Lecture 12: Mass transport to or from atmospheric particles : Condensation and Evaporation

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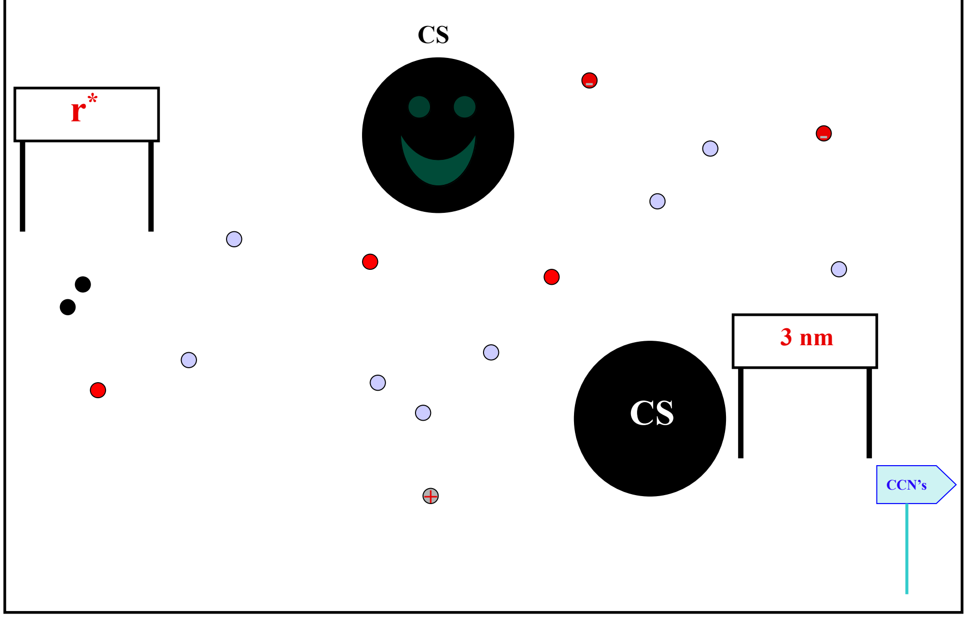

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Nucleation and growth events

in the boundary atmosphere

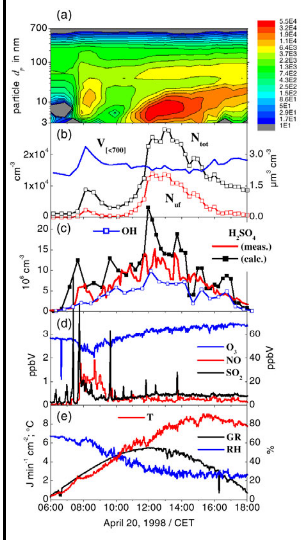

Figure 1. Time evolution of aerosol, gas phase and meteorological parameters at Hohenpeissenberg on April 20, 1998. (a) Particle size distribution $dN/d\log d_p$ in cm^{-3}. (b) Total particle concentration N_{tot} (3–700 nm), UF particle concentration N_{uf} (3–11 nm), and particle volume < 700 nm in $\mu m^3 \cdot cm^{-3}$ (assuming spherical particles). (c) Measured H_2SO_4 and OH concentrations, and $[H_2SO_4]$ derived from steady-state calculation. (d) NO, SO_2 (left axis), and O_3 (right axis). (e) Dry temperature T, RH, and global radiation "GR".

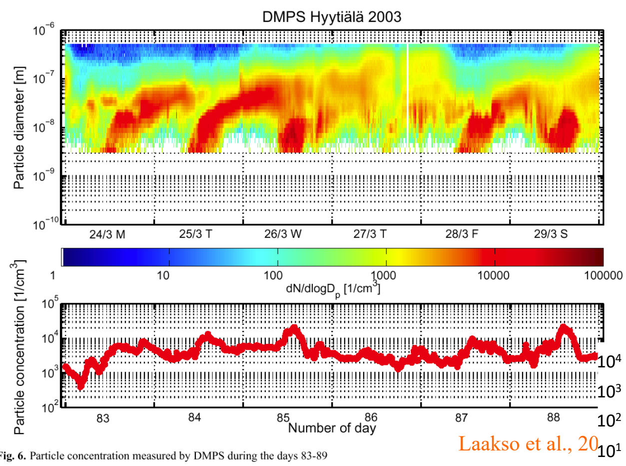

Fig. 6. Particle concentration measured by DMPS during the days 83-89

Laakso et al., 20

Birmili et al., 2000

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Mass transfer: Diffusion flux

