A Variational Transition State Theory Approach to Cluster Evaporation and Condensation Important in Homogeneous Vapor-Phase Nucleation

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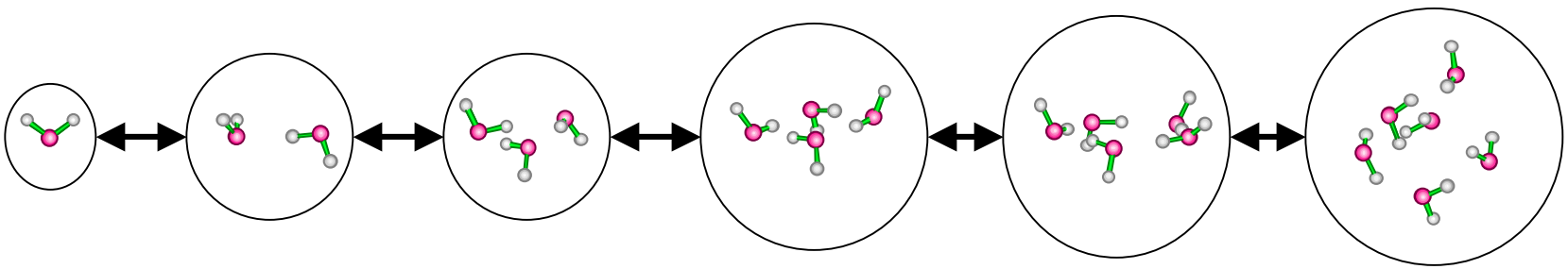

Support

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Nucleation: a Macroscopic Phenomena Controlled by Molecular Scale Processes

Homogeneous vapor-phase nucleation is important in:

- aerosol production in the atmosphere (aerosols have impact on global change, health effects, oxidant concentrations)
- nanotechnology (competition of nucleation and growth controls particle size)
- ultrasensitive detection of trace species (e.g., mercury concentration in atmosphere)

Theoretical approaches view nucleation as cluster evolution:

- Nucleation controlled by the competition of cluster condensation and evaporation
- Critical clusters (i.e., condensation and evaporation rates equal) typically small (10's of molecules)

Classical Nucleation Theory

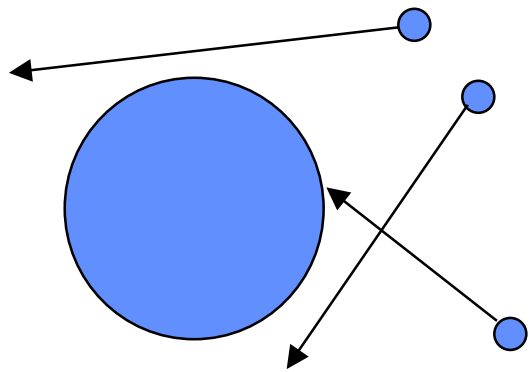
(Volmer & Weber, 1926; Becker & Doring, 1935; Zeldovich, 1942)

- Nucleation is treated as the evolution of cluster populations

$$A + A_{i-1} \underset{\alpha_i}{\overset{\beta_{i-1}}{\rightleftharpoons}} A_i$$

- Condensation rate constant, β_i, is approximated by the gas kinetic collision rate of molecules with the cluster, assuming unit sticking probability

$$\beta_i \approx \beta_i^{coll} = (c/4)\,(4\pi r_i^2)\,\rho_1$$
$$\approx (c/4)\,(4\pi r_i^2)\,(p_1/kT)$$



c = average gas-phase velocity, r_i = cluster radius,
ρ_1 = gas-phase monomer density

- Evaporation rate constant, α_i, is obtained from the condensation rate constant by detailed balance

$$\alpha_i = \beta_{i-1}\,(N_{i-1}^{EQ} / N_i^{EQ})$$

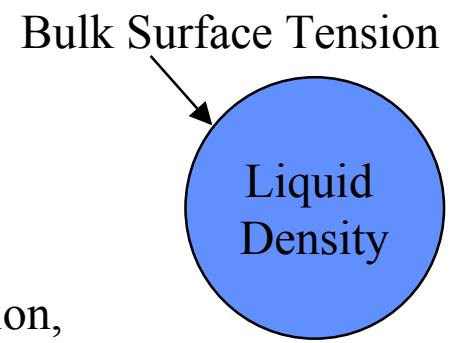
Classical Nucleation Theory

(continued)

- Equilibrium cluster distributions approximated from bulk properties (e.g., solvation energies and surface tensions)

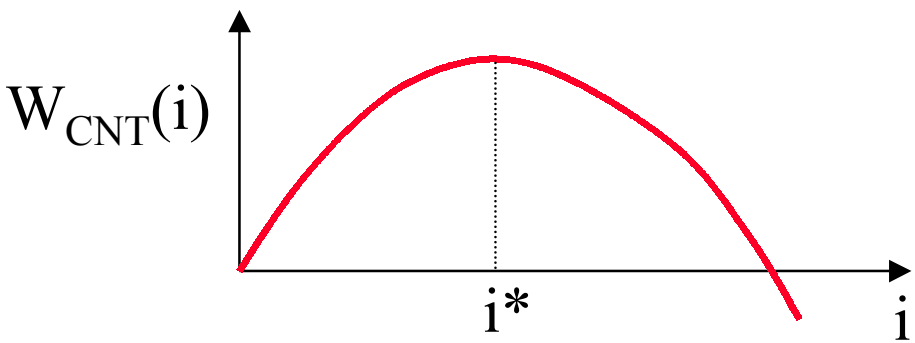
$$N_i^{EQ} = N_1 \exp(-W_{CNT}(i)/kT)$$

$$W_{CNT}(i) = -(4/3)\pi r_i^3 (kT/v_1) \ln S + 4\pi r_i^2 \sigma$$



v_1 = monomer volume in liquid, $S = N_1/N_1^{EQ}$ = supersaturation, σ = surface tension, r_i = cluster radius

- Kinetics is assumed to be pseudo-steady state and nucleation rate is approximated by flux through critical cluster that has lowest equilibrium cluster population



Molecular Description of Nucleation

<u>Accurate description of the molecular interactions</u>

- Electronic structure calculations of interaction energies
- Reliable fit to analytical functional form (direct dynamics approaches not affordable in MC simulations)

We use the Dang-Chang polarizable water potential

<u>Consistent theory of the phenomena – requires dynamics</u>

- Dynamical Nucleation Theory - focus on reaction dynamics and relevant kinetic parameters, rather than equilibrium properties of clusters

Focus of this presentation

<u>Adequate sampling of the relevant phase space for free energies</u>

- MC simulation in NPT for relative Helmholtz free energy
- Bennett's method for free energy differences
- Reinhardt's excess work method

Converged simulation require billions of MC moves - use MPP

Molecular Approaches to Nucleation

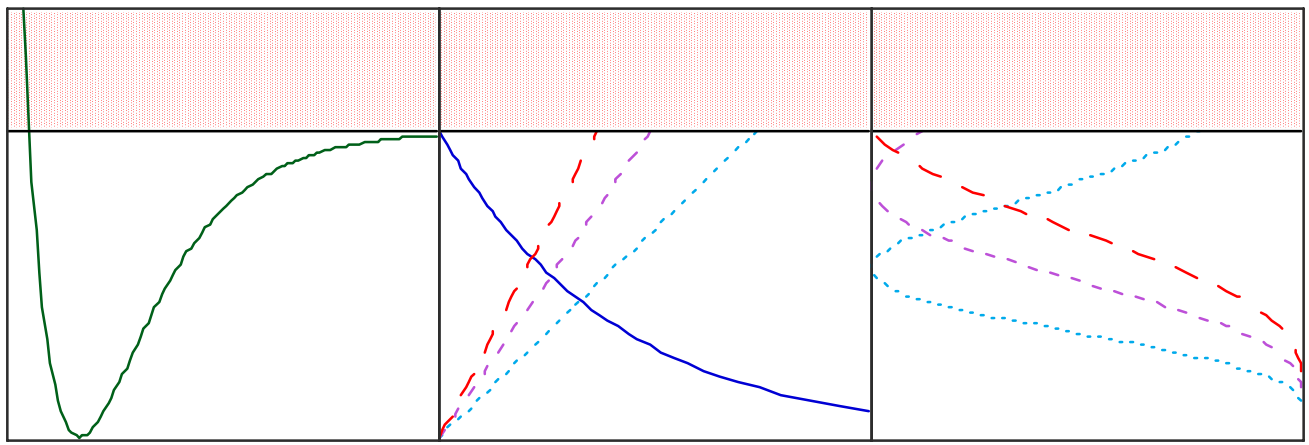
(e.g., Lee, Barker, Abraham, *JCP* ***58***, *3166*, 1973; Weakliem, Reiss, *JCP* ***99***, *5374*, 1993; Hale, *Aust. J. Phys.* ***49***, *425*, 1996; Kusaka, Wang, Seinfeld, *JCP* ***108***, *3416*, 1998)

