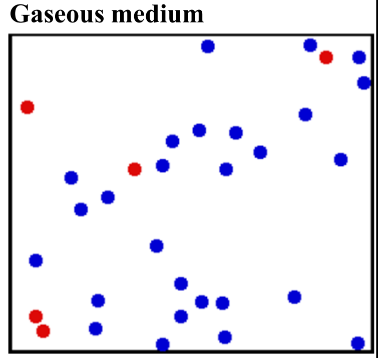
Lectures 6-7: Dynamics of single aerosol particles

Some important parameters



Under room T (20 ^{o}C) and P (1 atm):

1. Number of molecules per cm^3 air:

2. Mean diameter of air molecules:

3. Mean distance between air molecules:

4. Mean velocity of air molecules:

5. Mean free path of air molecules:

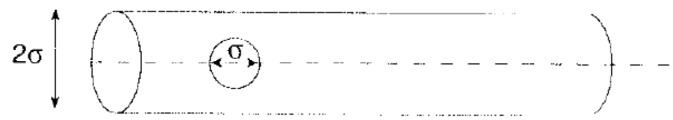


Figure 3.3 Schematic of tunnel to estimate mean free path.

Mean free path of a <u>pure</u> gas:

Associated with relative velocity of molecules

Collision rate of B molecules, $Z_{BB} = \sqrt{2}\pi\sigma_B^2\bar{c}_B N_B$

$$\lambda_{BB} = \frac{\bar{c}_B}{Z_{BB}}$$

$$\lambda_{BB} = \frac{1}{\sqrt{2}\pi\sigma_B^2 N_B}$$

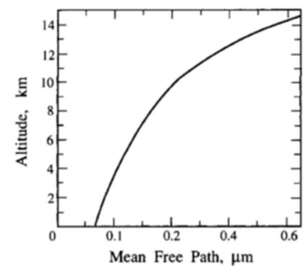


FIGURE 9.3 Mean free path of air as a function of altitude for the standard U.S. atmosphere (Hinds 1999).

Mean free path of molecule A in a binary mixture of A and B:

$$\lambda_{AB} = \frac{1}{\sqrt{2}\pi N_A\sigma_A^2 + \pi(1+z)^{1/2}N_B\sigma_{AB}^2}$$

$$z = m_A/m_B = M_A/M_B$$

Mean free path of a gas cannot be measured directly. However, the mean free path can be theoretically related to measurable gas microscopic properties, such as viscosity, thermal conductivity, or molecular diffusivity.

Diffusion coefficient and mean free path

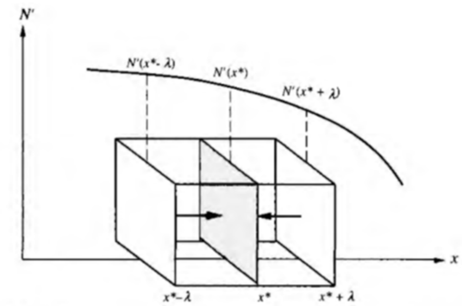


FIGURE 9.4 Control surfaces for molecular diffusion as envisioned in the elementary kinetic theory of gases.

$$J = -D(\partial N'/\partial x)$$

The net left-to-right flux of painted molecules through the plane of x^* is (in molecules $\mathrm{cm}^{-2}\ \mathrm{s}^{-1}$)

$$J = \frac{1}{4}\bar{c}[N'(x^* - \lambda) - N'(x^* + \lambda)] \qquad (9.17)$$

Expanding both $N'(x^* - \lambda)$ and $N'(x^* + \lambda)$ in Taylor series about x^*, we obtain

$$J = -\frac{1}{2}\bar{c}\lambda\left(\frac{\partial N'}{\partial x}\right)_{x=x^*} \qquad (9.18)$$

$$\lambda = 2\frac{D}{\bar{c}}$$

Diffusion coefficient and mean free path

$$\lambda_{AB} = \frac{32}{3\pi(1+z)}\frac{D_{AB}}{\bar{c}_A} \qquad (9.13)$$

$$\begin{aligned} \lambda_{AB} &= 3.397\frac{D_{AB}}{\bar{c}_A} && z \ll 1 \\ &= 1.7\frac{D_{AB}}{\bar{c}_A} && z = 1 \qquad (9.14) \\ &= \frac{3.397}{z}\frac{D_{AB}}{\bar{c}_A} && z \gg 1 \end{aligned}$$

