Atmospheric Aerosols

Lecture 15

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Particle Diffusion

The movement of particles due to Brownian motion can also be viewed as a macroscopic diffusion process.

Let us discuss the connection between these two different perspectives on the same process.

If $N(x, y, z, t)$ is the number concentration of particles undergoing Brownian motion, then we can define a Brownian diffusivity D, such that

$$\boxed{\frac{\partial N(x,y,z,t)}{\partial t} = D\nabla^2 N(x,y,z,t)} \quad *$$

If we relate the Brownian diffusivity D to the mean square displacements given by

$$\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = \frac{2kTC_c}{3\pi\mu D_p} t$$

then *can provide a convenient framework for describing aerosol diffusion.

To do so, let us repeat the experiment above, namely, let us follow the Brownian diffusion of N_0 particles placed at t = 0 at the y-z plane.

To simplify our discussion we assume that N does not depend on y or z.

Multiplying

$$\frac{\partial N(x,y,z,t)}{\partial t} = D\nabla^2 N(x,y,z,t)$$

by x^2 and integrating the resulting equation over x from -∞ to ∞, we get

$$\int_{-\infty}^{+\infty} x^2 \frac{\partial N}{\partial t} dx = \int_{-\infty}^{+\infty} x^2 D \frac{\partial^2 N}{\partial x^2} dx$$

The LHS can also be written as

$$\int_{-\infty}^{+\infty} x^2 \frac{\partial N}{\partial t} dx = N_0 \frac{\partial \langle x^2 \rangle}{\partial t}$$

and the RHS of equation as

$$\int_{-\infty}^{+\infty} x^2 D \frac{\partial^2 N}{\partial x^2} dx = 2DN_0$$

Combining equations results in $$\frac{\partial\langle x^2\rangle}{\partial t} = 2D$$

or after integration $$\langle x^2\rangle = 2Dt$$

We can now equate this result for $\langle x^2\rangle$ with that of $\langle x^2\rangle = \langle y^2\rangle = \langle z^2\rangle = \frac{2kTC_c}{3\pi\mu D_p}t$ to obtain an explicit relation for D

$$\boxed{D = \frac{kTC_c}{3\pi\,\mu D_p}}$$

which, without the correction factor Cc, is the Stokes-Einstein-Sutherland relation.

Note that for particles that are larger than the mean free path of air, $Cc \simeq 1$ and their diffusivity varies as D_p^{-1}

As expected, larger particles diffuse more slowly.

In the other extreme,

When $D_p \ll \lambda$ $C_c = 1 + 1.657(2\lambda / D_p)$

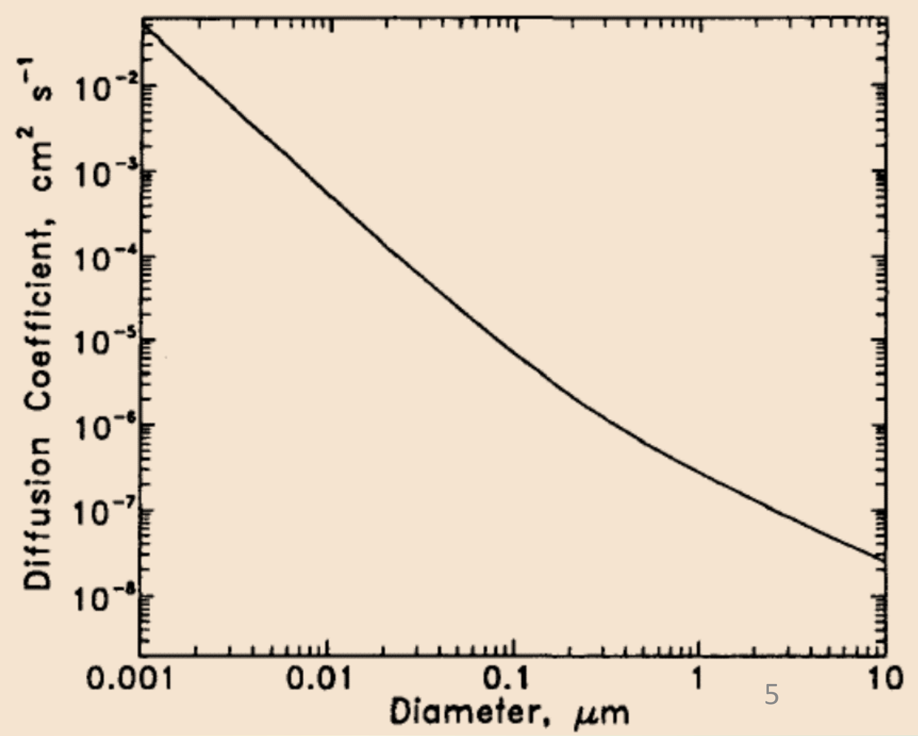
and D can be approximated by $2(1.657)\lambda kT / 3\pi\mu D_p^2$