- Nucleation is treated as the evolution of cluster populations (same as classical nucleation theory)
- Condensation rate constant, β_i, is approximated from the gas kinetic collision rate (same as classical nucleation theory)
- Evaporation rate constant, α_i, is obtained from condensation rate constant by detailed balance (same as classical nucleation theory)
- Equilibrium cluster populations obtained using statistical mechanics (requires calculating cluster partition functions or free energies)
- Problem - "nucleation is a dynamical process and should be described by a dynamical theory rather than an equilibrium one" (Reiss, Tabazadeh, Talbot). In the equilibrium molecular approach, this problem requires that the cluster be operationally defined.

Statistical Mechanics of Weakly Bound Clusters

- Equilibrium properties (thermochemistry) obtained using statistical mechanics from cluster partition functions
- The partition function of a dissociative cluster is arbitrarily large depending on the volume of the configuration space (entropy wins out).

$$Q = \int dE\ \rho(E)\ e^{-E/kT}$$



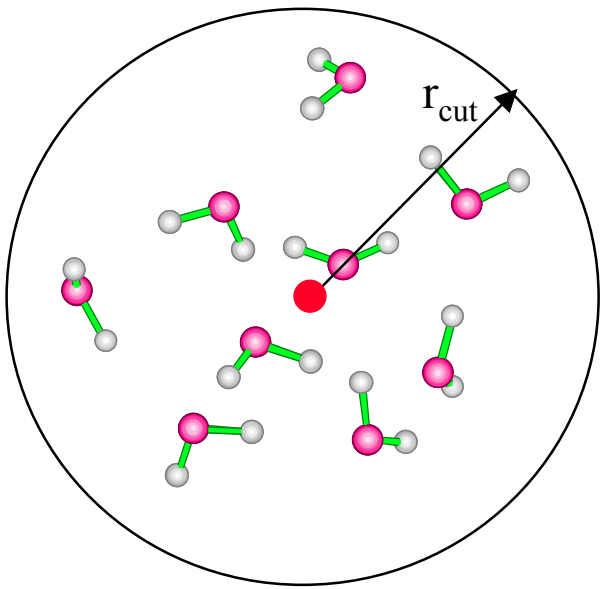
- Need an operational definition of a cluster that limits the phase space of the cluster, e.g., energy cut off, radial cut off, lifetime of dissociative states, etc.

Physically Consistent Cluster

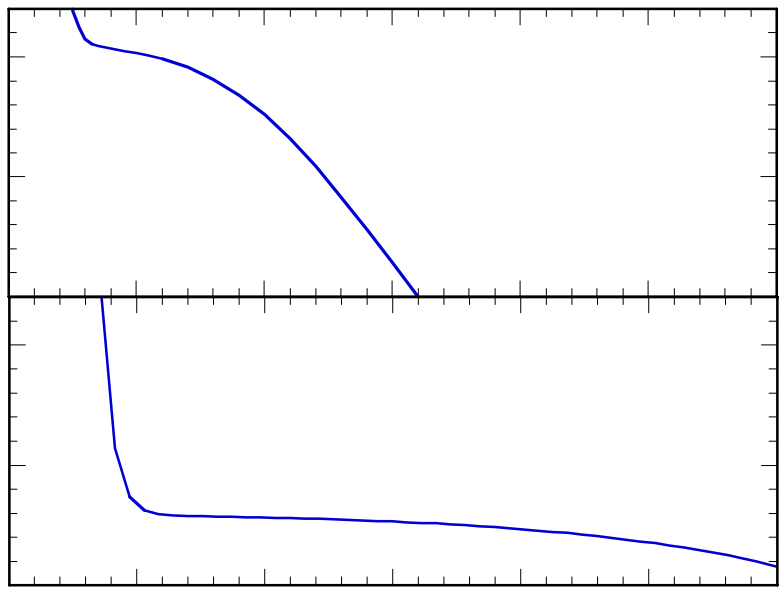
(Reiss, Katz, Cohen, *JCP* ***48****, 5553*, 1968;
Lee, Barker, Abraham, *JCP* ***58****, 3166*, 1973;

Reiss, Tabazadeh, Talbot, *JCP* ***92,*** *1266*, 1990)

Cluster defined to lie within a spherical shell of radius r_{cut} with center fixed on the center of mass of the cluster.



Helmholtz free energy for forming water clusters



Dynamical Nucleation Theory: A New Molecular Approach to the Kinetics of Nucleation

- Nucleation is treated as the evolution of cluster populations (same as classical nucleation theory)
- Dynamics of evaporation treated explicitly by approximating rate constant, α_i, using variational transition state theory (VTST) - cluster radius, r_i, (or volume v_i) consistently defined by TST dividing surface that minimizes the reactive flux
- Condensation rate constant, β_i, consistently obtained using VTST (VTST obeys detailed balance) - requires equilibrium constants
- Nucleation rates obtained by solving kinetic equations

$$A + A_{i-1} \underset{\alpha_i}{\overset{\beta_{i-1}}{\rightleftharpoons}} A_i$$

DNT Outline

- VTST calculation of rate constant, α_i, for evaporation of a monomer from an i-cluster

- Calculation of rate constant, β_i, for condensation of a monomer onto an i-cluster using detailed balance

$$\beta_{i-1} = \alpha_i K_{i,i-1}^{EQ} = \alpha_i (N_i^{EQ}/N_{i-1}^{EQ})$$

- Solve kinetic equations to obtain nucleation rate

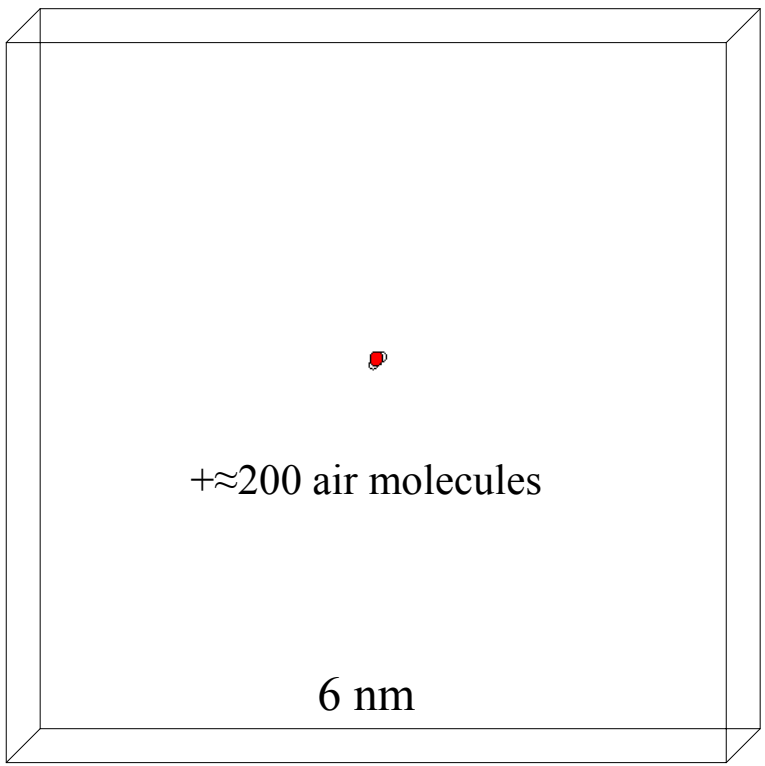
$$dN_i/dt = J_{i-1} - J_i$$

$$J_i = \beta_{i-1} N_{i-1} - \alpha_i N_i$$

Gas-Phase Perspective for Vapor-Phase Nucleation

- Condensation and evaporation processes are considered gas-phase association and dissociation reactions - rate constants can be calculated using variational transition state theory (VTST)

