Bulk vs. stochastic kinetics to describe the oxidation of organic aerosol components

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Simple aerosol oxidation system

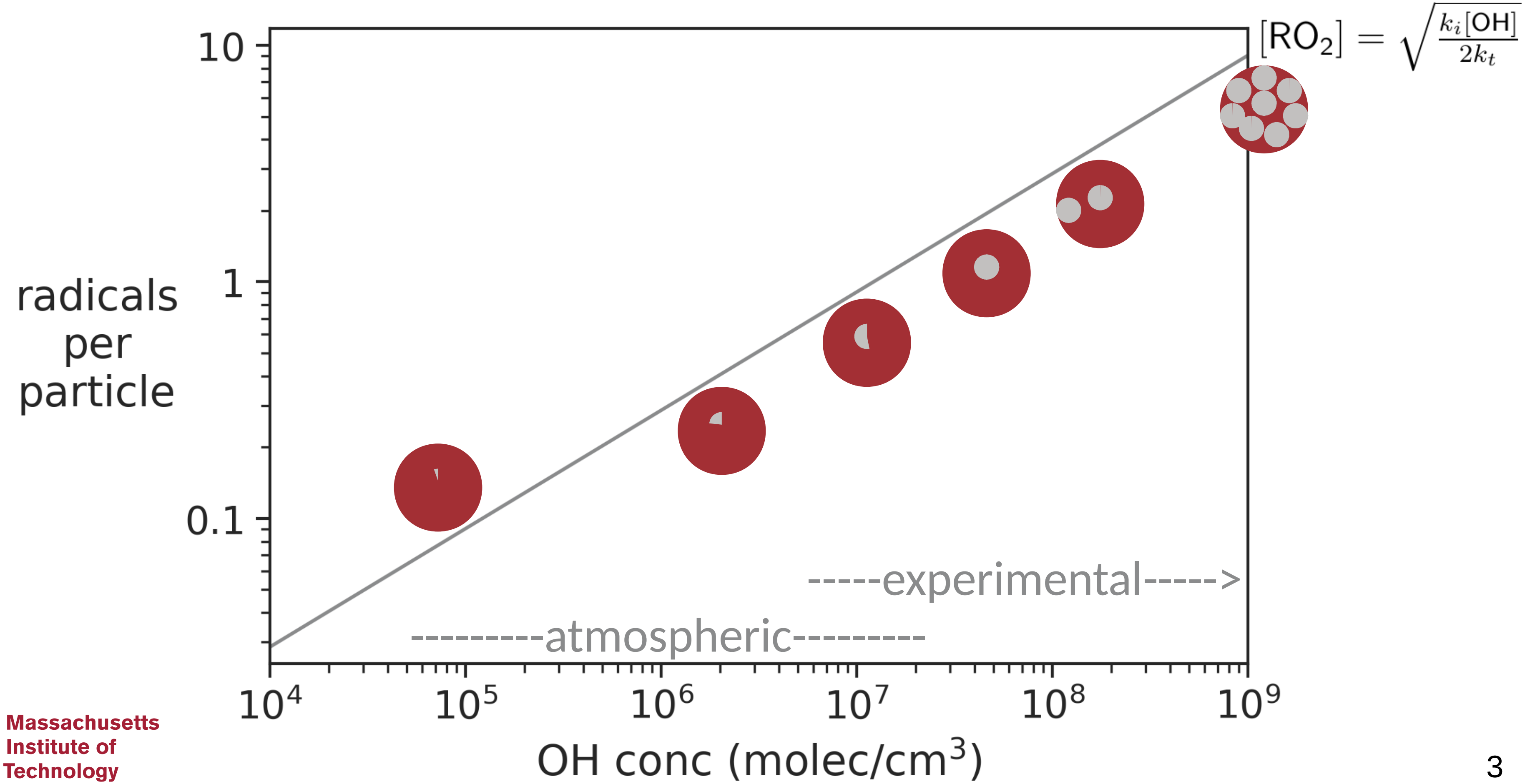
initiation	$\mathrm{OH} + \mathrm{RH} + \mathrm{O_2} \longrightarrow \mathrm{H_2O} + \mathrm{RO_2}$	$r_i = k_i(d_p, T, \gamma)[\mathrm{OH}]$
termination	$\mathrm{RO_2} + \mathrm{RO_2} \longrightarrow \mathrm{R{=}O} + \mathrm{ROH}$	$r_t = k_t[\mathrm{RO_2}]^2$

$$\gamma = \frac{\text{num reactions with OH}}{\text{num OH collisions}}$$

0

$$\frac{d[\mathrm{RO_2}]}{dt} = r_i - 2r_t \qquad [\mathrm{RO_2}] = \sqrt{\frac{k_i[\mathrm{OH}]}{2k_t}}$$