binary diffusivity of A in B, D_{AB}

$z = M_A/M_B$

Knudsen Number and three regimes of gas-particle interactions

Knudsen number:

$$Kn = \frac{2\lambda}{D_p} = \frac{\lambda}{R_p}$$

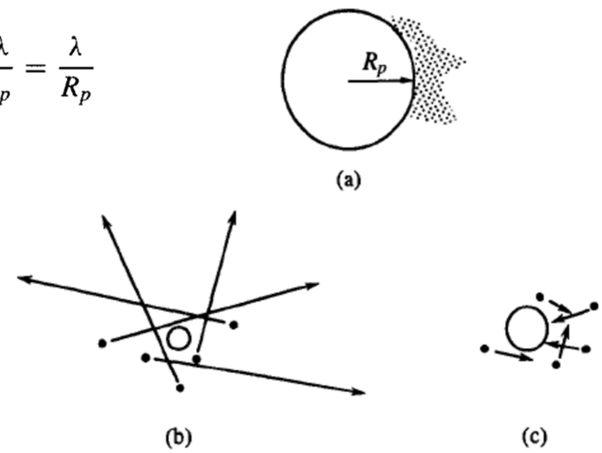
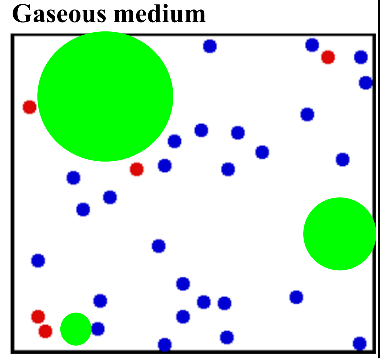


FIGURE 9.1 Schematic of the three regimes of suspending fluid–particle interactions: (a) continuum regime ($\mathrm{Kn} \to 0$), (b) free molecule (kinetic) regime ($\mathrm{Kn} \to \infty$), and (c) transition regime ($\mathrm{Kn} \sim 1$).

What about particles?

Gaseous medium



Under room T (20 °C) and P (1 atm):

1. **Number of particles in per cm^3 air:**

2. **Mean diameter of particles:**

3. **Mean distance between particles:**

4. **Mean velocity of particles:**

5. **Mean free path of particles:**

Mean Free Path of an Aerosol Particle

Gas molecules

$$\bar{c}_B = \left(\frac{8RT}{\pi M_B}\right)^{1/2}$$

$$\lambda = 2\frac{D}{\bar{c}}$$

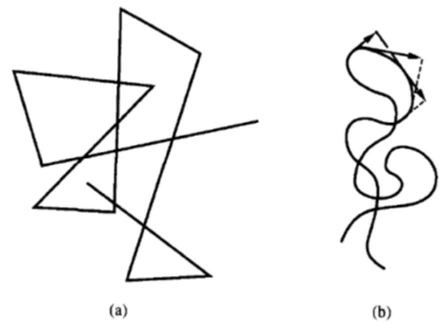


FIGURE 9.11 A two-dimensional projection of the path of (a) an air molecule and (b) the center of a 1-μm particle. Also shown is the apparent mean free path of the particle.

Particles

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

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

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

$$\lambda_p = \frac{C_c}{6\mu}\sqrt{\frac{\rho k T D_p}{3}}$$

C_c*: slip correction factor*
*(*noncontinuum effects)

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}

The drag on a single particle : **Stokes' Law**

We start our discussion of the dynamical behavior of aerosol particles by considering the motion of a particle in a viscous fluid. As the particle is moving with a velocity u_∞, there is a drag force exerted by the fluid on the particle equal to F_{drag}. This drag force will always be present as long as the particle is not moving in a vacuum.To calculate F_{drag}, one must solve the equations of fluid motion to determine the velocity and pressure fields around the particle.