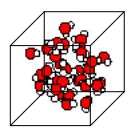
Water Vapor (298 K, S=10)



Water Vapor (S=10)

	T = 243 K	T = 298 K
$\rho^{-1/3}$ (nm)	19	6
$l_{W\text{-}W}$ (nm)	1000	300
$l_{W\text{-}Air}$ (nm)	70	80
$1/\beta_{30}$ (ns)	11	10
τ_{30} (ps)	70	60

Liquid water (298 K)



0.6 nm

Fundamentals of VTST

- Calculate equilibrium rate constants for elementary chemical reactions (forward and backward reactions obey detailed balance)
- Assume classical mechanics is valid to describe motion of nuclei (quantum mechanical effects can be added later)

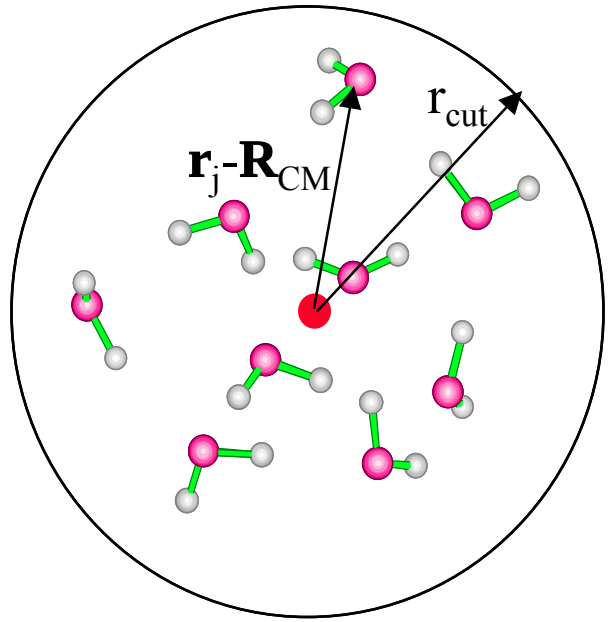
Wigner's fundamental assumption [Trans. Faraday Soc. **34**, 70 (1938)]:

- *Reactive trajectories originating in reactants must cross the dividing surface only once and proceed to products, i.e., reactive flux at dividing surface approximated by forward flux*

Corollaries to the fundamental assumption (Wigner, Horiuti, Keck)

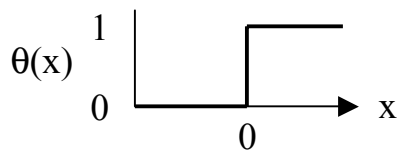
- *TST overcounts reactive trajectories and overestimates the exact classical rate constant*
- *The best dividing surface can be found variationally to minimize the TST rate constant*

VTST for Cluster Evaporation



- Dividing surface $S_i(r_{cut},\mathbf{r}^{(i)})=0$ chosen as sphere of radius r_{cut} centered as center of mass of i-cluster $[\mathbf{r}^{(i)}=\{\mathbf{r}_j\}_{j=1,\ldots,i}]$:

$$\Theta(S_i)=\prod_j \theta(r_{cut}-|\mathbf{r}_j-\mathbf{R}_{CM}|)$$



- Reactant partition function $q_i^R(r_{cut})$ and Helmholtz free energy $A_i(r_{cut})$ defined by:

$$q_i^R(r_{cut}) = \exp[-\beta A_i(r_{cut})] = (i!\, h^{3i})^{-1} \int d\mathbf{r}^{(i)}\, d\mathbf{p}^{(i)}\, e^{-\beta H}\, \Theta(S_i)$$

- TST approximation to the evaporation rate constant defined by:

$$\alpha_i(r_{cut}) = [i!\, h^{3i}\, q_i^R(r_{cut})]^{-1} \int d\mathbf{r}^{(i)}\, d\mathbf{p}^{(i)}\, e^{-\beta H}\, |\partial\Theta(S_i)/\partial t|/2$$

$$\partial\Theta(S_i)/\partial t = (\mathbf{p}^{(i)}/m)\bullet(\partial\Theta(S_i)/\partial\mathbf{r}^{(i)})$$

VTST for Cluster Evaporation (con't.)

- For the choice of a spherical dividing surface, the evaporation rate takes the form:

$$\alpha_i(r_{cut}) = (c/4)\,(4\pi r_{cut}^2)\,(-dA_i/dv)/kT = (c/4)\,(4\pi r_{cut}^2)\,(p_{int}/kT)$$

Note similarity to approximate expression for condensation:

$$\beta_i^{coll} = (c/4)\,(4\pi r_i^2)\,\rho_1 \approx (c/4)\,(4\pi r_i^2)\,(p_1/kT)$$

c = average gas-phase velocity, r_{cut} = cluster radius,

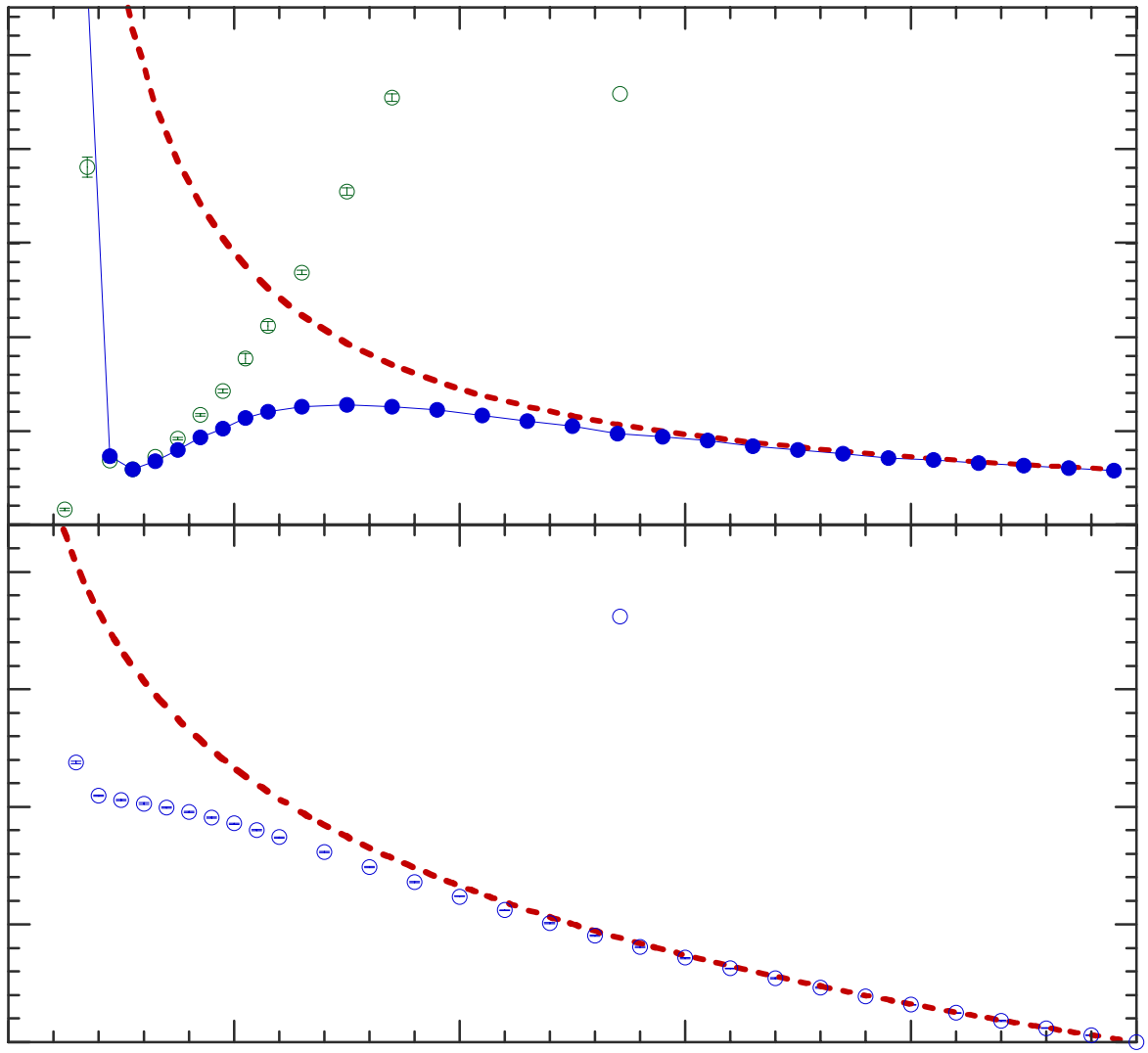
ρ_1 = gas-phase monomer density, $v = 4\pi r_{cut}^3/3$

