Nucleation and Growth of Atmospheric Aerosols

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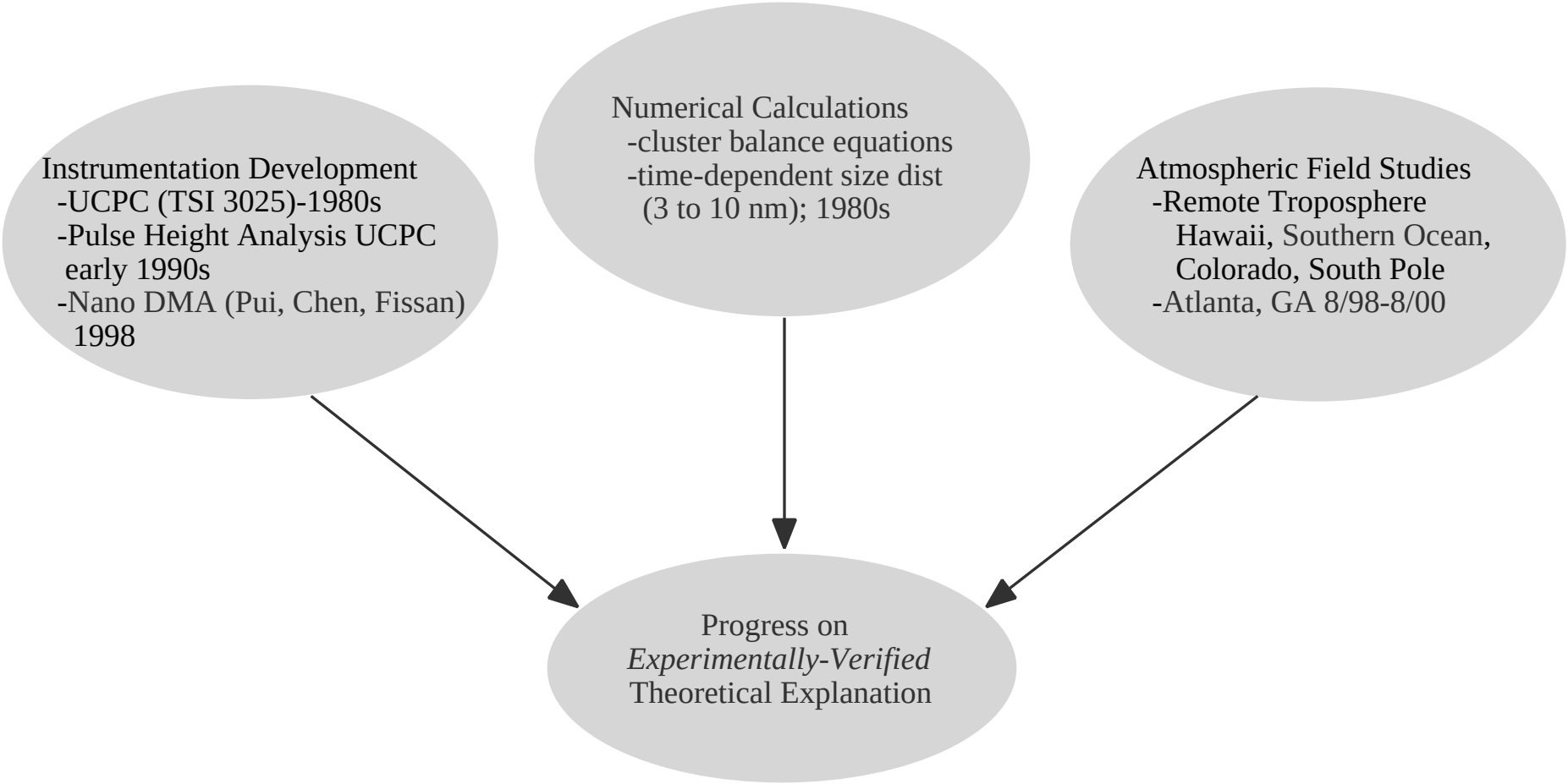
Lecture Outline



Monomer and Cluster Population Balance Equations for Nucleating Aerosol

Monomer:

$$\frac{dN_1}{dt} = R - N_1 \sum_{j=1}^{\infty} \beta_{1\,j} N_j + \sum_{j=2}^{\infty} (1+\delta_{2\,j})\, N_j - \frac{N_1 \bar{c}_1}{4} I$$

g → p *coagulation* *evaporation* "*scavenging*"