The velocity and pressure in an incompressible Newtonian fluid are governed by the equation of continuity (a mass balance)

$$\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} = 0 \tag{9.20}$$

and the Navier–Stokes equations (a momentum balance) (Bird et al. 1960), the x component of which is

$$\rho\left(\frac{\partial u_x}{\partial t} + u_x\frac{\partial u_x}{\partial x} + u_y\frac{\partial u_x}{\partial y} + u_z\frac{\partial u_x}{\partial z}\right) = -\frac{\partial p}{\partial x} + \mu\left(\frac{\partial^2 u_x}{\partial x^2} + \frac{\partial^2 u_x}{\partial y^2} + \frac{\partial^2 u_x}{\partial z^2}\right) + \rho g_x \tag{9.21}$$

where $\mathbf{u} = (u_x, u_y, u_z)$ is the velocity field, $p(x, y, z)$ is the pressure field, μ is the viscosity of the fluid, and g_x is the component of the gravity force in the x direction. To simplify our discussion let us assume without loss of generality that $g_x = 0$. The y and z components of the Navier–Stokes equations are similar to (9.21).

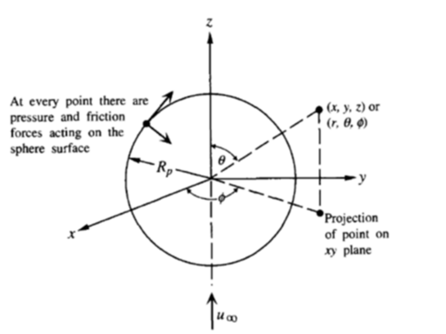
The drag on a single particle : **Stokes' Law**

Reynolds number

$$\boldsymbol{Re} = \frac{\text{Inertial force}}{\text{Viscous force}} = \frac{\rho u_\infty D_p}{\mu}$$

Re<<1 (inertial term negligible) and Kn<<1 (continuous regime):

$$p = p_0 - \frac{3}{2}\frac{\mu u_\infty R_p}{r^2}\cos\theta$$



$$F_{\text{drag}} = 3\pi\mu D_p u_\infty$$

FIGURE 9.5 Coordinate system used in describing the flow of a fluid about a rigid sphere.

TABLE 9.2 Reynolds Number for Particles in Air Falling at Their Terminal Velocities at 298 K

Diameter, μm	Re
0.1	7×10^{-9}
1	2.8×10^{-6}
10	2.5×10^{-3}
20	0.02
60	0.4
100	2
300	20

For particles smaller than 20 μm (virtually all atmospheric aerosols) Stokes' law is an accurate formula for the drag exerted by the air

Corrections to Stokes' Law: The Drag Coefficient

Stokes' law has been derived for $\mathrm{Re} \ll 1$, neglecting the inertial terms in the equation of motion. If $\mathrm{Re} = 1$, the drag predicted by Stokes' law is 13% low, due to the errors introduced by the assumption that inertial terms are negligible. To account for these terms, the drag force is usually expressed in terms of an empirical *drag coefficient* C_D as

$$F_{\mathrm{drag}} = \frac{1}{2} C_D A_p \rho u_\infty^2 \tag{9.30}$$

where A_p is the projected area of the body normal to the flow. Thus for a spherical particle of diameter D_p

$$\boxed{F_{\mathrm{drag}} = \frac{1}{8} \pi C_D \rho D_p^2 u_\infty^2 \qquad (9.31)}$$

$$\begin{aligned} C_D &= \frac{24}{\mathrm{Re}} \qquad \mathrm{Re} \lesssim 1 \quad \text{(Stokes' law)} \\ C_D &= 18.5\ \mathrm{Re}^{-0.6} \qquad \mathrm{Re} \gtrsim 1 \end{aligned} \tag{9.32}$$

Stokes' Law and Noncontinuum Effects: Slip Correction Factor

Stokes' law is based on the solution of equations of continuum fluid mechanics and therefore is applicable to the limit Kn $\to$ 0. The nonslip condition used as a boundary condition is not applicable for high Kn values. When the particle diameter D_p approaches the same magnitude as the mean free path λ of the suspending fluid (e.g., air), the drag force exerted by the fluid is smaller than that predicted by Stokes' law. To account for noncontinuum effects that become important as D_p becomes smaller and smaller, the *slip correction factor* C_c is introduced into Stokes' law, written now in terms of particle diameter D_p as

$$F_{\text{drag}} = \frac{3\pi \mu u_\infty D_p}{C_c} \qquad (9.33)$$

where

$$C_c = 1 + \frac{2\lambda}{D_p}\left[1.257 + 0.4\exp\left(-\frac{1.1D_p}{2\lambda}\right)\right] \qquad (9.34)$$

TABLE 9.3 Slip Correction Factor C_c for Spherical Particles in Air at 298 K and 1 atm