- The variational procedure minimizes the reactive flux to find the best dividing surface:

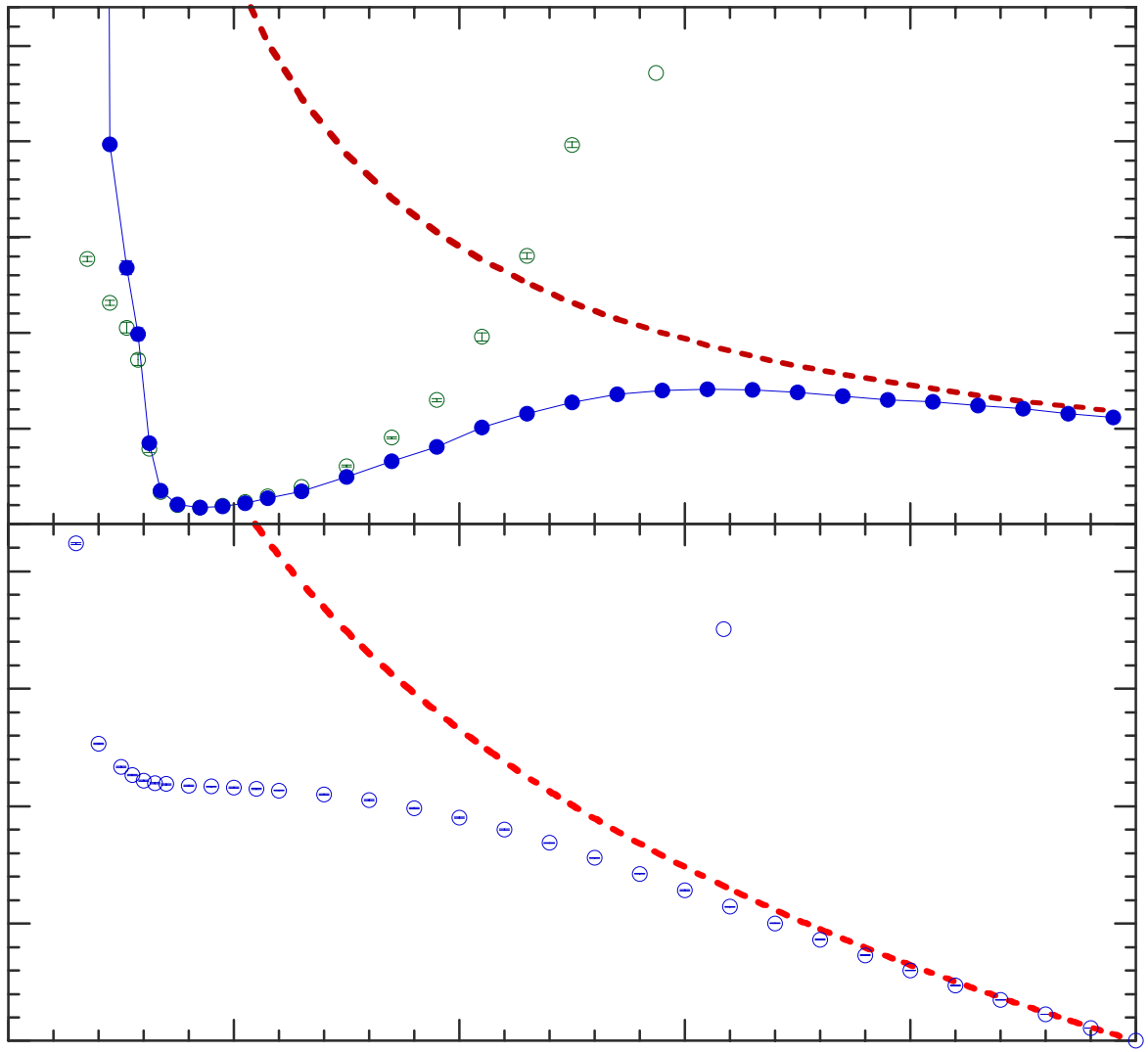
$$d[\exp(-A_i/kT)\,\alpha_i]/dr_{cut} = 0$$

PRL **82**, 3484 (1999), JCP **110**, 7951 (1999)

Helmholtz Free Energy for Forming $(H_2O)_2$ at 243 K



Helmholtz Free Energy for Forming $(H_2O)_3$ at 243 K



DNT Outline

- VTST calculation of rate constant, α_i, for evaporation of a monomer from an i-cluster

- Calculation of rate constant, β_i, for condensation of a monomer onto an i-cluster using detailed balance

$$\beta_{i-1} = \alpha_i K_{i,i-1}^{EQ} = \alpha_i (N_i^{EQ}/N_{i-1}^{EQ})$$

- Solve kinetic equations to obtain nucleation rate

$$dN_i/dt = J_{i-1} - J_i$$

$$J_i = \beta_{i-1} N_{i-1} - \alpha_i N_i$$

VTST for Condensation Rate Constant: Equilibrium Theory of the Vapor

(JCP **111**, 4688, 1999)

- Condensation rate constant obtained from evaporation rate constant using detailed balance: $\beta_{i-1} = \alpha_i K_{i,i-1}^{EQ} = \alpha_i (N_i^{EQ}/N_{i-1}^{EQ})$
- Equilibrium distribution is the most probable distribution subject to constant total number of molecules and volume

(Reiss, Katz, Cohen, *JCP* ***48****, 5553,* 1968; Reiss, Tabazadeh, Talbot, *JCP* ***92,*** *1266,* 1990)

$$N_i^{EQ} = \exp\{-[A_i^{\ddagger} + pv_i^{\ddagger} - kT \ln(i^{3/2} \gamma V) - i\mu_1]/kT\}$$