Clusters:

$$\frac{dN_k}{dt} = \frac{1}{2} \sum_{i+j=k} \beta_{kj} N_i N_j - N_k \sum_{j=1}^{\infty} \beta_{kj} N_j + E_{k+1} N_{k+1} - E_k N_k - \frac{N_k \bar{c}_k}{4} I$$

coagulation *evaporation* "*scavenging*"

gain *loss* *gain* *loss*

Dimensionless Population Balance Equations for Monomer and Clusters

Monomer:

$$\frac{d\tilde{N}_1}{d\tilde{t}} = 1 - \tilde{N}_1 \sum_{j=1}^{\infty} \tilde{\beta}_{1j} \tilde{N}_j + \sum_{j=2}^{\infty} (1+\delta_{2j}) \tilde{E}_j \tilde{N}_j - \sqrt{L}\, \tilde{N}_1$$

g → p *coagulation* *evaporation* *"scavenging"*

Clusters:

$$\frac{d\tilde{N}_k}{d\tilde{t}} = \frac{1}{2} \sum_{i+j=k} \tilde{\beta}_{kj} \tilde{N}_i \tilde{N}_j - \tilde{N}_k \sum_{j=1}^{\infty} \tilde{\beta}_{kj} \tilde{N}_j + \tilde{E}_{k+1} \tilde{N}_{k+1} - \tilde{E}_k \tilde{N}_k - \sqrt{\frac{L}{k}}\, \tilde{N}_k$$

coagulation *evaporation* *"scavenging"*

gain *loss* *gain* *loss*

Parameters that Regulate Steady-State 3 to 10 nm Size Distributions

Parameters that determine significance of monomer evaporation from molecular clusters:

Dimensionless Evaporation Rate Parameter: $E = N_s \left(\frac{\beta_{11}}{R} \right)^{1/2}$

Dimensionless Surface Tension Parameter: $A = 4 \left(\frac{\pi}{6} \right)^{1/3} \frac{v_1^{2/3} \sigma}{k_b T}$

Parameter that determines rate of monomer and cluster loss to preexisting aerosol:

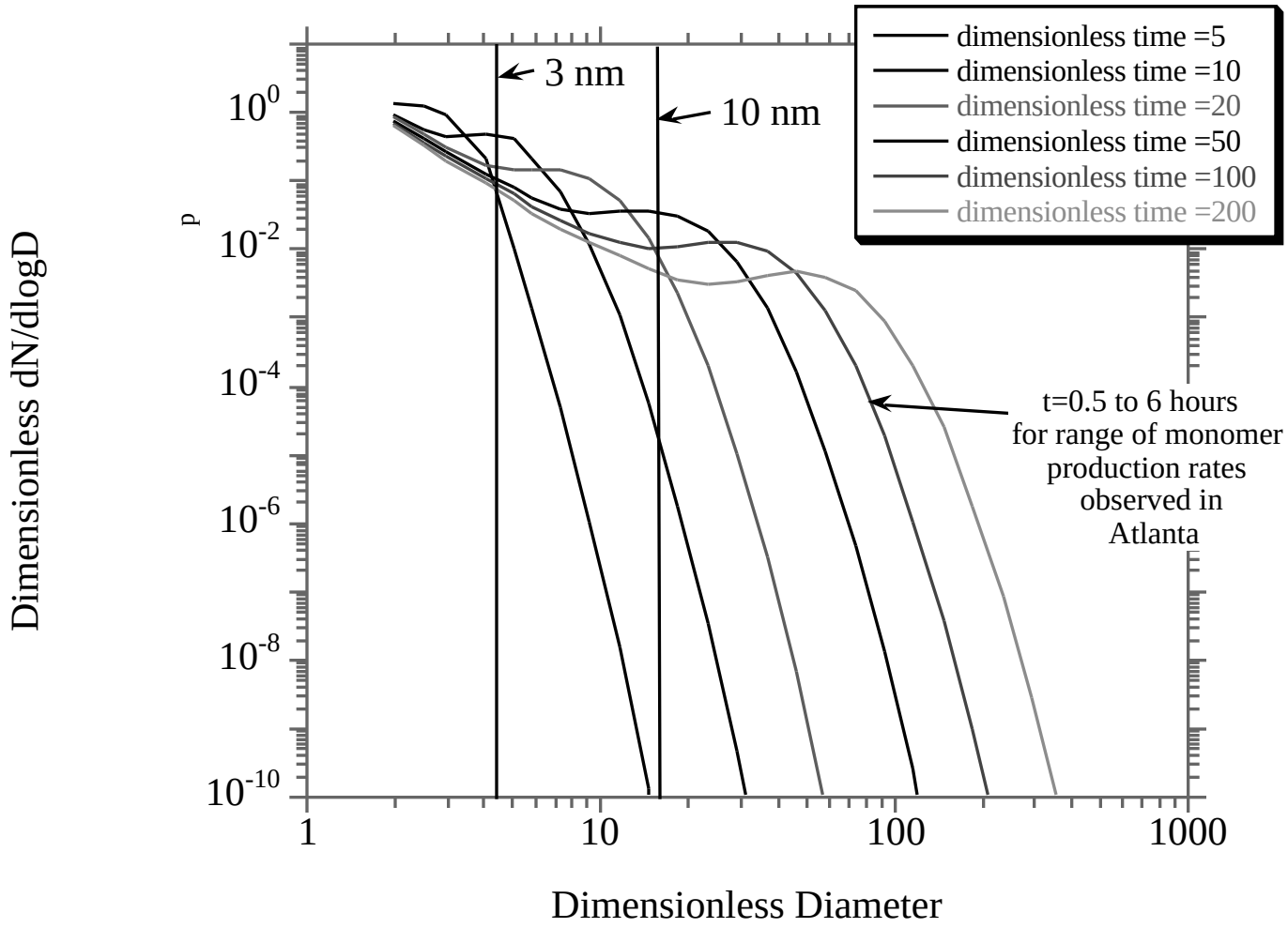
Dimensionless "Scavenging" Parameter: $\sqrt{L} = \left(\frac{k_b T}{2\pi m_1} \right)^{1/2} \frac{I}{\sqrt{\beta_{11} R}}$