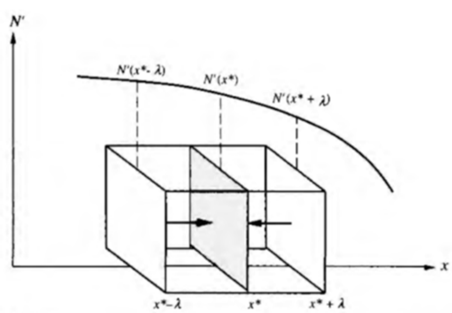

FIGURE 9.4 Control surfaces for molecular diffusion as envisioned in the elementary kinetic theory of gases.

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

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Knudsen Number and three regimes of gas-particle interactions

Knudsen number:

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

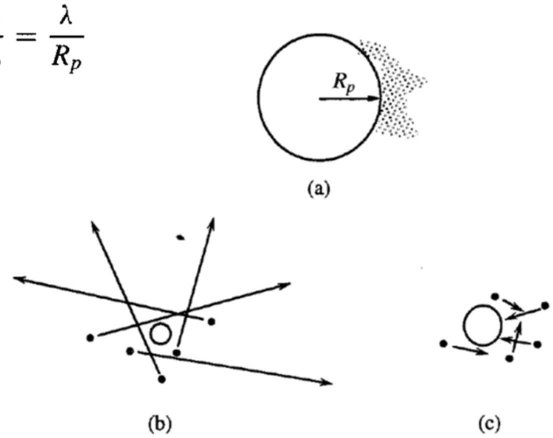

FIGURE 8.1 Schematic of the three regimes of suspending fluid–particle interactions: (a) continuum regime ($Kn \to 0$), (b) free molecule (kinetic) regime ($Kn \to \infty$), and (c) transition regime ($Kn \sim 1$).

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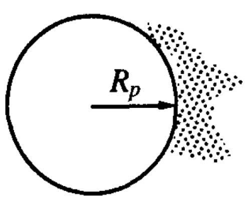
The Continuum Regime

$$\frac{\partial c}{\partial t} = -\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 \tilde{J}_{A,r}) \qquad \tilde{J}_{A,r} = -D_g \frac{\partial c}{\partial r}$$



$c(r, t)$ is the concentration of A, and $\tilde{J}_{A,r}(r, t)$ is the molar flux of A (moles area^{-1}time^{-1}) at any radial position r.

$$\frac{\partial c}{\partial t} = D_g\left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right)$$

$$c(r, 0) = c_\infty, \quad r > R_p$$
$$c(\infty, t) = c_\infty$$
$$c(R_p, t) = c_s$$

$$c(r) = c_\infty - \frac{R_p}{r}(c_\infty - c_s)$$

The total flow of A (moles time^{-1}) toward the particle is denoted by J_c, the subscript c referring to the continuum regime, and is given by

$$J_c = -4\pi R_p^2(\tilde{J}_A)_{r=R_p} \qquad J_c = 4\pi R_p D_g (c_\infty - c_s)$$

Maxwellian flux

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A mass balance on the growing or evaporating particle is

$$\frac{\rho_p}{M_A}\frac{d}{dt}\left(\frac{4}{3}\pi R_p^3\right) = J_c$$

$$\boxed{\frac{dR_p}{dt} = \frac{D_g M_A}{\rho_p R_p}(c_\infty - c_s)}$$

$$R_p^2 = R_{p0}^2 + \frac{2D_g M_A}{\rho_p}(c_\infty - c_s)\,t$$

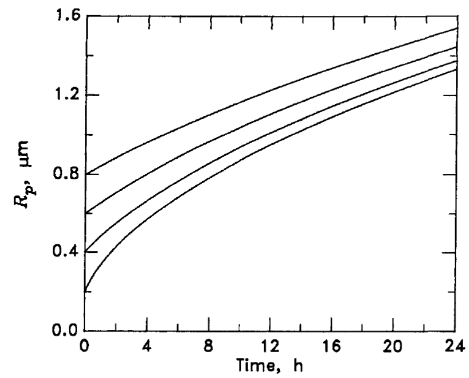

FIGURE 12.1 Growth of aerosol particles of different initial radii as a function of time for a constant concentration gradient of 1 µg m^{-3} between the aerosol and gas phases ($D_g = 0.1$ cm^2 s^{-1}, $\rho_p = 1$ g cm^{-3}).