p = system pressure, $v_i^{\ddagger}$ = cluster volume, V = system volume

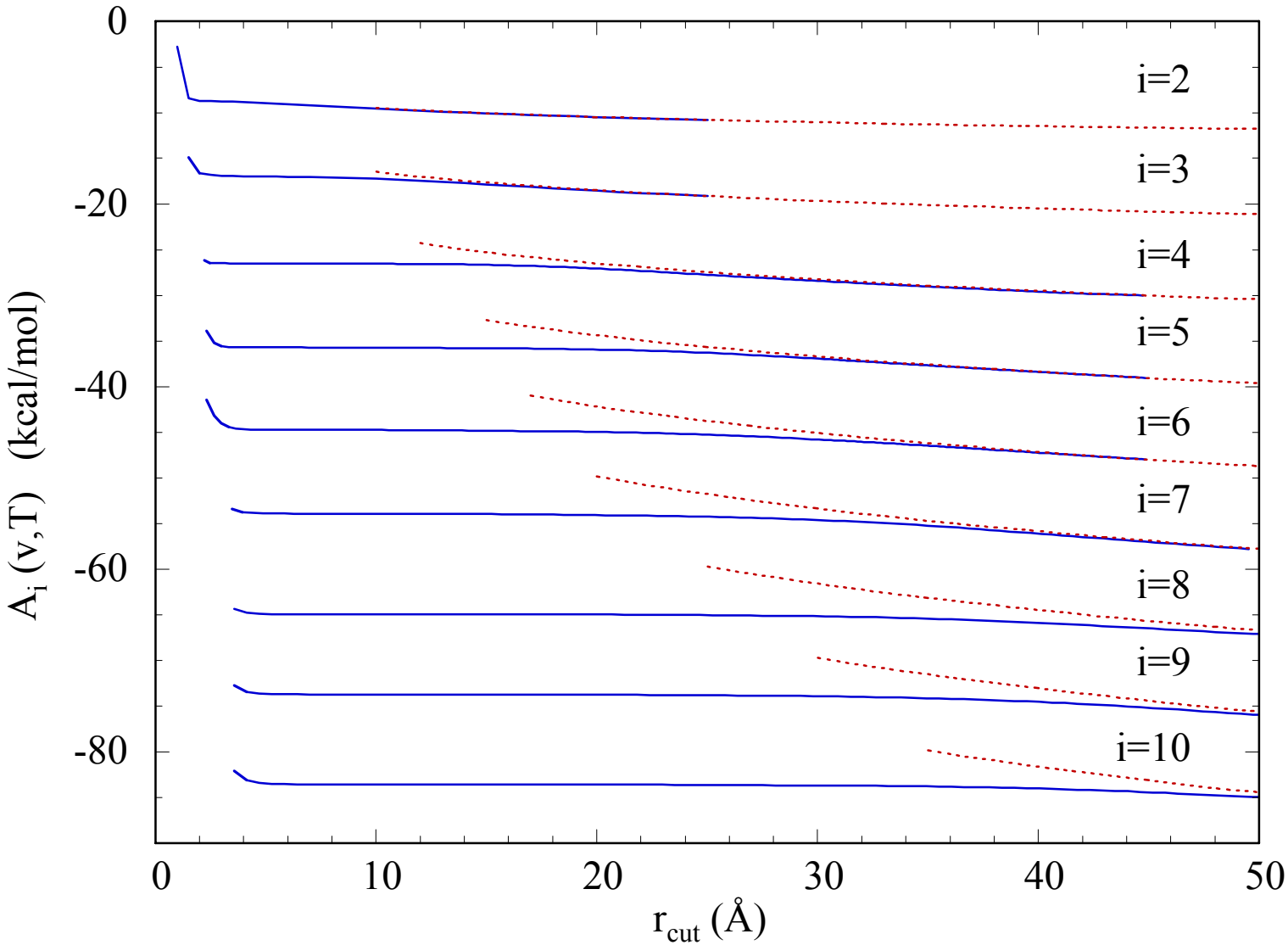
$N_1/V = q_1 \exp(\mu_1/kT)$ = monomer concentration

μ_1 = monomer chemical potential, q_1 = monomer p.f. (trans. & rot.)

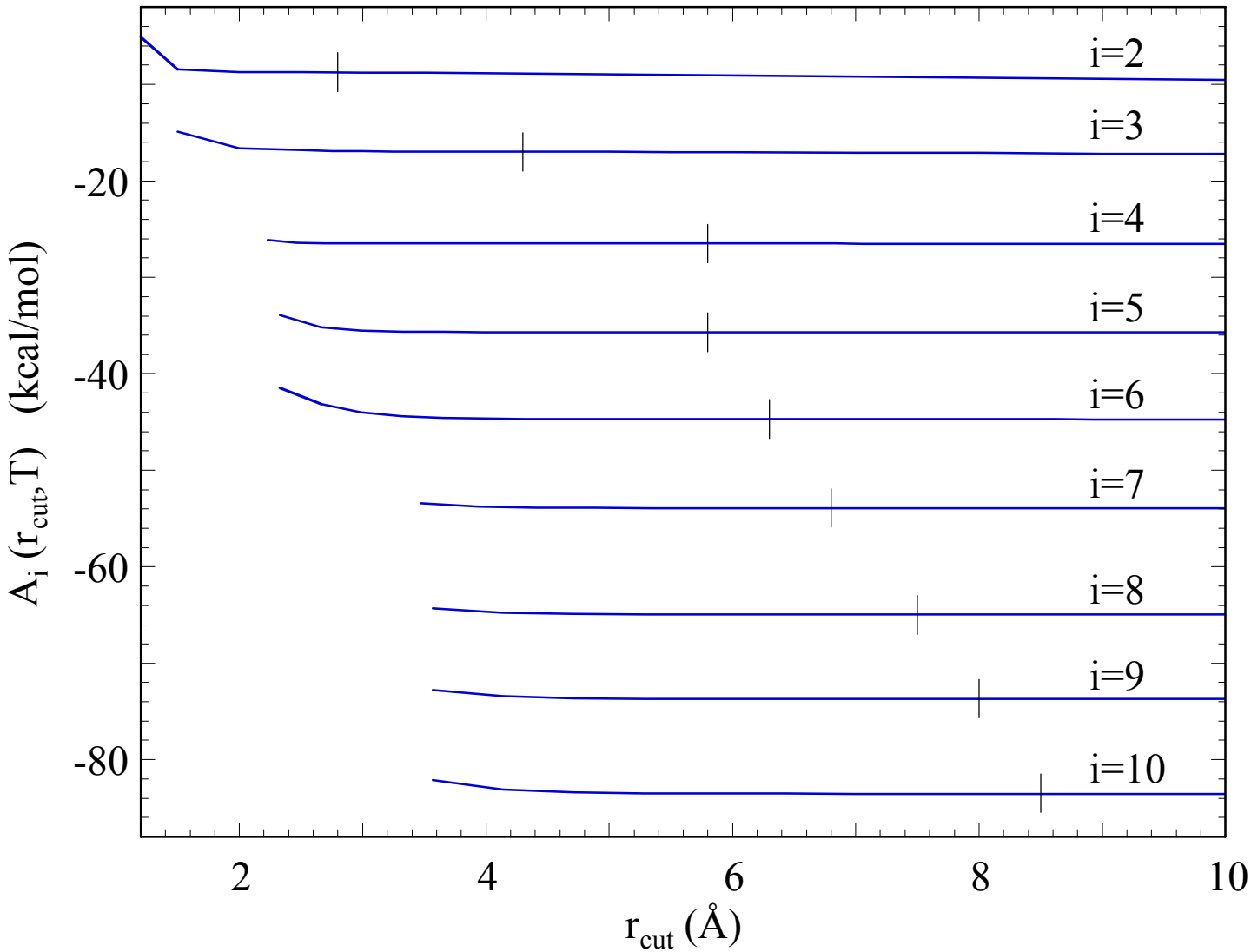
γ = monomer trans. p.f.

- Equilibrium constants require differences in absolute Helmholtz free energies $(A_i^{\ddagger} - A_{i-1}^{\ddagger})$

Helmholtz Free Energy for Forming $(H_2O)_i$ (i = 2 -10) at 243 K



Helmholtz Free Energy for Forming $(H_2O)_i$ (i = 2 -10) at 243 K



Kinetics of Water Cluster Evaporation and Condensation

($T = 243$ K, $\rho_1 = 1.5 \times 10^{17}$ cm^{-3})

i	r_i (Å)	$(-dA_{iv}/dv)$ (torr)	α_i (10^9 s^{-1})	β_i (10^7 s^{-1})	$K_{i-1,i}^{EQ}$
2	2.8	32000	160	6.9	0.0004
3	4.3	4000	49	17	0.0034
4	5.8	210	4.7	18	0.039
5	5.8	450	10.0	22	0.023
6	6.3	490	12.8	26	0.021
7	6.8	310	9.4	29	0.031
8	7.5	190	7.2	26	0.037
9	8.0	120	5.2	33	0.064
10	8.5	96	4.6	28	0.061
11	8.5		4.4		
12	9.0		4.2		
13	9.5		3.5		
14	9.5		3.0		
15	9.5		3.3		