Therefore, in the free molecule regime, D varies as D_p^{-2}

Diffusion coefficients for particles ranging from 0.001 to 10.0 μm diameter in air at 20°C are shown in Figure.

The change from D_p^{-2} dependence is indicated by the change of slope of the line of D versus D_p.

Aerosol diffusion coefficients in air at 20°C as a function of diameter.



$$t = 1s,\ R = 1\mu m \rightarrow d = 4\mu m$$

$$t = 1s,\ R = 0.1\mu m \rightarrow d = 20\mu m$$

$$t = 1s,\ R = 0.01\mu m \rightarrow d = 1000$$

Aerosol Mobility and Drift Velocity

In the development of Brownian motion up to this point, we have assumed that the only external force acting on the particle is the fluctuating Brownian force $m_p \mathbf{a}$.

If we generalize $m_p \frac{d\mathbf{v}}{dt} = -\frac{3\pi \mu D_p}{C_c}\mathbf{v} + m_p \mathbf{a}$ to include an external force F_{ext}, we get

$$m_p \frac{d\mathbf{v}}{dt} = \mathbf{F}_{\text{ext}} - \frac{m_p}{\tau}\mathbf{v} + m_p \mathbf{a}$$

As before, assuming that we are interested in times for which $t \gg \tau$, and taking mean values, the approximate force balance is at steady state:

$$0 = \mathbf{F}_{\text{ext}} - \frac{m_p}{\tau}\langle \mathbf{v} \rangle$$

The ensemble mean velocity <v> is identified as the drift velocity $\mathbf{v}_{\text{drift}}$, where $\mathbf{v}_{\text{drift}} = \frac{\mathbf{F}_{\text{ext}}\tau}{m_p}$

The drift velocity is the mean velocity experienced by the particle population due to the presence of the external force F_{ext}.

For example, in the case where the external force is simply gravity, $\mathbf{F}_{ext} = m_p \mathbf{g}$, and the drift velocity (or settling velocity) will simply be $\vec{V}_{drift} = \vec{g}\tau$

When the external force is electrical, the drift velocity is the electrical migration velocity

$$\mathbf{v}_e = \frac{qC_c}{3\pi\mu D_p}\mathbf{E}$$

Therefore our analysis presented in the previous sections is still valid even after the introduction of Brownian motion.

It is customary to define the generalized particle *mobility B* by

$$\mathbf{v}_{\text{drift}} = B\mathbf{F}_{\text{ext}}$$

Therefore the particle mobility is given by $$B = \frac{\tau}{m_p} = \frac{C_c}{3\pi \mu D_p} \quad *$$

The mobility can also be viewed as the drift velocity that would be attained by the particles under unit external force.

Recall $$B_e = \frac{qC_c}{3\pi \mu D_p}$$ which is the mobility in the special case of an electrical force.

By definition, the electrical mobility is related to the particle mobility by $B_e = qB$, where q is the particle charge.

A particle with zero charge, has a mobility given by * and zero electrical mobility.

Finally, the Brownian diffusivity can be written in terms of the mobility by

$$D = BkT$$

a result known as the *Einstein relation.*

Gravitational Settling and the Vertical Distribution of Aerosol Particles

Let us consider the simultaneous Brownian diffusion and gravitational settling of particles above a surface at $z = 0$.