Radicals in 100 nm particle



Stochastic kinetic oxidation

typical kinetics

$[RO_2]$

$$r_t = k_t[RO_2]^2$$

stochastic kinetics

probability → p_x ← number of RO_2 in particle

$$r_t = k_t \sum_{x=2}^{\infty} x(x-1)p_x$$

$r_t(p_0 = 1) = 0$

$r_t(p_1 = 1) = 0$

$r_t(p_2 = 1) = 2k_t$

$r_t(p_3 = 1) = 6k_t$

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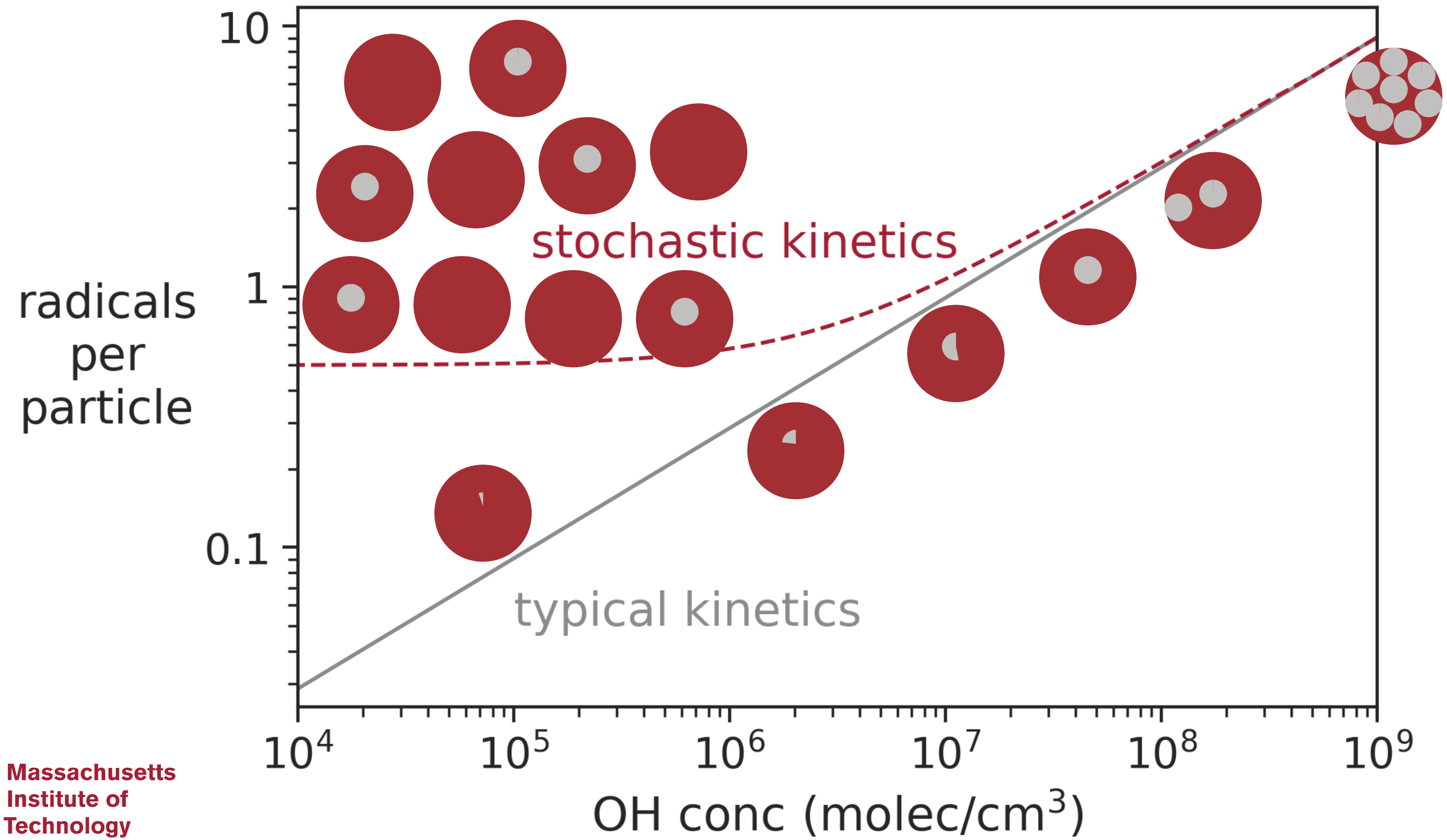
Radicals in 100 nm particle