DNT Outline

- VTST calculation of rate constant, α_i, for evaporation of a monomer from an i-cluster

- Calculation of rate constant, β_i, for condensation of a monomer onto an i-cluster using detailed balance

$$\beta_{i-1} = \alpha_i K_{i,i-1}^{EQ} = \alpha_i (N_i^{EQ}/N_{i-1}^{EQ})$$

- Solve kinetic equations to obtain nucleation rate

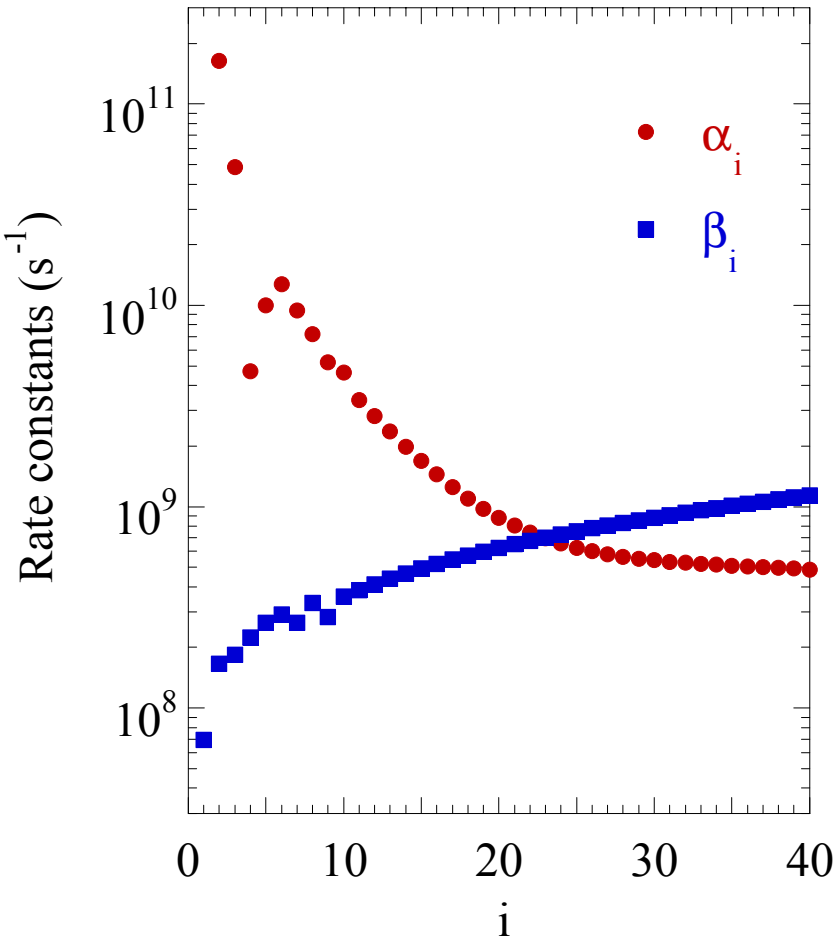
$$dN_i/dt = J_{i-1} - J_i$$

$$J_i = \beta_{i-1} N_{i-1} - \alpha_i N_i$$

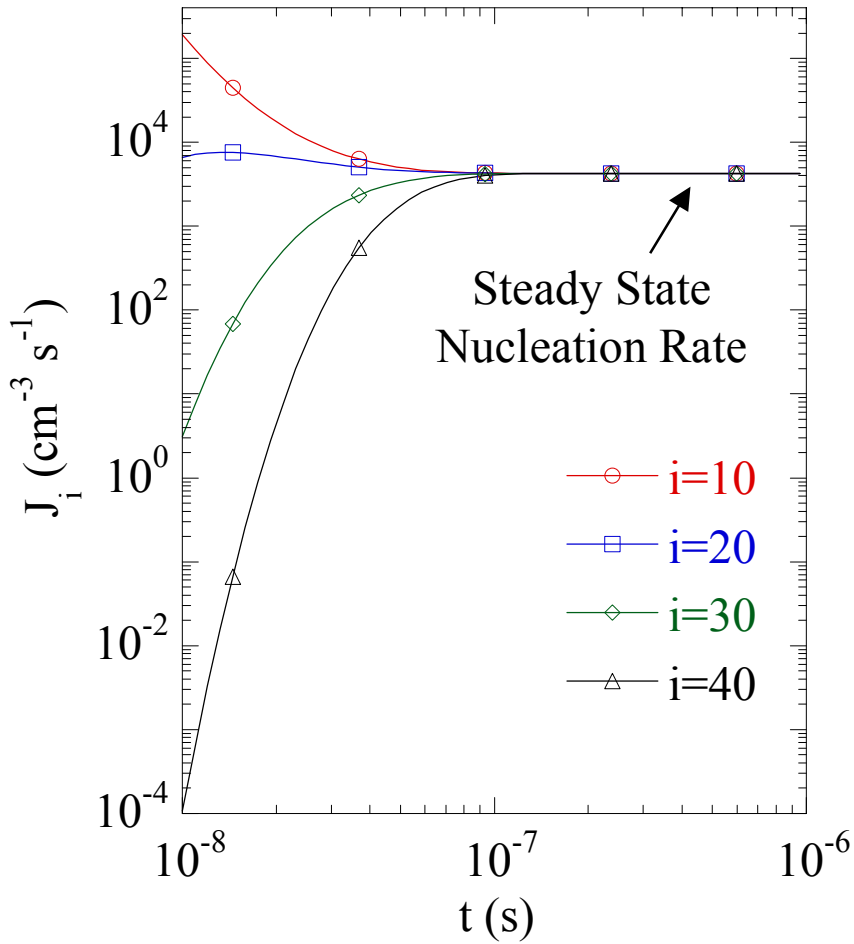
Kinetics of Water Nucleation

($T = 243$ K, $\rho_1 = 1.5\times10^{17}$ cm^{-3})

Rate Constants for Evaporation (α_i) and Condensation (β_i)



Transient Flux From Cluster i to Cluster i+1, J_i

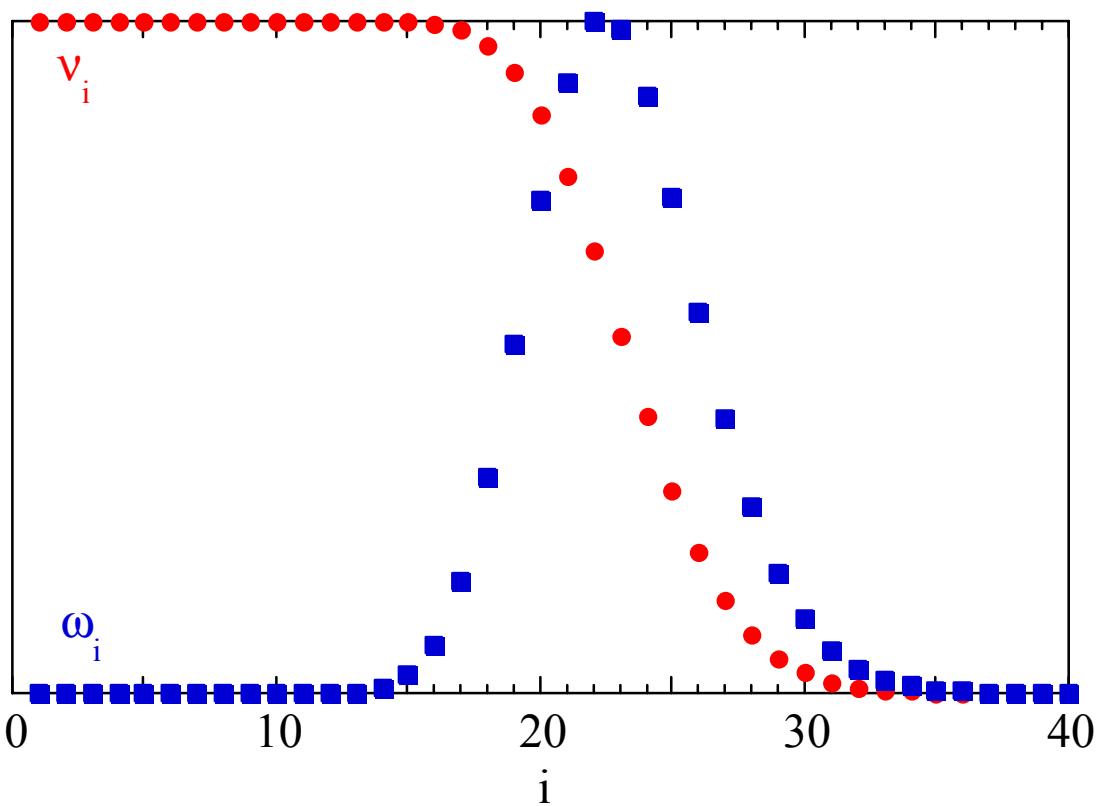


Sensitivity of Nucleation Rate to Kinetic Parameters

Water Nucleation ($T = 243$ K, $\rho_1 = 1.5\times10^{17}$ cm^{-3})