At $t = 0$, a uniform concentration $N_0 = 1000\ cm^{-3}$ of particles is assumed to exist for $z > 0$ and at all times the concentration of particles right at the surface is zero as a result of their removal at the surface.

1. What is the particle concentration as a function of height and time, N(z,t)?
2. What is the removal rate of particles at the surface?

The concentration distribution of aerosol particles in a stagnant fluid in which the particles are subject to Brownian motion and in which there is a velocity *vt* in the -*z* direction is described by

$$\frac{\partial N}{\partial t} - v_t \frac{\partial N}{\partial z} = D \frac{\partial^2 N}{\partial z^2}$$

subject to the conditions

$$\begin{aligned} N(z,0) &= N_0 \\ N(0,t) &= 0 \\ N(z,t) &= N_0 \quad z \to \infty \end{aligned}$$

where the z coordinate is taken as vertically upward.

The solution of these equations for the vertical profile of the number distribution $N(z, t)$ is

$$N(z,t) = \frac{N_0}{2}\left[1 + \mathrm{erf}\left(\frac{z+v_t t}{2\sqrt{Dt}}\right) - \exp\left(-\frac{v_t z}{D}\right)\mathrm{erfc}\left(\frac{z-v_t t}{2\sqrt{Dt}}\right)\right]$$

We can calculate the deposition rate of particles on the z = 0 surface from the expression for the flux of particles at z = 0,

$$J = D\left(\frac{\partial N}{\partial z}\right)_{z=0} + v_t N(0,t)$$

$N(0, t) = 0$

$$J = N_0\left\{\frac{v_t}{2}\left[1 - \mathrm{erf}\left(-\frac{v_t t}{2\sqrt{Dt}}\right)\right] + \left(\frac{D}{\pi t}\right)^{1/2}\exp\left(-\frac{v_t^2 t}{4D}\right)\right\}$$

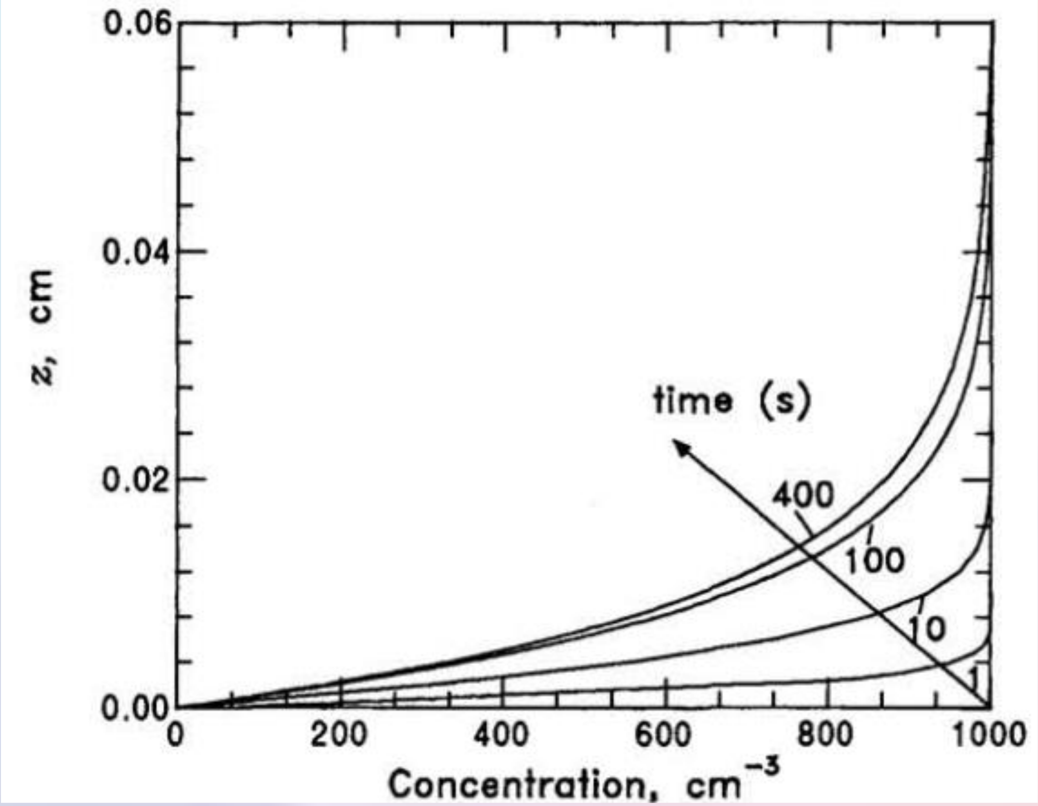
According this equation, there is an infinite removal flux at t=0, because of our artificial specification of an infinite concentration gradient at z=t=0.