D_p, μm	C_c
0.001	216
0.002	108
0.005	43.6
0.01	22.2
0.02	11.4
0.05	4.95
0.1	2.85
0.2	1.865
0.5	1.326
1.0	1.164
2.0	1.082
5.0	1.032
10.0	1.016
20.0	1.008
50.0	1.003
100.0	1.0016

Motion of particle in gas medium

$$m_p \frac{d\mathbf{v}}{dt} = \sum_i \mathbf{F}_i$$

Motion of particle in gas medium

GRAVITATIONAL SETTLING OF AN AEROSOL PARTICLE

in a fluid with velocity **u**

$$m_p \frac{d\mathbf{v}}{dt} = m_p\mathbf{g} + \frac{3\pi\mu D_p}{C_c}(\mathbf{u} - \mathbf{v}) \qquad \text{for } Re < 0.1$$

$$\tau \frac{d\mathbf{v}}{dt} = \tau\mathbf{g} + \mathbf{u} - \mathbf{v}$$

$$\tau = \frac{m_p C_c}{3\pi\mu D_p}$$

TABLE 9.4 Characteristic Time Required for Reaching Terminal Settling Velocity

D_p, μm	τ, s
0.05	4×10^{-8}
0.1	9.2×10^{-8}
0.5	1×10^{-6}
1.0	3.6×10^{-6}
5.0	7.9×10^{-5}
10.0	3.14×10^{-4}
50.0	7.7×10^{-3}

is the characteristic *relaxation time* of the particle.

Motion of particle in gas medium

Let us consider the case of a particle in a quiescent fluid ($\mathbf{u} = \mathbf{0}$) starting with zero velocity and let us take the z axis as positive downward. Then the equation of motion becomes

$$\tau \frac{dv_z}{dt} = \tau g - v_z \quad v_z(0) = 0 \tag{9.39}$$

and its solution is

$$v_z(t) = \tau g[1 - \exp(-t/\tau)] \tag{9.40}$$

For $t \gg \tau$, the particle attains a characterstic velocity, called its *terminal settling velocity* $v_t = \tau g$ or

$$v_t = \frac{m_p C_c g}{3\pi\mu D_p} \tag{9.41}$$

For a spherical particle of density ρ_p in a fluid of density ρ, $m_p = (\pi/6)D_p^3(\rho_p - \rho)$, where the factor $(\rho_p - \rho)$ is needed to account for both gravity and buoyancy. However, since generally $\rho_p \gg \rho, m_p = (\pi/6)D_p^3\rho_p$ and (9.41) can be rewritten in the more convenient form:

$$\boxed{v_t = \frac{1}{18}\frac{D_p^2 \rho_p g C_c}{\mu} \tag{9.42}}$$

$$C_c = 1 + \frac{2\lambda}{D_p}\left[1.257 + 0.4\exp\left(-\frac{1.1D_p}{2\lambda}\right)\right]$$

The viscosity of air (μ) depends mostly on the temperature. At 15 °C, the viscosity of air is 1.81×10^{-5} kg/(m·s) , 18.1 μPa·s or 1.81×10^{-5} Pa·s .

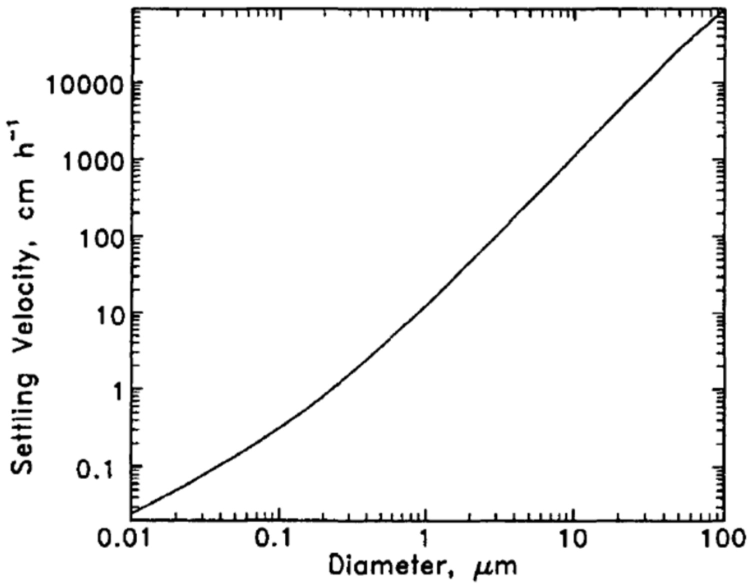


FIGURE 9.6 Settling velocity of particles in air at 298 K as a function of their diameter.