ν_i = sensitivity with respect to rate parameters, α_i and β_i

ω_i = sensitivity with respect to condensation rate, β_i, and equilibrium cluster distribution, N_i^{EQ}

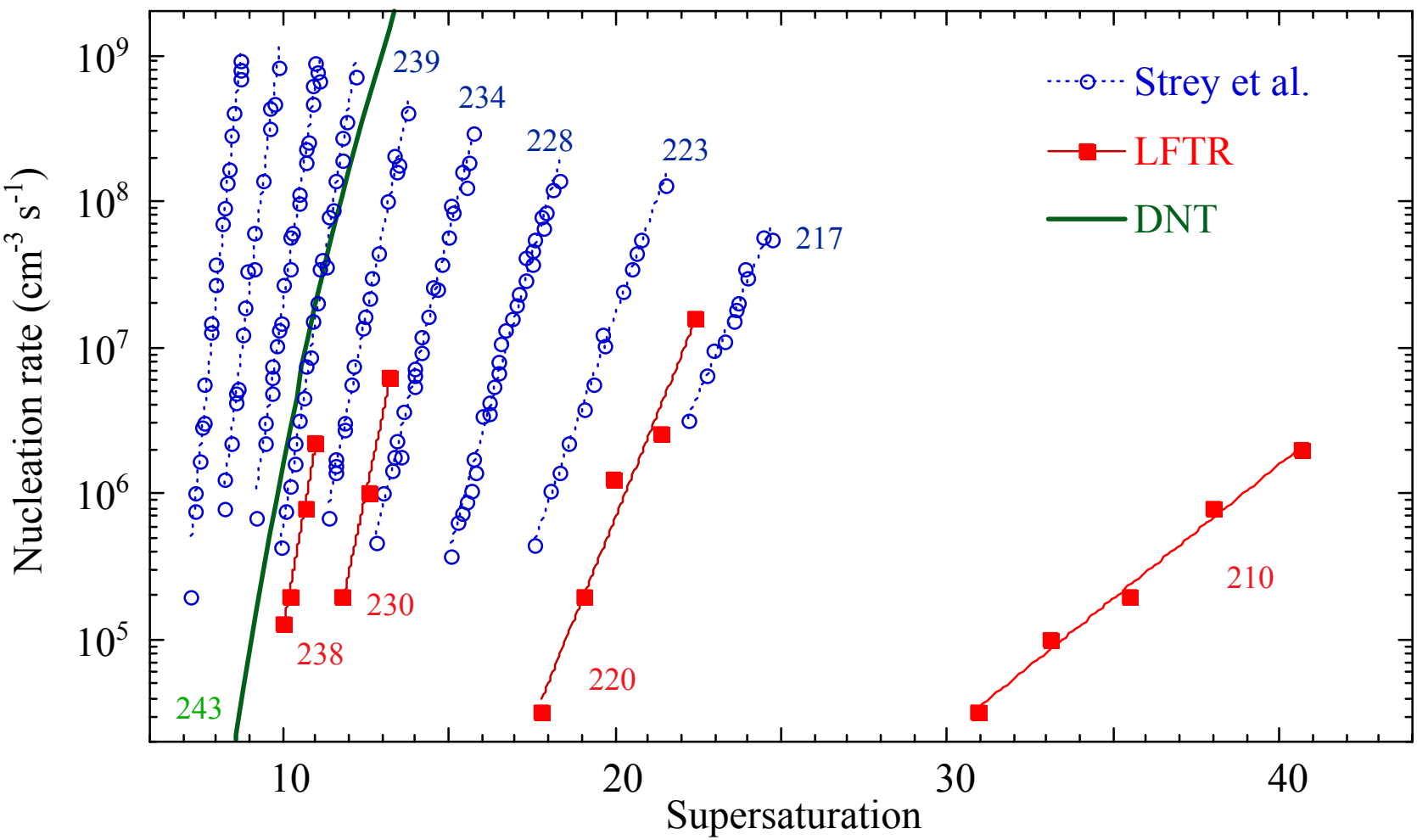


$$N_i^{EQ} = \frac{\beta_{i-1}}{\alpha_i} N_{i-1}^{EQ}$$

$$N_i^{EQ} = N_1 \prod_{i'=1}^{i-1} \frac{\beta_{i'}}{\alpha_{i'+1}}$$

Comparison of Measured and Calculated Nucleation Rates for Water

(Temperatures in K – Strey et al. high temperatures are 259, 254, 249, 244)



Critique of DNT

- Current formalism is limited to monomer addition and loss, *but* VTST can be extended to loss/gain of clusters (requires new definition of dividing surfaces describing these processes)
- Evaporation rate constants computed using classical mechanics, *but* tunneling is unimportant (no intrinsic barrier) and quantum effects on bound vibrations can be included using Feynmann path integrals
- Breakdown of 'no recrossing assumption' can lead to overestimates of the rate constants, *but* recrossing effects can be mitigated by improved dividing surfaces or can be calculated from classical trajectories
- Equilibrium of reactant energy states may break down if evaporation is faster than thermalizing collisions with buffer gases, *but* this approximations becomes better for larger clusters and effects on smaller clusters can be estimated using RRKM theory
- Computed rate constants are sensitive to the intermolecular potentials, *and* obtaining highly accurate potentials for many molecule clusters remains a challenge

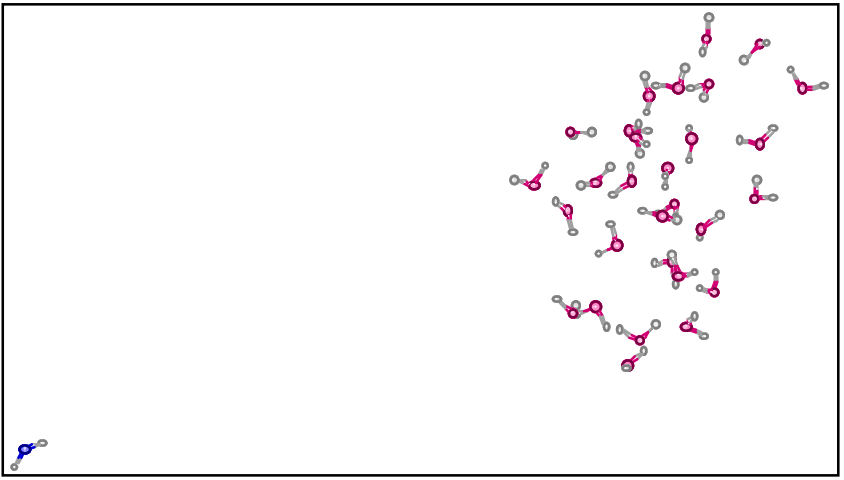
Validity of the Fundamental Assumption of TST for Cluster Kinetics