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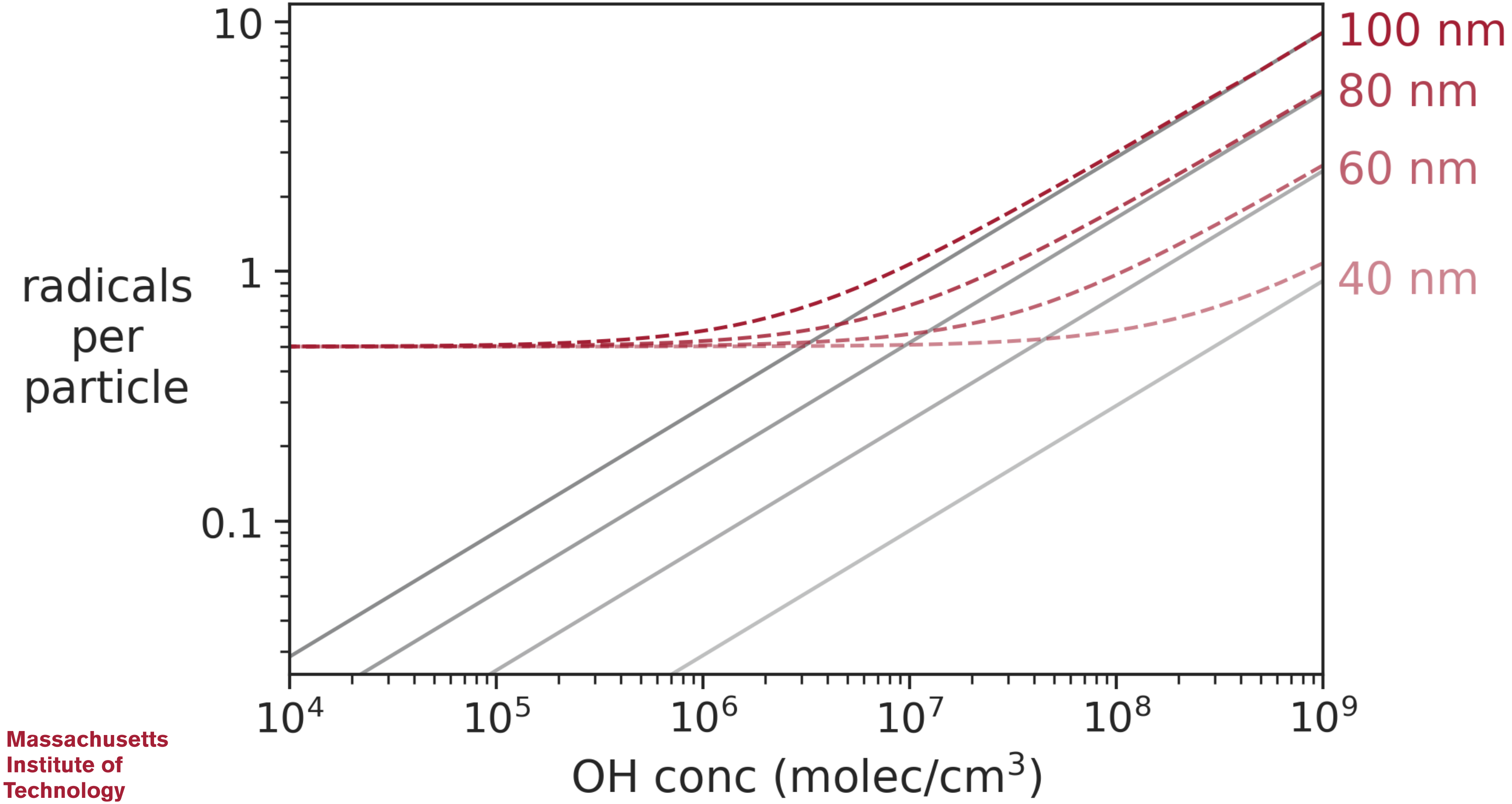
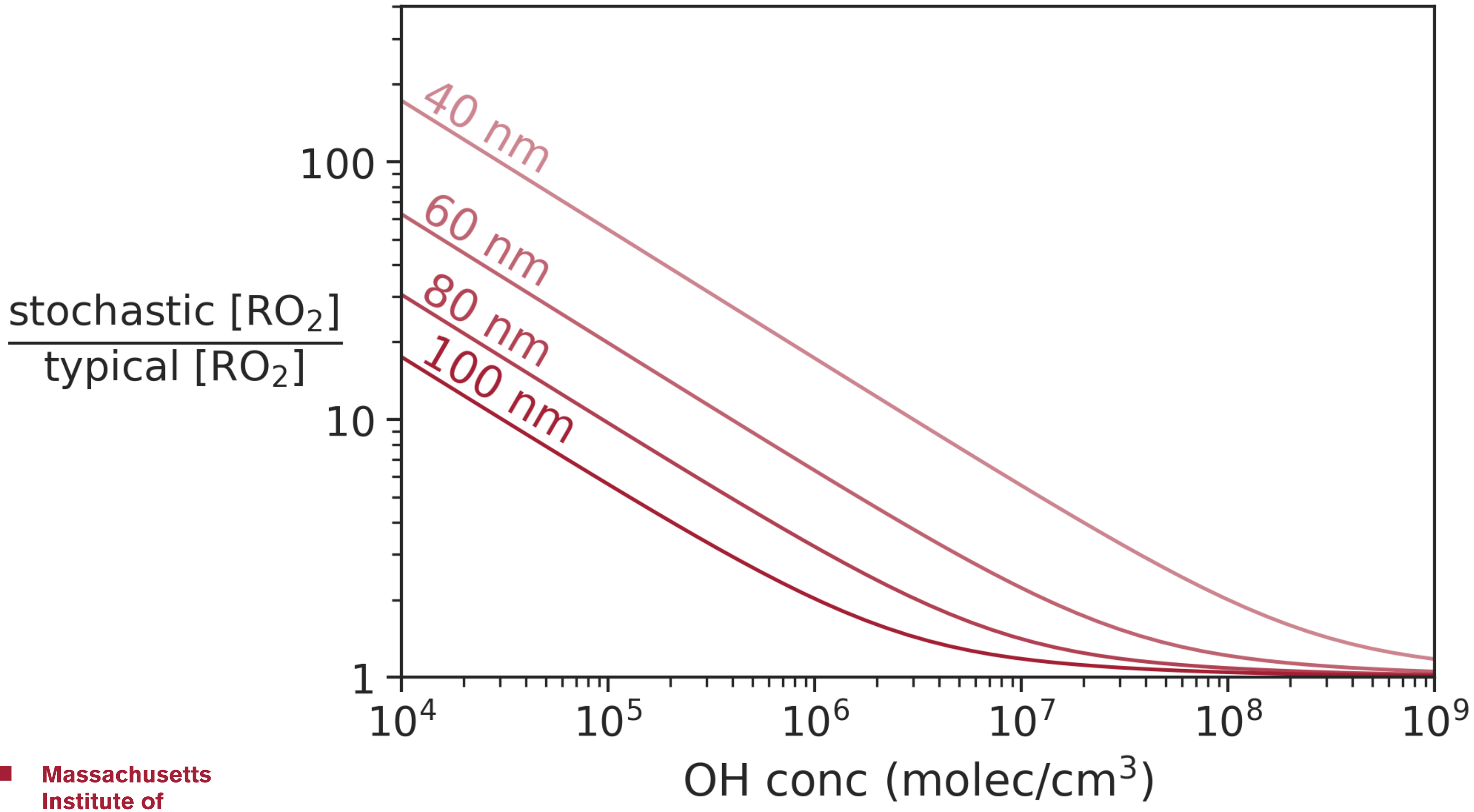
Asymptote independent of size