Calculating R from Slope and Intercept

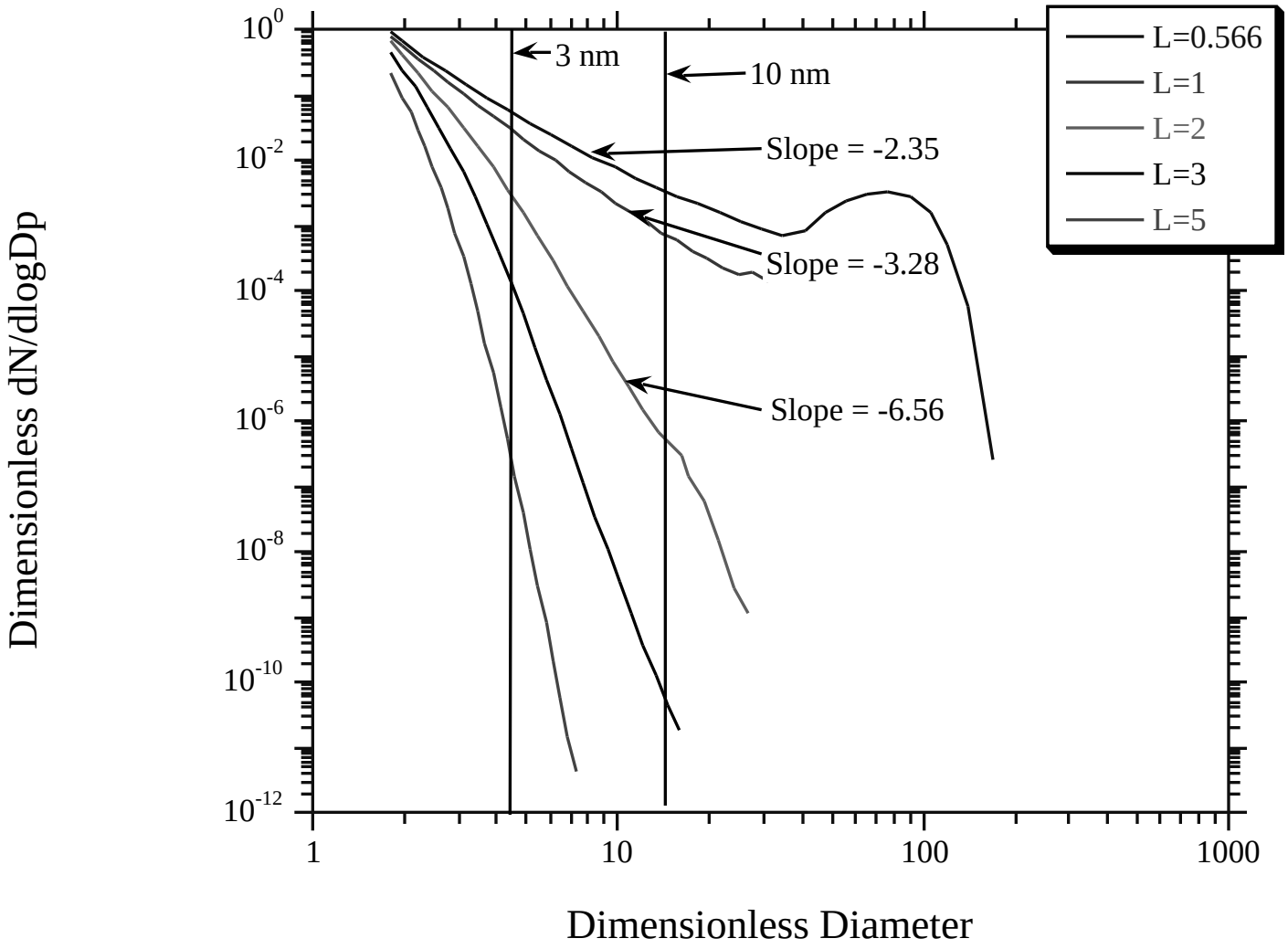
$$\left.\frac{dN}{d\log D_p}\right|_{dimensional} = \left(\frac{R}{\beta_{11}}\right)^{1/2} \left.\frac{d\tilde{N}}{d\log \tilde{D}_p}\right|_{dimensionless}$$

$$\left. D_p \right|_{dimensional} = v_1^{1/3} \left. \tilde{D}_p \right|_{dimensionless}$$