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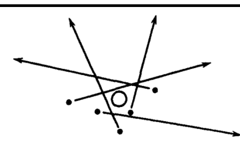
The Kinetic Regime



For molecules in three-dimensional random motion the number of molecules Z_N striking a unit area per unit time is (Moore 1962)

$$Z_N = \frac{1}{4}N\bar{c}_A \qquad (12.23)$$

where $\bar{c}_A$ is the mean speed of the molecules:

$$\bar{c}_A = \left(\frac{8kT}{\pi m_A}\right)^{1/2} \qquad (12.24)$$

Under these conditions the molar flow J_k (moles time^{-1}) to a particle of radius R_p is

$$J_k = \pi R_p^2 \bar{c}_A \alpha (c_\infty - c_s)$$

where α is the molecular accommodation coefficient $\alpha = \dfrac{\text{number of molecules entering the liquid phase}}{\text{number of molecular collisions with the surface}}$

$$\frac{J_k}{J_c} = \frac{\alpha \bar{c}_A}{4D_g} R_p$$

$0 \le \alpha \le 1$

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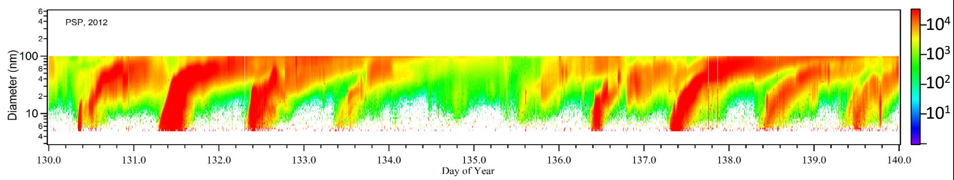
Growth rates of ultrafine particles



$$\frac{\rho_p}{M_A}\frac{d}{dt}\left(\frac{4}{3}\pi R_p^3\right) = J_k = \pi R_p^2 \bar{c}_A \alpha (c_\infty - c_s)$$

$$\frac{dR_p}{dt} = ?$$

$$\frac{dD_p}{dt} = 2\frac{dR_p}{dt} = ?$$

Q: If the observed growth rate (diameter) of 5-10 nm particles is 3 nm/hr and H_2SO_4 is assumed to be the only condensing gas, what is the concentration of H_2SO_4 gas ?

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The Transition Regime

$$Kn \approx 1$$

Flux matching: Flux matching assumes that the noncontinuum effects are limited to a region $R_p \le r \le \Delta + R_p$ beyond the particle surface and that continuum theory applies for $r \ge \Delta + R_p$. The distance Δ is then of the order of the mean free path λ and within this inner region the basic kinetic theory of gases is assumed to apply.

$R_p \le r \le \Delta + R_p$ **Kinetic theory applies**

$r \ge \Delta + R_p.$ **Continuum theory applies**

Fuchs Theory

$$4\pi R_p^2 (\tfrac{1}{4}\bar{c}_A)[c(R_p + \Delta) - c_s] = D\left(\frac{dc}{dr}\right)_{r=R_p+\Delta} 4\pi (R_p + \Delta)^2$$

Then solving the steady-state continuum transport equation for a dilute system,

$$\frac{d^2c}{dr^2} + \frac{2}{r}\frac{dc}{dr} = 0$$

$$c(r) = c_\infty - \frac{R_p}{r}(c_\infty - c_s)\beta_F \qquad \beta_F = \frac{[1 + (\Delta/R_p)]\bar{c}_A R_p}{\bar{c}_A R_p + 4D[1 + (\Delta/R_p)]}$$

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Fuchs Theory

$$\alpha \; 4\pi R_p^2(\tfrac{1}{4}\bar{c}_A)[c(R_p+\Delta)-c_s] = D\left(\frac{dc}{dr}\right)_{r=R_p+\Delta} 4\pi(R_p+\Delta)^2$$