Stochasticity impacts smaller particles



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Mozurkewich 1997 GRL, 24, 3209-3212

Simple aerosol oxidation system

$$\text{initiation} \quad \mathsf{OH + RH + O_2 \longrightarrow H_2O + RO_2}$$

$$\text{termination} \quad \mathsf{RO_2 + RO_2 \longrightarrow R{=}O + ROH}$$

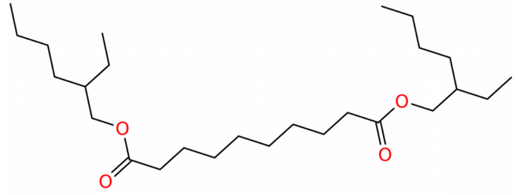
$$[\mathsf{R_{Ox}}] = [\mathsf{R{=}O}] + [\mathsf{ROH}] + [\mathsf{ROOH}] + \ldots$$

$$\frac{d[\mathsf{R_{Ox}}]}{dt} = 2r_t = r_i = k_i[\mathsf{OH}]$$

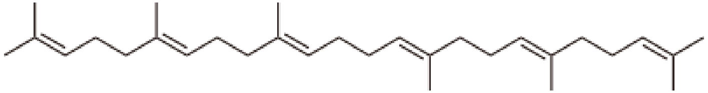
Lushnikov et al. 2003 JAS, 34, 9, 1117

Propagation chemistry happens

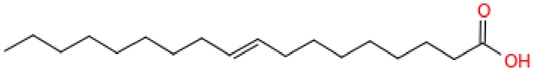
$$\gamma_{eff} = \frac{\text{num oxidations}}{\text{num OH collisions}}$$