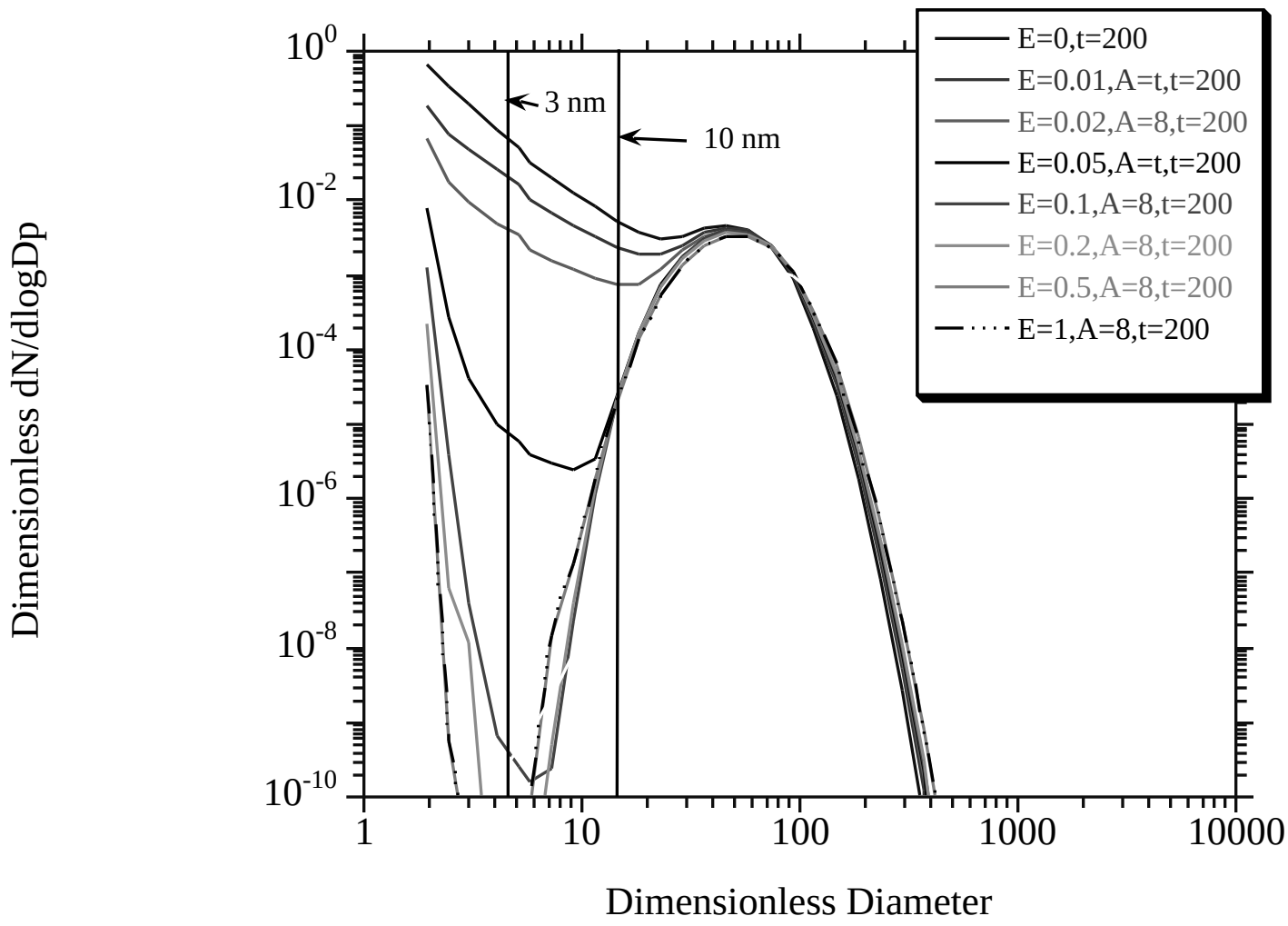
Evolution of Aerosol Size Distribution for Collision-Controlled Nucleation (E=0)



