

Let us focus attention on a fixed particle. Consider a spherical shell from \( r \) to \( r + dr \), Figure 2.7.2-left. The rate of increase of particles inside the shell is

\[
\frac{\partial n}{\partial t} = 4\pi r^2 dr
\]

which must be equal to the net influx through the two surfaces of the shell

\[
-\frac{\partial}{\partial r} \left( -4\pi r^2 D \frac{\partial n}{\partial r} \right) dr
\]

thus,

\[
\frac{\partial n}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial n}{\partial r} \right)
\]

\[ (2.7.13) \]
Assume that whenever two particles come into contact they stick to each other and become one. Therefore the spherical surface of radius $2a$ concentric with the stationary particle acts as a sink, on which $n = 0$, i.e.,

$$n = 0 \quad r = 2a \quad (2.7.14)$$

$$n \to n_\infty \quad r \to \infty \quad (2.7.15)$$

See Figure 2.7.2-right. The initial condition is

$$n = n_\infty, \quad 2a < r < \infty \quad t = 0 \quad (2.7.16)$$

The solution can be facilitated by introducing

$$w = \frac{n_\infty - n}{n_\infty} \left( \frac{r}{2a} \right) \quad (2.7.17)$$

and

$$x = \frac{r - 2a}{2a} \quad (2.7.18)$$

it is shown in Appendix A that

$$\frac{\partial w}{\partial t} = D' \frac{\partial^2 w}{\partial x^2} \quad (2.7.19)$$

where

$$D' = \frac{D}{(2a)^2} \quad (2.7.20)$$

The boundary conditions become,

$$w = 1, \quad x = 0 \quad (2.7.21)$$

while

$$w = 0, \quad x = \infty \quad (2.7.22)$$

The initial condition is

$$w = 0, \quad t = 0, x > 0 \quad (2.7.23)$$

The solution, which can be obtained by the similarity method (see Appendix B), is:

$$w = 1 - \text{erf} \left( \frac{x}{2 \sqrt{Dt}} \right) = 1 - \sqrt{\frac{2}{\pi}} \int_0^{\frac{r-2a}{2\sqrt{Dt}}} e^{-z^2} \, dz \quad (2.7.24)$$

or,

$$\frac{n_\infty - n(r,t)}{n_\infty} = 1 - \sqrt{\frac{2}{\pi}} \int_0^{\frac{r-2a}{2\sqrt{Dt}}} e^{-z^2} \, dz$$

or

$$1 - \frac{n}{n_\infty} = 1 - \frac{2a}{r} \left[ 1 - \sqrt{\frac{2}{\pi}} \int_0^{\frac{r-2a}{2\sqrt{Dt}}} e^{-z^2} \, dz \right]$$
Finally, the number concentration near a fixed particle is

\[ n(r, t) = n(0) \left( 1 - \frac{2a}{r} + \frac{2a}{r} \sqrt{\frac{2}{\pi}} \int_0^{\frac{r}{2a}} e^{-z^2} dz \right) = 1 - \frac{2a}{r} + \frac{2a}{r} \text{erf} \left( \frac{r - 2a}{2Dt} \right) \] (2.7.25)

We now use this information to find the rate of coagulation when all particles are moving, by calculating the number density of particles in the process of collision. Starting from one particle, the rate of flux of particle across the sphere of radius \( r = 2a \) is

\[ J(t) = 4\pi r^2 D \left( \frac{\partial n}{\partial r} \right)_{r=2a} = 4\pi D(2a)n(0) \left( 1 + \frac{2a}{\sqrt{\pi Dt}} \right) \] (2.7.26)

When

\[ t \gg \frac{(2a)^2}{D} \]

we get the steady state limit,

\[ J(\infty) = 4\pi D(2a)n(\infty) = 8\pi Dn(\infty) \] (2.7.27)

Let us estimate \( D = 10^{-4} \text{ cm}^2/\text{sec} \), and \( 2a = 10^{-6} \text{ cm} \), then the time to steady state is \( \frac{(2a)^2}{D} = 10^{-8} \text{ sec} \) and is very short.

Each stationary particle will be hit, hence coagulate with, \( 8\pi D \) a \( n(\infty) \) particles per second. Since all particles are moving, the steady rate of collision (coagulation) must be doubled, i.e., \( 16\pi Dn(\infty) \). As the consequence, the number density of particles must decrease. Each collision reduces the number of particles by 1. Hence

\[ \frac{dn(\infty)}{dt} = -16\pi aDn(\infty)^2 \] (2.7.28)

Thus

\[ \frac{dn(\infty)}{dt} = -16\pi aDn(\infty)^2 \quad \text{where} \quad D = \frac{kT}{6\pi \mu a} \]

or

\[ \frac{dn(\infty)}{n(\infty)^2} = -16\pi aDt \]

which may integrated to

\[- \left[ \frac{1}{n(\infty)} - \frac{1}{n(\infty)(0)} \right] = -16\pi aDT \]

Note that

\[ 16\pi aD = \frac{16\pi a kT}{6\pi \mu a} = \frac{8kT}{3\mu} \]

Finally,

\[ n(\infty)(t) = \frac{n(\infty)(0)}{1 + [16\pi aDn(\infty)(0)t]} = \frac{n(\infty)(0)}{1 + K_n n(\infty)(0)t} \] (2.7.29)
where
\[ K_o = 16\pi aD = \frac{8kT}{3\mu} \] (2.7.30)
is the coagulation constant while
\[ T_{\text{coag}} = \frac{1}{K_\circ n_\infty(0)} \] (2.7.31)
is the coagulation time.