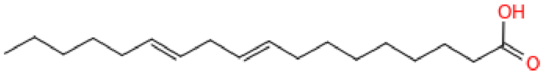
$$\gamma_{eff} = 2 \pm 0.5$$



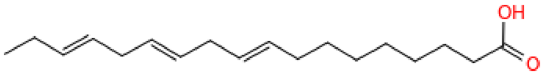
$$\gamma_{eff} = 2\text{–}100$$



$$\gamma_{eff} = 1.72 \pm 0.08$$



$$\gamma_{eff} = 3.75 \pm 0.18$$



$$\gamma_{eff} = 5.73 \pm 0.14$$

Hearn & Smith 2006 GRL, 33, L17805

Nah et al. 2014. JPCA, 118, 4106-4119

Nah et al. 2013. PPCP, 15, 18649-18663

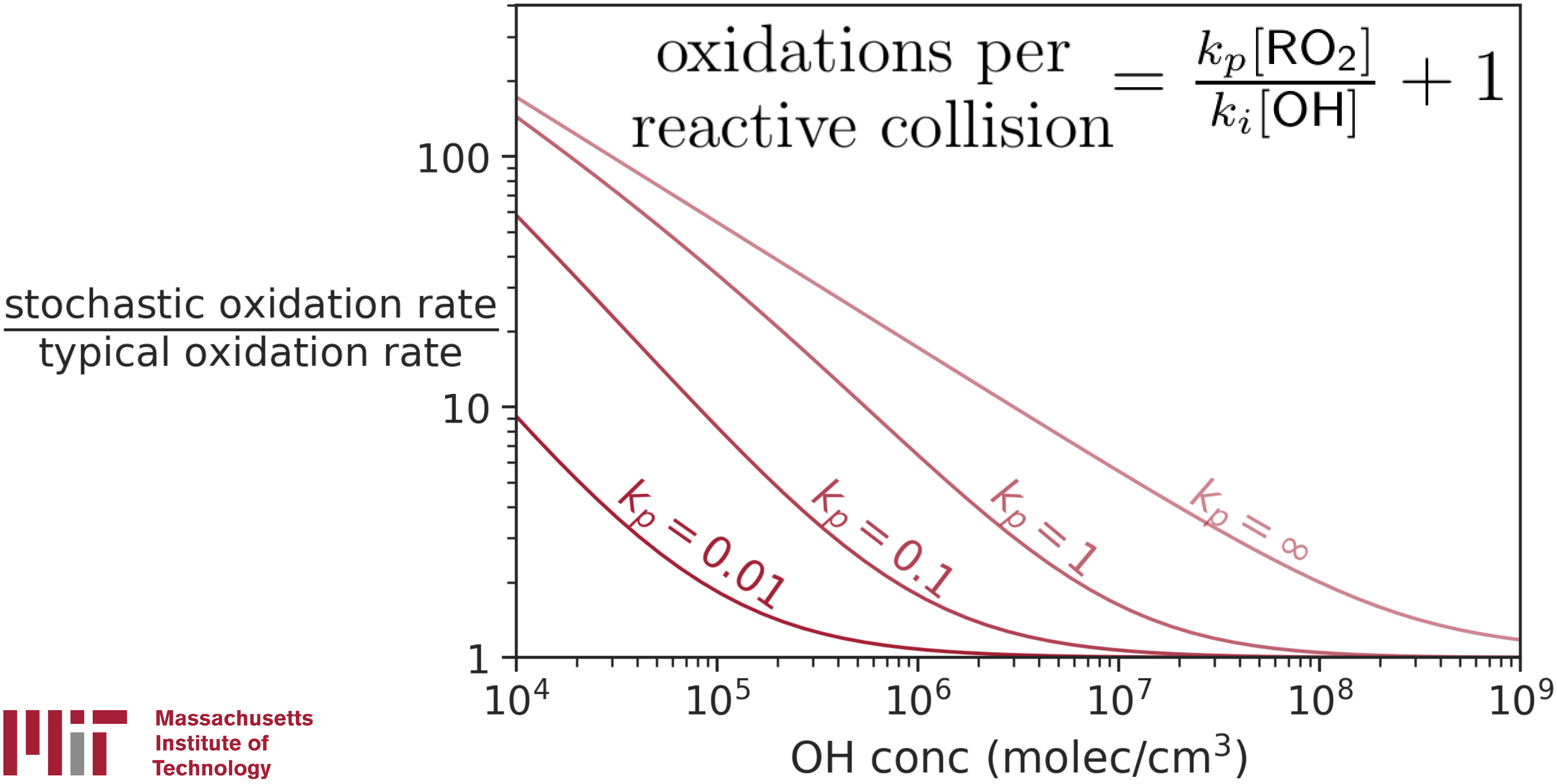
Heine & Wilson. 2016. ACS, 251, 373

Aerosol oxidation with propagation

initiation	$\mathsf{OH} + \mathsf{RH} + \mathsf{O_2} \longrightarrow \mathsf{H_2O} + \mathsf{RO_2}$
termination	$\mathsf{RO_2} + \mathsf{RO_2} \longrightarrow \mathsf{R{=}O} + \mathsf{ROH}$
propagation	$\mathsf{RO_2} + \mathsf{RH} + \mathsf{O_2} \longrightarrow \mathsf{ROOH} + \mathsf{RO_2}$

$$\frac{d[\mathsf{R}_{\mathsf{Ox}}]}{dt} = 2r_t + r_p = k_i[\mathsf{OH}] + k_p[\mathsf{RO_2}]$$