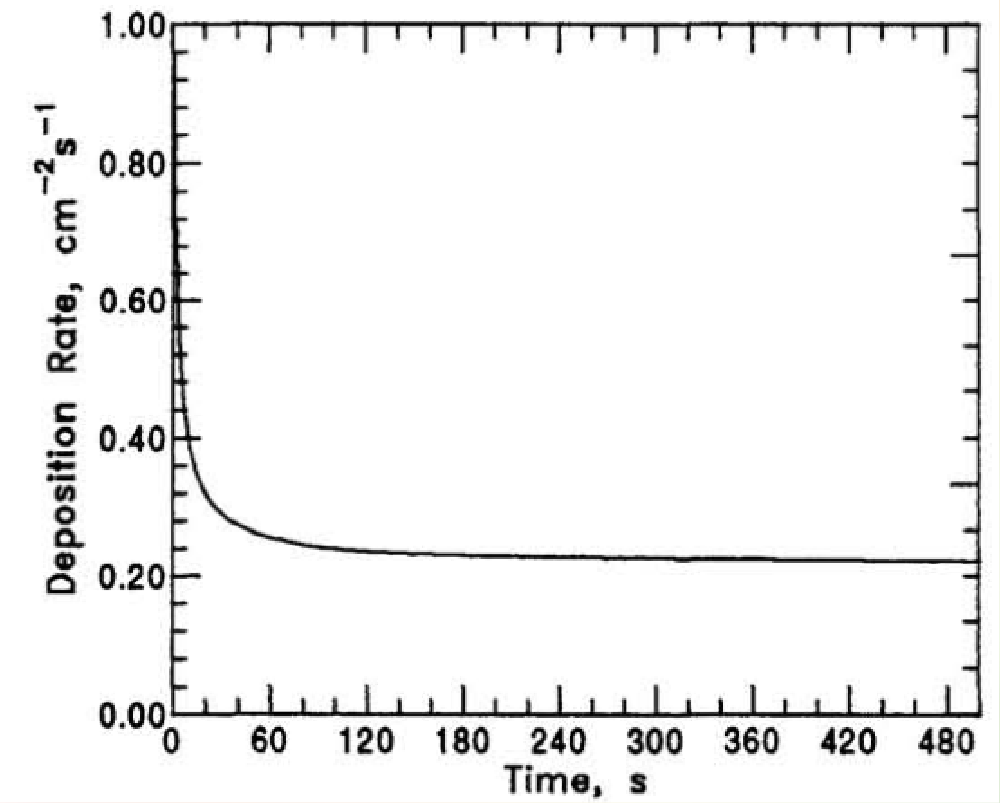
We can identify a characteristic time τ_{ds} for the organization $\tau_{ds} = \frac{4D}{v_t^2}$

and observe the following limiting behavior for the particle flux at short and long times:

$$J(t) = N_0\left[\left(\frac{D}{\pi t}\right)^{1/2} + \frac{v_t}{2}\right] \qquad t \ll \tau_{ds}$$