From Fuchs, Table 28, p 291.

<table>
<thead>
<tr>
<th>a (cm)</th>
<th>10^{-7}</th>
<th>10^{-6}</th>
<th>10^{-5}</th>
<th>10^{-4}</th>
<th>10^{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_o \times 10^{10}$ (cm$^3$/sec)</td>
<td>323</td>
<td>34</td>
<td>5.56</td>
<td>3.19</td>
<td>2.98</td>
</tr>
</tbody>
</table>

How long does it take for $n_\infty(t)$ to drop to one-tenth of its initial value?
\[ t = \frac{n_\infty(0) - 1}{K_\circ n_\infty(0)} \] (2.7.32)
where
\[ K = \frac{4kT}{3\mu} \]

It can be estimated that $t_{\text{coag}} \sim 125$ sec, if $2a = 0.1 \mu m$, and $T = 293^\circ K$.

### 2.7.3 Appendix A: Proof of (2.7.19)

\[
\frac{\partial w}{\partial t} = -\frac{r}{2a} \frac{\partial n}{\partial t} - \frac{1}{n_\infty} \frac{\partial n}{\partial r} - \frac{r}{n_\infty} \frac{\partial^2 n}{\partial r^2}
\]

Substituting these results in (2.7.19), we get
\[
\frac{\partial n}{\partial t} = D'(2a)^2 \left( \frac{\partial^2 n}{\partial r^2} + \frac{2}{r} \frac{\partial n}{\partial r} \right) = \frac{D}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial n}{\partial r} \right)
\] (2.7.33)

with
\[ D = D'(2a)^2 \]
2.7.4 Appendix B: Solution of (2.7.19) by the method of similarity

Let us seek a transformation

\[ x = \lambda^a x' \quad t = \lambda^b t' \quad w = \lambda^c w' \]

such that the initial-boundary-value problem retains the same form.

\[
\frac{\partial}{\partial t} \rightarrow \frac{\partial}{\partial t'} \lambda^{-b} \quad \frac{\partial}{\partial x} \rightarrow \frac{\partial}{\partial x'} \lambda^{-a} \\
\frac{\partial w}{\partial t} = D' \frac{\partial^2 w}{\partial x^2} \rightarrow \lambda^{-b+c} \left( \frac{\partial w'}{\partial t'} \right) = D' \lambda^{-2a+c} \left( \frac{\partial^2 w'}{\partial x'^2} \right)
\]

For invariance we require, \(-2a = -b, \ a = b/2\). Clearly

\[
\xi = \frac{x}{2\sqrt{D't}} = \frac{\lambda^{b/2}x}{2\sqrt{D'\lambda^b t'}} = \frac{x'}{2\sqrt{D't'}}
\]

satisfies the requirement. From the boundary conditions,

\[ x'\lambda^a = 0 \quad \lambda^c w' = 1 \]

which requires that

\[ c = 0 \quad (2.7.34) \]

The initial condition as well as the boundary condition at \( x'\lambda^a = \infty \) are trivially satisfied.

The similarity solution is

\[ w = w(\xi) = w \left( \frac{x}{2\sqrt{D't}} \right) \]

Some algebra:

\[
\frac{\partial w}{\partial t} = w \frac{\partial}{\partial t} \xi = w' \frac{x}{2\sqrt{D'}} \left( -\frac{1}{2t^{2/3}} \right) = -\frac{w'\xi}{2t} \\
D' \frac{\partial^2 w}{\partial x^2} = D' \frac{w''}{4D't} = \frac{w''}{4t'}
\]

hence

\[ -\frac{w'\xi}{2} = \frac{w''}{4} \]

or

\[ \frac{w''}{w'} = -2\xi \]

\[ \frac{d \log w'}{d\xi} = -2\xi \]

Integrating

\[ \log(w') = -\xi^2 + \text{Const}, \]
and
\[ w' = ce^{-\xi^2} = \frac{dw}{d\xi} \]
Thus
\[ w = -c \int_\xi^\infty e^{-z^2} \, dz \]
so that \( w(\infty) = 0 \). Since
\[ w = 1, \; \xi = 0 \]
\[ 1 = -c \int_0^\infty e^{-z^2} \, dz \]
The integral is \( \sqrt{\pi}/2 \). Hence
\[ c = -\sqrt{\frac{2}{\pi}} \]
\[ w = \sqrt{\frac{2}{\pi}} \int_\xi^\infty e^{-z^2} \, dz = \sqrt{\frac{2}{\pi}} \left[ \int_0^\infty - \int_0^\xi e^{-z^2} \, dz \right] \]
\[ = 1 - \sqrt{\frac{2}{\pi}} \int_0^\frac{\xi}{\sqrt{2\pi}} e^{-z^2} \, dz \]