Large impact with radical propagation



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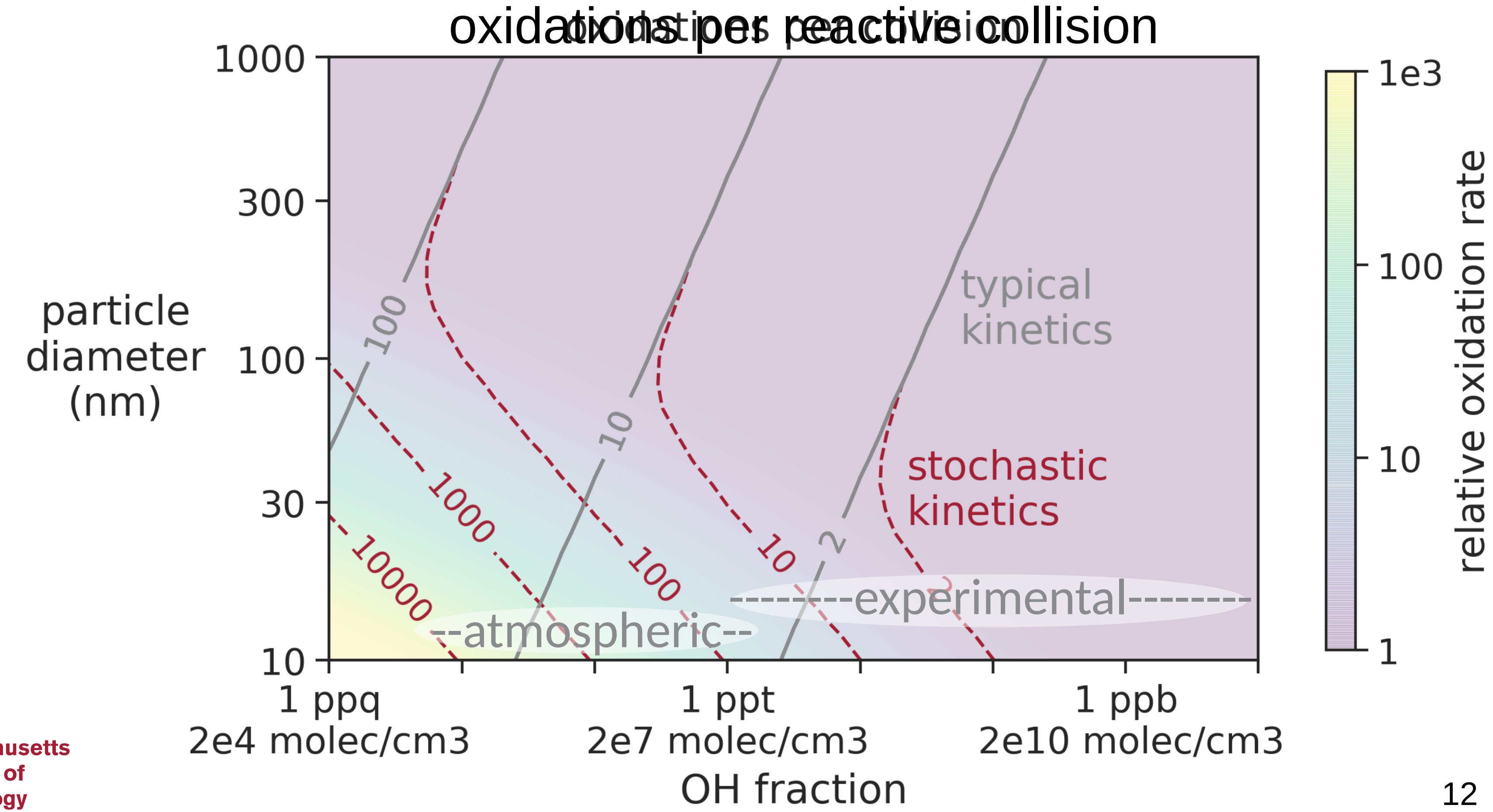
Stochasticity impacts oxidation rate