Motion of a Charged Particle in an Electric Field

$$m_p \frac{d\mathbf{v}}{dt} = \frac{3\pi \mu D_p}{C_c}(\mathbf{u} - \mathbf{v}) + q\mathbf{E}$$

At steady state in the absence of a background fluid velocity, the particle velocity is such that the electrical force is balanced by the drag force and

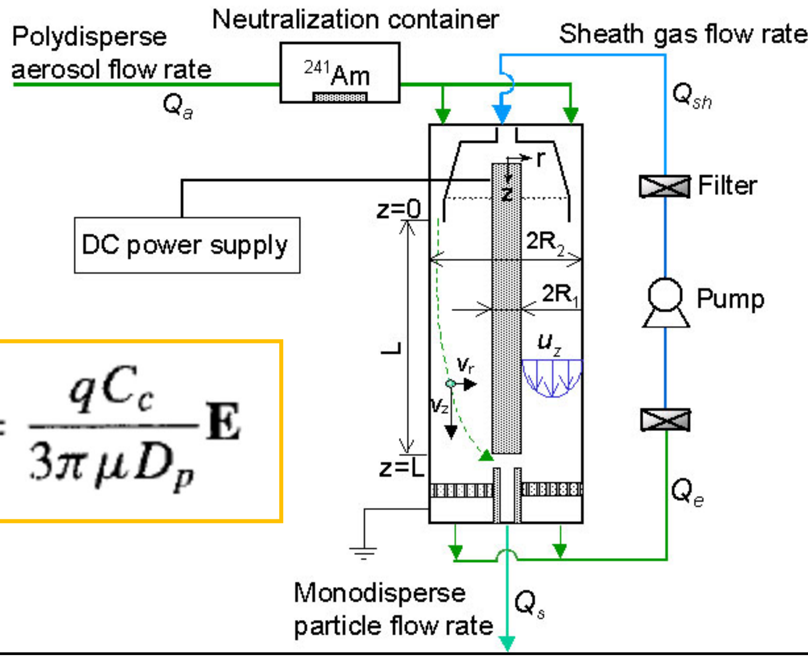
$$\mathbf{v}_e = \frac{qC_c}{3\pi \mu D_p}\mathbf{E}$$

where $\mathbf{v}_e$ is termed the *electrical migration velocity*.

Defining the electrical mobility of a charged particle B_e as $$B_e = \frac{qC_c}{3\pi \mu D_p}$$

$$\mathbf{v}_e = B_e\mathbf{E}$$

Differential mobility analyzers (DMAs)



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

BROWNIAN MOTION OF AEROSOL PARTICLES

Langevin equation

$$m_p \frac{d\mathbf{v}}{dt} = -\frac{3\pi\mu D_p}{C_c}\mathbf{v} + m_p\mathbf{a}$$

$$\frac{d\mathbf{v}}{dt} = -\frac{1}{\tau}\mathbf{v} + \mathbf{a}$$

The random acceleration **a** is a discontinuous term, since it represents the random force exerted by the suspending fluid molecules that imparts an irregular, jerky motion to the particle.

dot product
$$\mathbf{r}\cdot\frac{d\mathbf{v}}{dt} = -\frac{1}{\tau}\mathbf{r}\cdot\mathbf{v} + \mathbf{r}\cdot\mathbf{a}$$

ensemble averaging
$$<\mathbf{r}\cdot\frac{d\mathbf{v}}{dt}> = -\frac{1}{\tau}<\mathbf{r}\cdot\mathbf{v}> + <\mathbf{r}\cdot\mathbf{a}> \; = -\frac{1}{\tau}<\mathbf{r}\cdot\mathbf{v}>$$

$$\frac{d}{dt}<\mathbf{r}\cdot\mathbf{v}> = <\mathbf{r}\cdot\frac{d\mathbf{v}}{dt}> + <\frac{d\mathbf{r}}{dt}\cdot\mathbf{v}>$$