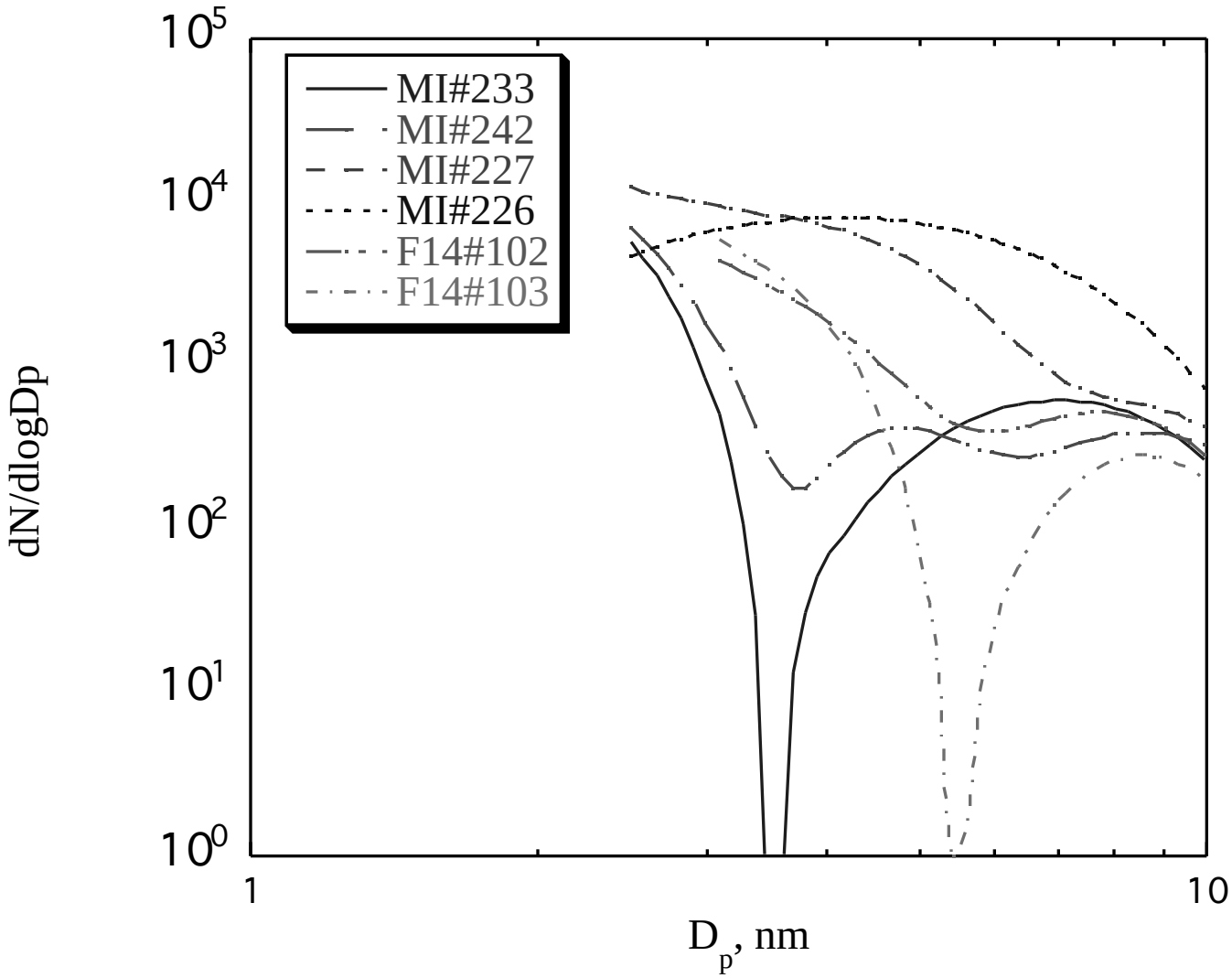
Dependence of Size Distributions on Pre-existing Aerosol "Surface Area" for Collision-controlled Nucleation (E=0)