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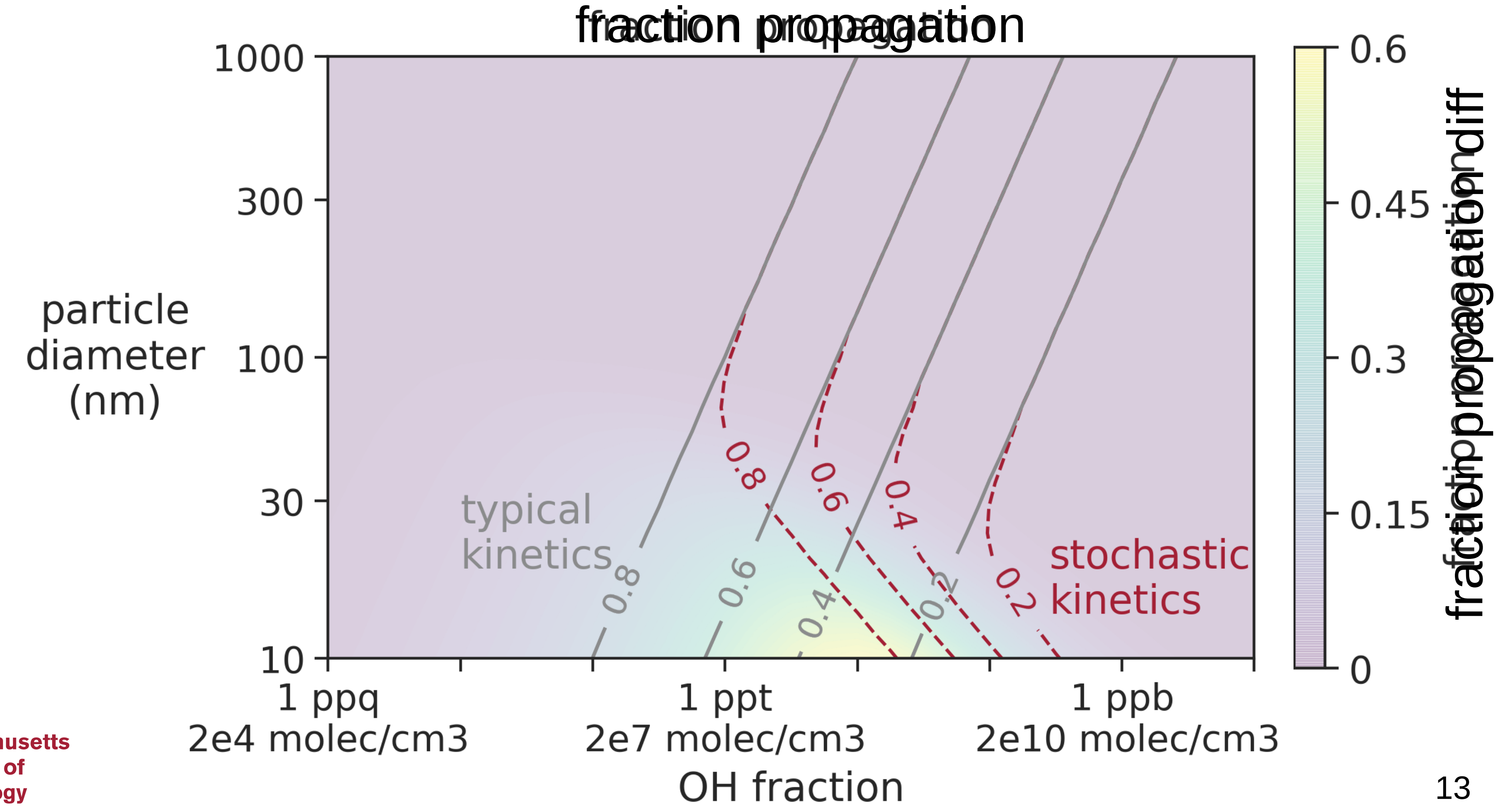
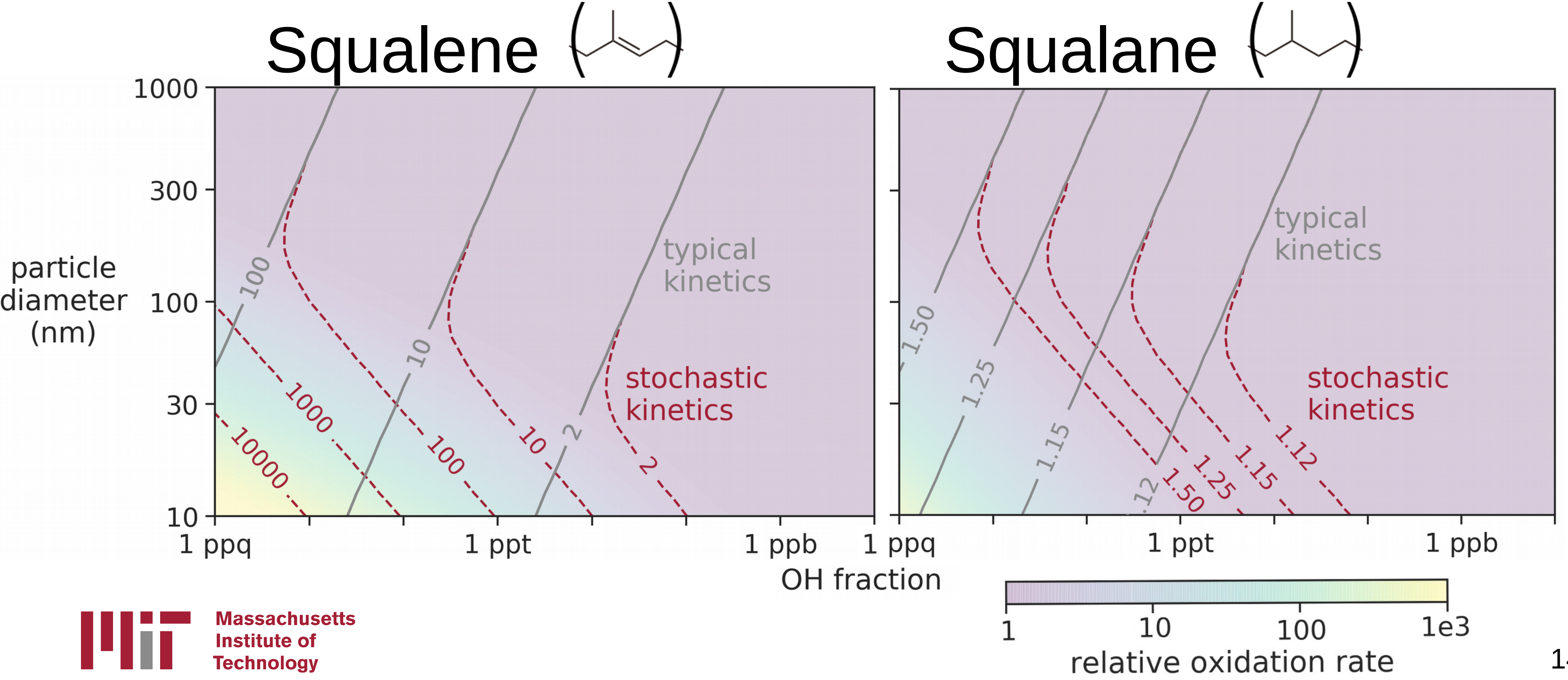
Stochasticity impacts functional groups