$$<\mathbf{r}\cdot\frac{d\mathbf{v}}{dt}> = \frac{d}{dt}<\mathbf{r}\cdot\mathbf{v}> - <v^2>$$

$$\frac{d}{dt}<\mathbf{r}\cdot\mathbf{v}> = -\frac{1}{\tau}<\mathbf{r}\cdot\mathbf{v}> + <v^2> = -\frac{1}{\tau}<\mathbf{r}\cdot\mathbf{v}> + \frac{3kT}{m_p}$$

$$< \mathbf{r}\cdot\mathbf{v} > = \frac{3kT\tau}{m_p} + c\exp(-t/\tau)$$

$$< \mathbf{r}\cdot\mathbf{v} > = < \mathbf{r}\cdot\frac{d\mathbf{r}}{dt} > = \frac{1}{2}\frac{d}{dt} < r^2 >$$

$$\frac{1}{2}\frac{d}{dt} < r^2 > = \frac{3kT\tau}{m_p} + c\exp(-t/\tau)$$

for $t \gg \tau$, $\quad \frac{1}{2}\frac{d}{dt} < r^2 > = \frac{3kT\tau}{m_p} \qquad < r^2 > = \frac{6kT\tau}{m_p}t = \frac{2kTC_c t}{\pi\mu D_p}$

$< x^2 > = < y^2 > = < z^2 > = \frac{1}{3} < r^2 >. \qquad < x^2 > = < y^2 > = < z^2 > = \frac{2kTC_c}{3\pi\mu D_p}t$

This result, first derived by Einstein by a different route, has been confirmed experimentally.

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

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

$$\frac{\partial < x^2 >}{\partial t} = 2D$$

$$< x^2 > = 2Dt \qquad \boxed{< x^2 > = < y^2 > = < z^2 > = \frac{2kTC_c}{3\pi\mu D_p}t}$$

Particle diffusion coefficient **Stokes-Einstein-Sutherland relation**

$$D = \frac{kTC_c}{3\pi\mu D_p} \qquad C_c = 1 + \frac{2\lambda}{D_p}\left[1.257 + 0.4\exp\left(-\frac{1.1D_p}{2\lambda}\right)\right]$$

Kn <<1, $D \propto$??; Kn >>1, $D \propto$??;

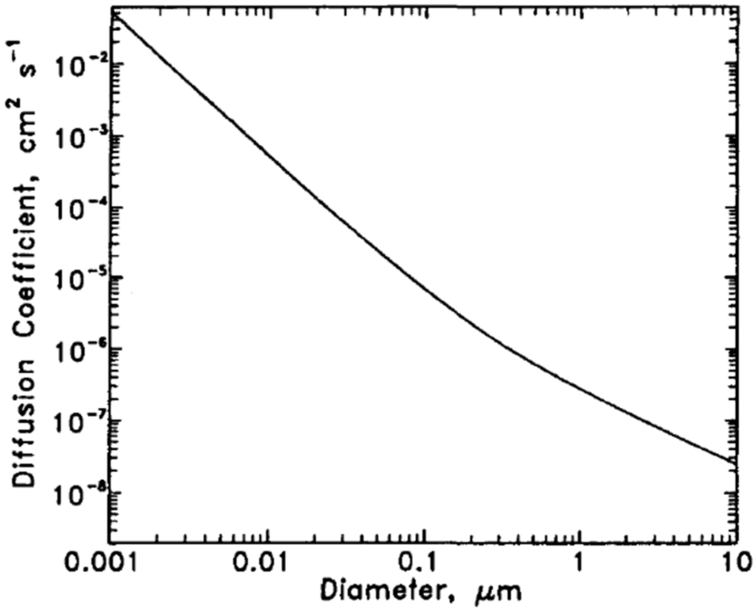


FIGURE 9.8 Aerosol diffusion coefficients in air at 20°C as a function of diameter.

Aerosol Mobility and Drift Velocity

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

at steady state

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

The ensemble mean velocity $< \mathbf{v} >$ is identified as the *drift velocity* $\mathbf{v}_{\text{drift}}$, where

$$\mathbf{v}_{\text{drift}} = \frac{\mathbf{F}_{\text{ext}}\tau}{m_p}$$

define the generalized particle *mobility* B by

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

$$B = \frac{\tau}{m_p} = \frac{C_c}{3\pi\mu D_p}$$

$D = BkT$ known as the *Einstein relation.*