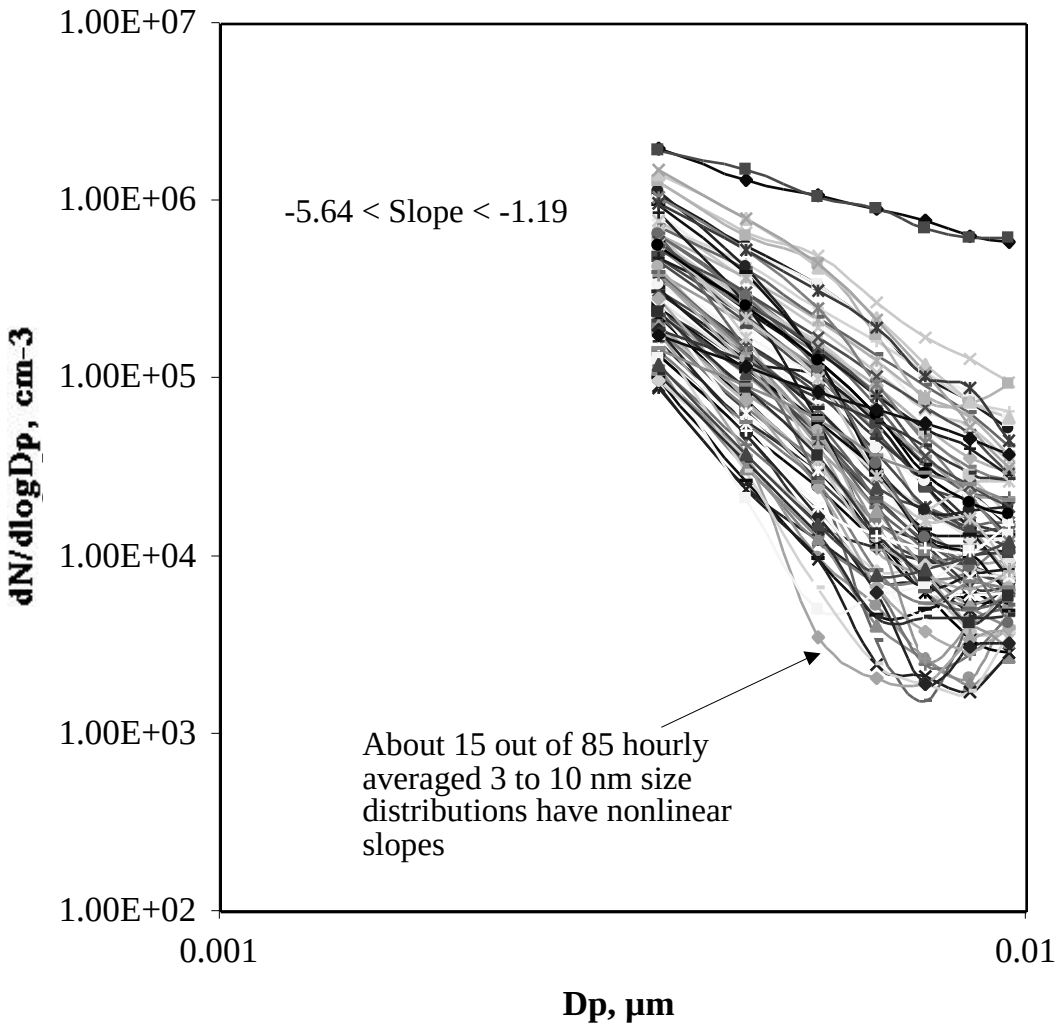
Dependence of Size Distributions on Evaporation Parameter, E, for Collision-Controlled Nucleation



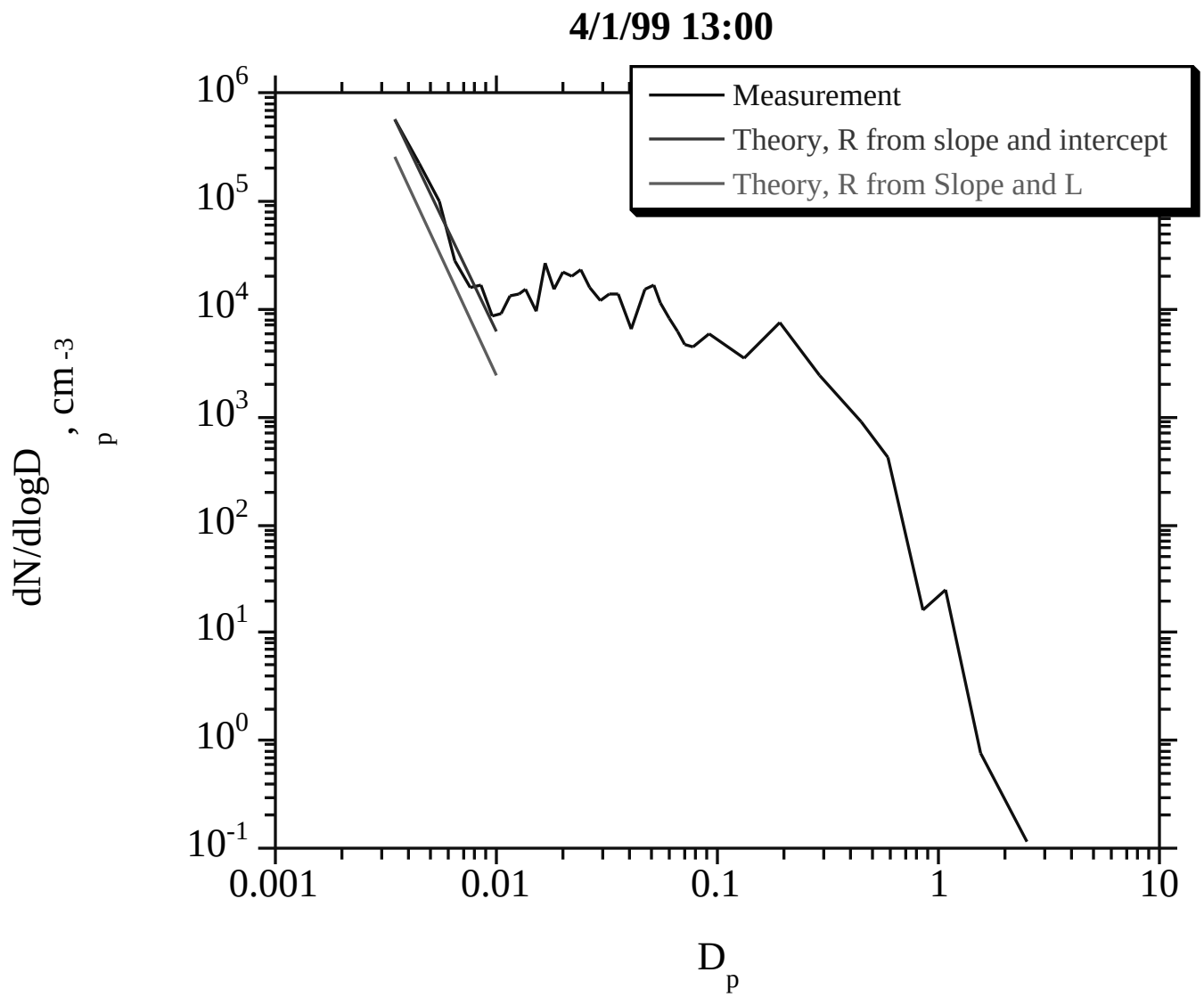
3 to 10 nm Size Distributions in the Remote Marine Troposphere