Impact is composition dependent



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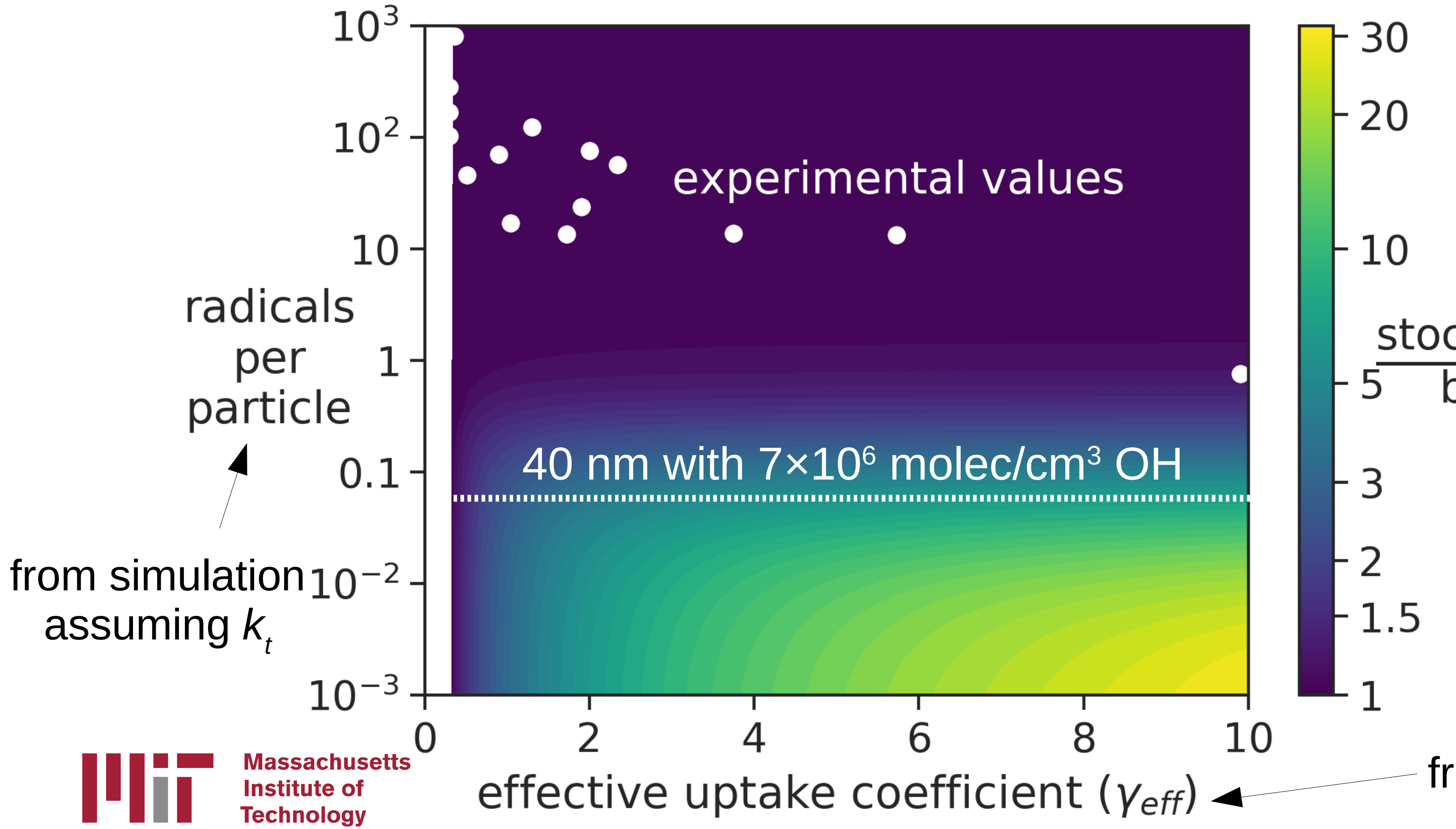
Experiments outside stochastic regime



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Nah et al. 2014 JPCA 118, 4106-4119
Heine & Wilson. 2016 ACS 251, 373
George et al. 2007 ACP 7, 4187-4201
McNeil et al. 2008 ACP 8, 5465-5476
Lambe et al. 2007 EST 41, 2357-2363
Ruehl et al. 2013 JPCA 117, 3990-4000
Lim et al. 2017 GRL 44, 2949-2957
Che et al. 2009 PCCP 11, 7885-7895
Smith et al. 2009 ACP 9, 3209-3222

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Conclusions

- Stochastic solvers necessary when:
  - propagation chemistry matters
  - few radicals per particle
- Largest impact on small particles at low oxidant concentrations
- Most experiments are outside stochastic regime
- Heterogeneous oxidation might be substantially faster than we currently assume

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