Relating the binary diffusivity and the mean free path using $D_{AB}/\lambda_{AB}\bar{c}_A = \frac{1}{3}$ and letting $\mathrm{Kn} = \lambda_{AB}/R_p$, one obtains

$$\frac{J}{J_c} = 0.75\alpha \frac{1 + Kn\Delta/\lambda_{AB}}{0.75\alpha + Kn + (\Delta/\lambda_{AB})Kn^2}$$

If $\alpha = 1$

$$\frac{J}{J_c} = 0.75 \frac{1 + Kn\Delta/\lambda_{AB}}{0.75 + Kn + (\Delta/\lambda_{AB})Kn^2}$$

$$\frac{J}{J_k} = \frac{1 + Kn\Delta/\lambda_{AB}}{1 + Kn\Delta/\lambda_{AB} + 0.75\, Kn^{-1}} \qquad \frac{J_k}{J_c} = \frac{3}{4\,Kn}$$

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TABLE 12.1 Transition Regime Formulas for Diffusion of Species A in a Background Gas B to an Aerosol

J/J_c	Mean Free Path Definition	Reference
$\dfrac{0.75\,\alpha(1+\mathrm{Kn}\Delta/\lambda_{AB})}{0.75\,\alpha+\mathrm{Kn}+(\Delta/\lambda_{AB})\mathrm{Kn}^2}$	$\dfrac{3D_{AB}}{\bar{c}_A}$	Fuchs (1964)
$\dfrac{0.75\,\alpha(1+\mathrm{Kn})}{\mathrm{Kn}^2+\mathrm{Kn}+0.283\,\mathrm{Kn}\alpha+0.75\,\alpha}$	$\dfrac{3D_{AB}}{\bar{c}_A}$	Fuchs and Sutugin (1971)
$\dfrac{1+\mathrm{Kn}}{1+2\,\mathrm{Kn}(1+\mathrm{Kn})/\alpha}$	$\dfrac{2D_{AB}}{\bar{c}_A}$	Dahneke (1983)
$\dfrac{1+1.333\,\mathrm{Kn}}{1+1.333\,\mathrm{Kn}+(1.333\sqrt{\pi}\mathrm{Kn}+1)\mathrm{Kn}}$	$\dfrac{4}{\sqrt{\pi}}\dfrac{D_{AB}}{\bar{c}_A}$	Loyalka (1983)
$\dfrac{b(1+a\mathrm{Kn})}{b+c\mathrm{Kn}+d\,\mathrm{Kn}^2}$	$4b\dfrac{D_{AB}}{\bar{c}_A}$ [see (12.39) for a, b, c, and d]	Sitarski and Nowakowski (1979)

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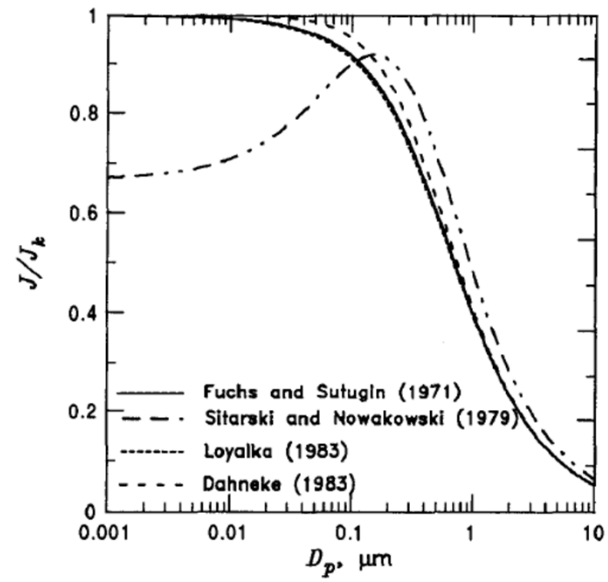

FIGURE 12.2 Mass transfer rate predictions for the transition regime by the approaches of (a) Fuchs and Sutugin (1971), (b) Dahneke (1983), (c) Loyalka (1983), and (d) Sitarski and Nowakowski (1979) ($z = 15$) as a function of particle diameter. Accommodation coefficient $\alpha = 1$.