3 to 10 nm Size Distributions from Atlanta: 8/98-8/99



Comparison of Measurements and Collision-Controlled Theory



Hypothesis: Rate limiting step is production of H_2SO_4 by OH + SO_2

If so, then:

$$[OH] = \frac{R}{k[SO_2]}$$

where

R = monomer production rate

k = OH + SO_2 rate constant.

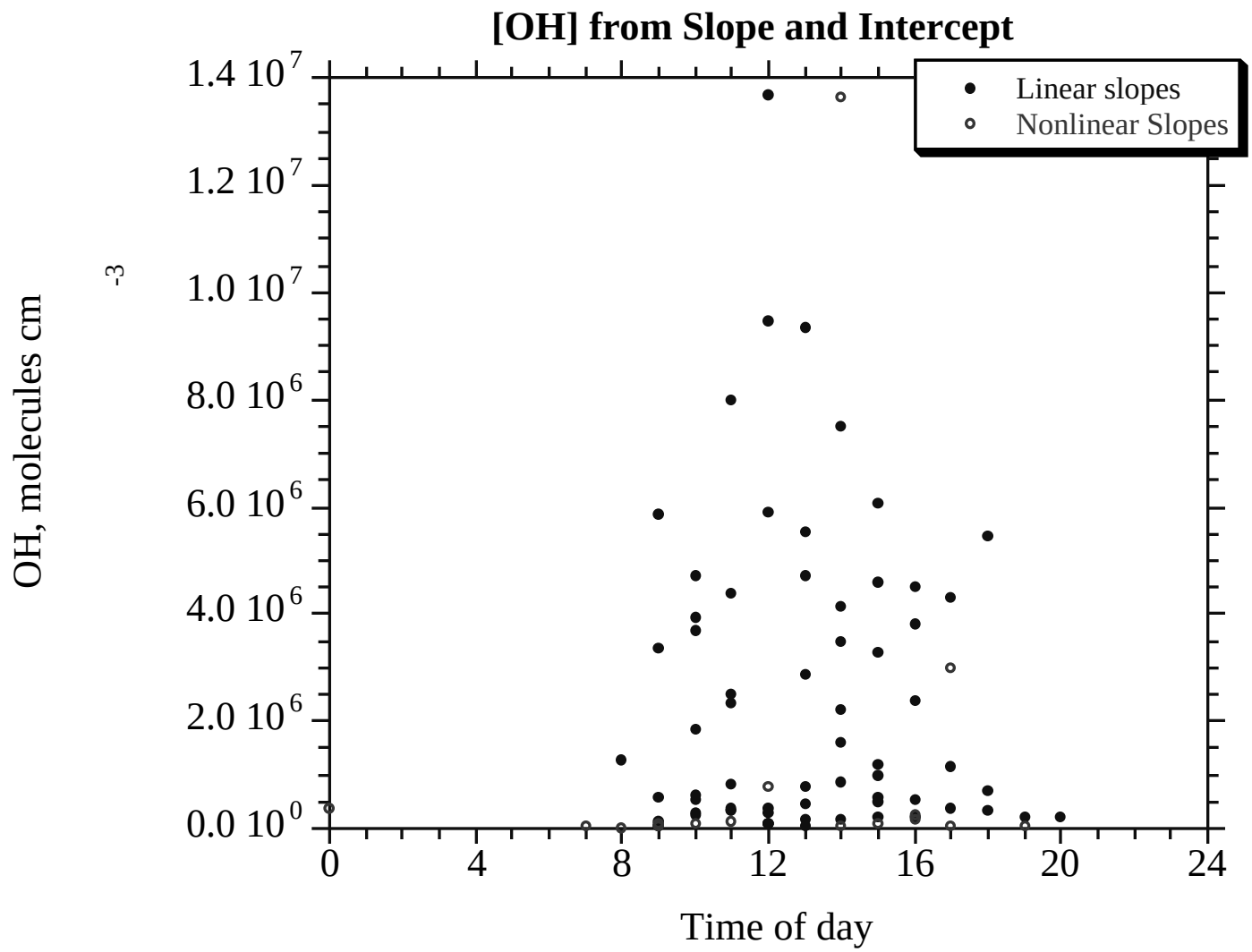
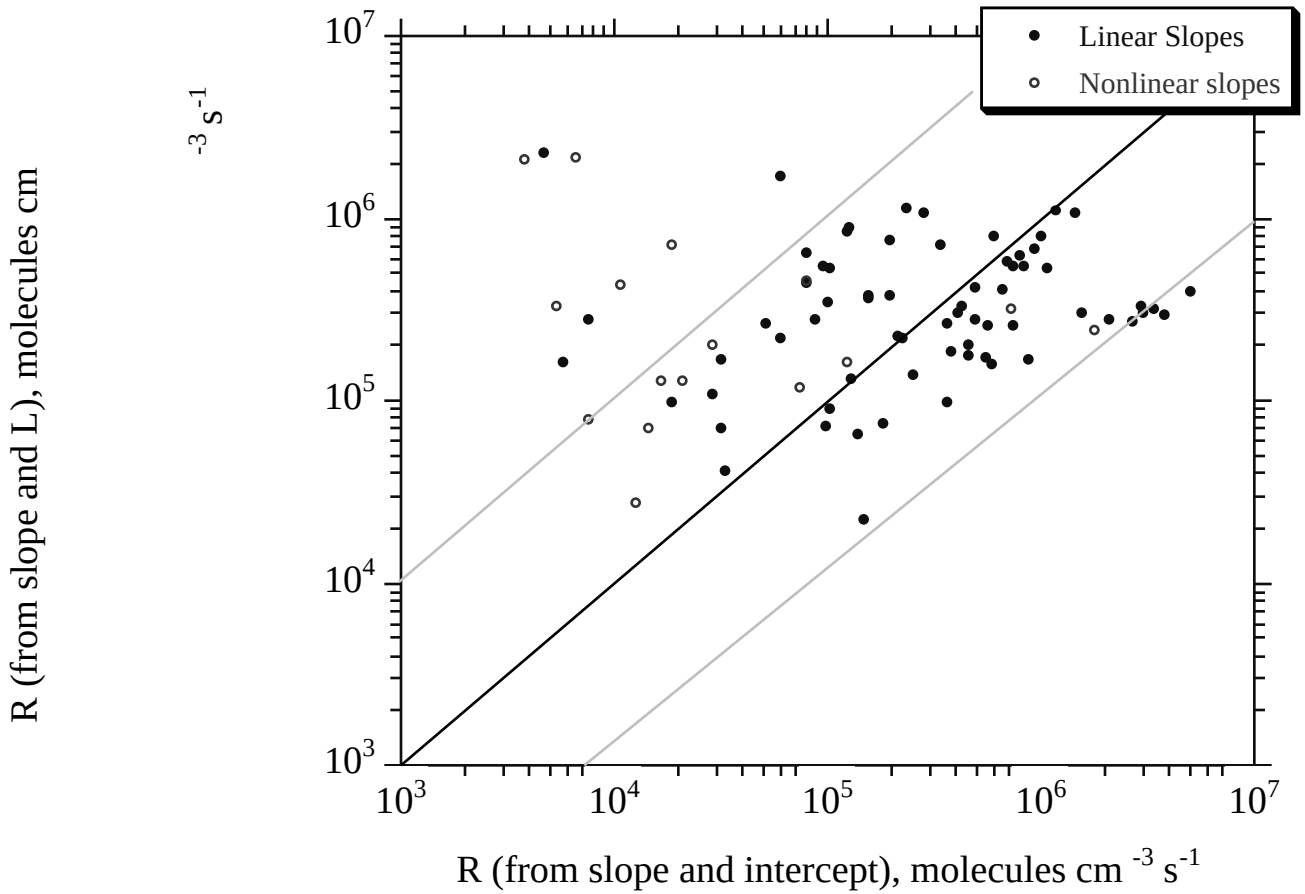
Conclusions

- Size Distributions of 3 to 10 nm aerosols during nucleation in Atlanta can be explained by collision-controlled theory
  - Does not apply to remote troposphere
- Monomer production rate is in reasonable agreement with H_2SO_4 production by SO_2+OH
- Nucleation is too fast to be explained by binary H_2SO_4 + H_2O nucleation
  - Other species must be involved

Future research

- Determine species that participate in nucleation
  - Measure composition of freshly nucleated particles
  - Measure concentration of trace gas phase species
    - » NH_3, amines, etc.
- Verify that $[H_2SO_4]$ is consistent with values calculated from collision-controlled theory
- Understand thermodynamic properties and reactivities of pertinent molecular clusters

$[OH] = R_{Slope\&Intercept}/k[SO_2]$



Comparison of Monomer Production Rates Calculated by Two Different Methods