$$J(t) = N_0 v_t \qquad t \gg \tau_{ds}$$



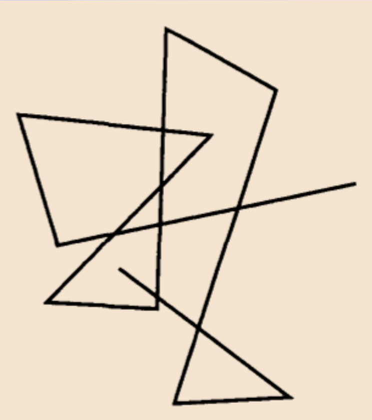


Removal rate of particles as a function of time for the conditions of Figure 9.9

Mean Free Path of an Aerosol Particle

The concept of mean free path is an obvious one for gas molecules. In the Brownian motion of an aerosol particle there is not an obvious length that can be identified as a mean free path.

This is depicted in Figure showing plane projections of the paths followed by an air molecule and an aerosol particle of radius roughly equal to 1 μm.



A two-dimensional projection of the path of (a) an air molecule and (b) the center of a 1-μm particle. Also shown is the apparent mean free path of the particle.

The particle motion can be characterized by a mean thermal speed $\bar{c}_p$:

$$\bar{c}_p = \left(\frac{8kT}{\pi m_p}\right)^{1/2}$$

To obtain the mean free path λ_p, we recall that in Section 9.1, using kinetic theory, we connected the mean free path of a gas to measured macroscopic transport properties of the gas such as its binary diffusivity.

A similar procedure can be used to obtain a particle mean free path λ_p from the Brownian diffusion coefficient and an appropriate kinetic theory expression for the diffusion flux.

Following an argument identical to that in Section 9.1, diffusion of aerosol particles can be viewed as a mean free path phenomenon so that

$$D = \frac{1}{2}\bar{c}_p\lambda_p$$

and the mean free path λ_p combining

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

$$\bar{c}_p = \left(\frac{8kT}{\pi m_p}\right)^{1/2}$$

$$D = \frac{1}{2}\bar{c}_p\lambda_p$$

$$\lambda_p = \frac{C_c}{6\mu}\sqrt{\frac{\rho kTD_p}{3}}$$

Certain quantities associated with the Brownian motion and the dynamics of single aerosol particles are shown as a function of particle size in Table 9.5.

All tabulated quantities in Table 9.5 depend strongly on particle size with the exception of the apparent mean free path *λp*, which is of the same order of magnitude right down to molecular sizes, with atmospheric values $\lambda_p \simeq 10\text{-}60$ nm.

TABLE 9.5 Characteristic Quantities in Aerosol Brownian Motion

D_p, μm	D, cm^2 s^{-1}	$\bar{c}_p$, cm s^{-1}	τ, s	λ_p (μm)
0.002	1.28×10^{-2}	4965	1.33×10^{-9}	6.59×10^{-2}
0.004	3.23×10^{-3}	1760	2.67×10^{-9}	4.68×10^{-2}
0.01	5.24×10^{-4}	444	6.76×10^{-9}	3.00×10^{-2}
0.02	1.30×10^{-4}	157	1.40×10^{-8}	2.20×10^{-2}
0.04	3.59×10^{-5}	55.5	2.98×10^{-8}	1.64×10^{-2}
0.1	6.82×10^{-6}	14.0	9.20×10^{-8}	1.24×10^{-2}
0.2	2.21×10^{-6}	4.96	2.28×10^{-7}	1.13×10^{-2}
0.4	8.32×10^{-7}	1.76	6.87×10^{-7}	1.21×10^{-2}
1.0	2.74×10^{-7}	0.444	3.60×10^{-6}	1.53×10^{-2}
2.0	1.27×10^{-7}	0.157	1.31×10^{-5}	2.06×10^{-2}
4.0	6.1×10^{-8}	5.55×10^{-2}	5.03×10^{-5}	2.8×10^{-2}
10.0	2.38×10^{-8}	1.40×10^{-2}	3.14×10^{-4}	4.32×10^{-2}
20.0	1.38×10^{-8}	4.96×10^{-3}	1.23×10^{-3}	6.08×10^{-2}

Characteristic Quantities in Aerosol Brownian Motion