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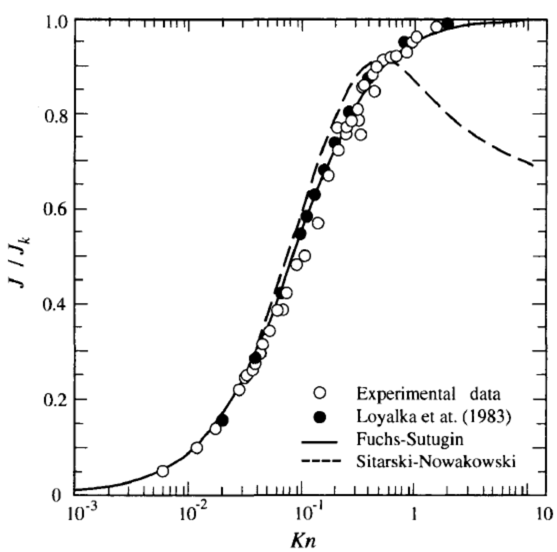

FIGURE 12.3 Comparison of experimental dibutyl phthalate evaporation data with the theories of Loyalka et al. (1989), Sitarski and Nowakowski (1979) (for $z = 15$), and the equation of Fuchs and Sutugin (1970). (Reprinted from *Aerosol Science and Technology*, **25**, Li and Davis, 11–21. Copyright 1995, with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington OX5 1GB, UK.)

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The Accommodation Coefficient

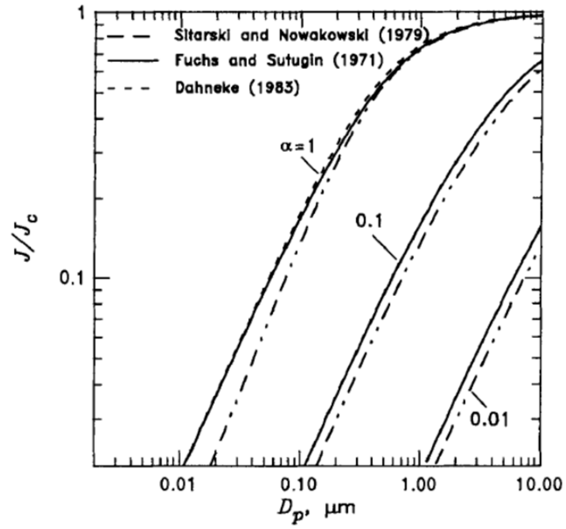

FIGURE 12.4 Mass transfer rates as a function of particle diameter for accommodation coefficient values 1.0, 0.1, and 0.01 for the approaches of Sitarski and Nowakowski (1979), Fuchs and Sutugin (1970), and Dahneke (1983).

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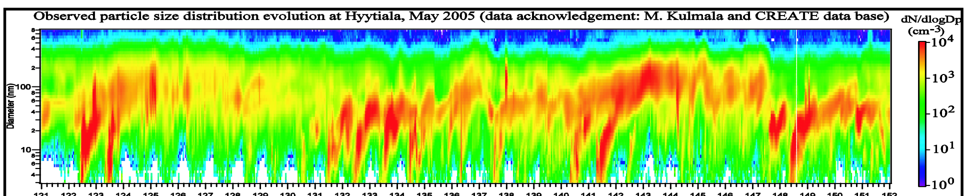
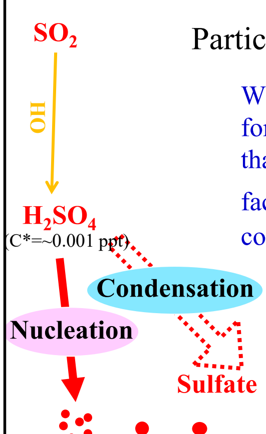
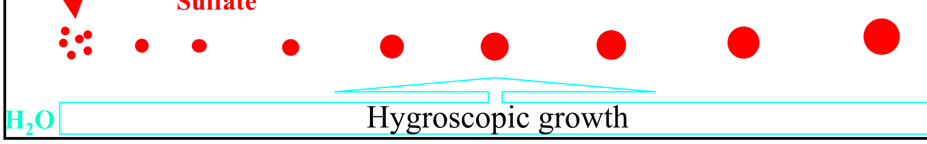


Particle formation = Nucleation + Growth

While the involvement of H_2SO_4 in atmospheric particle formation is well established, many field measurements indicate that the growth rates of nucleated particles are commonly a factor of ~ 2-20 higher than can be explained by the H_2SO_4 condensation alone (Kulmala et al., 2004; Kuang et al., 2010).



Secondary Organic Aerosol (SOA)



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