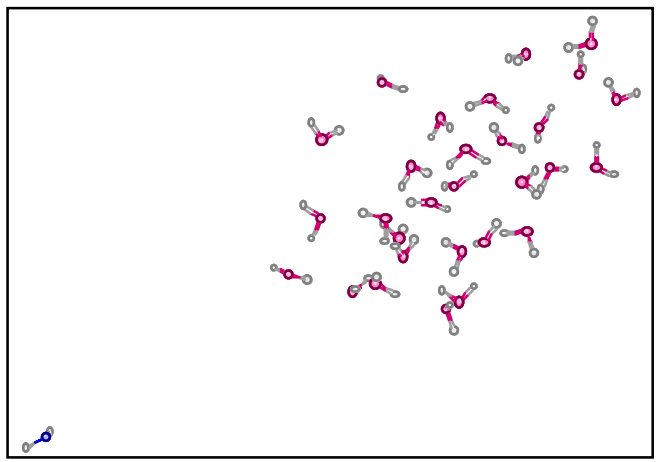
- Use classical trajectories to test for breakdown of the fundamental assumption, i.e., to calculate recrossing correction factor

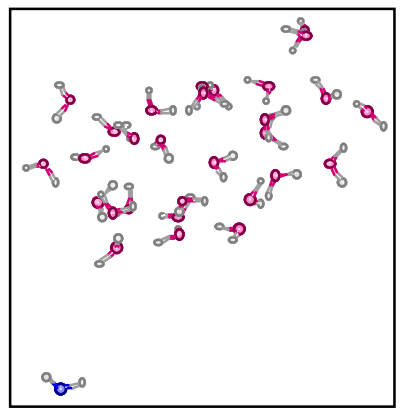
$$k^{Cl} = \kappa^{Recross}\, k^{VTST}$$

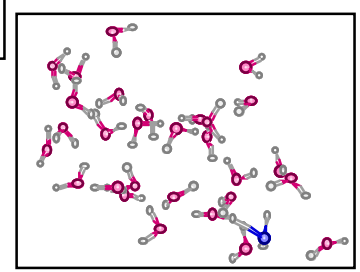
- Detailed balance insures that recrossing factor for β_{i-1} is the same as the recrossing factor for α_i; evaporation is an infrequent event, so use classical trajectories to simulate condensation

Snapshots from $H_2O + (H_2O)_{29}$ Trajectory

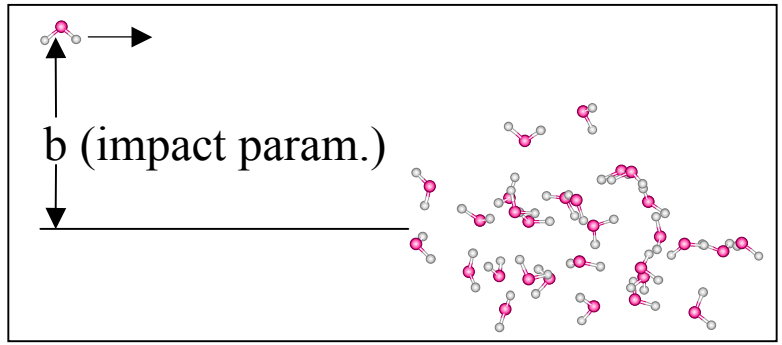




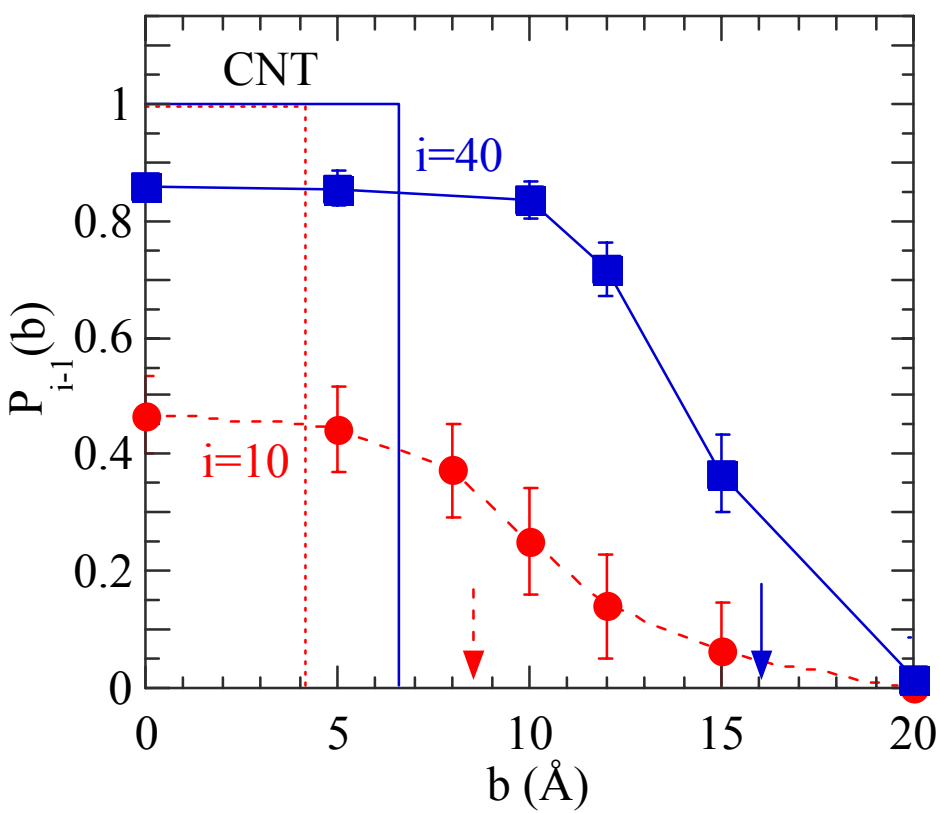




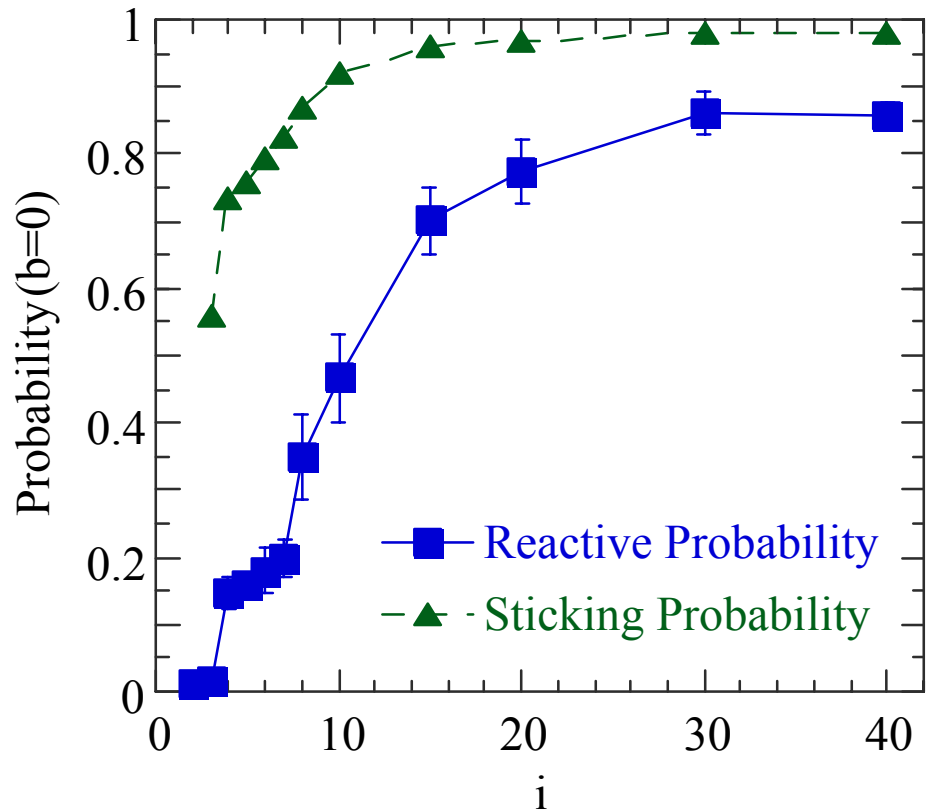
Trajectory Studies of Condensation Reaction



Reactive probability

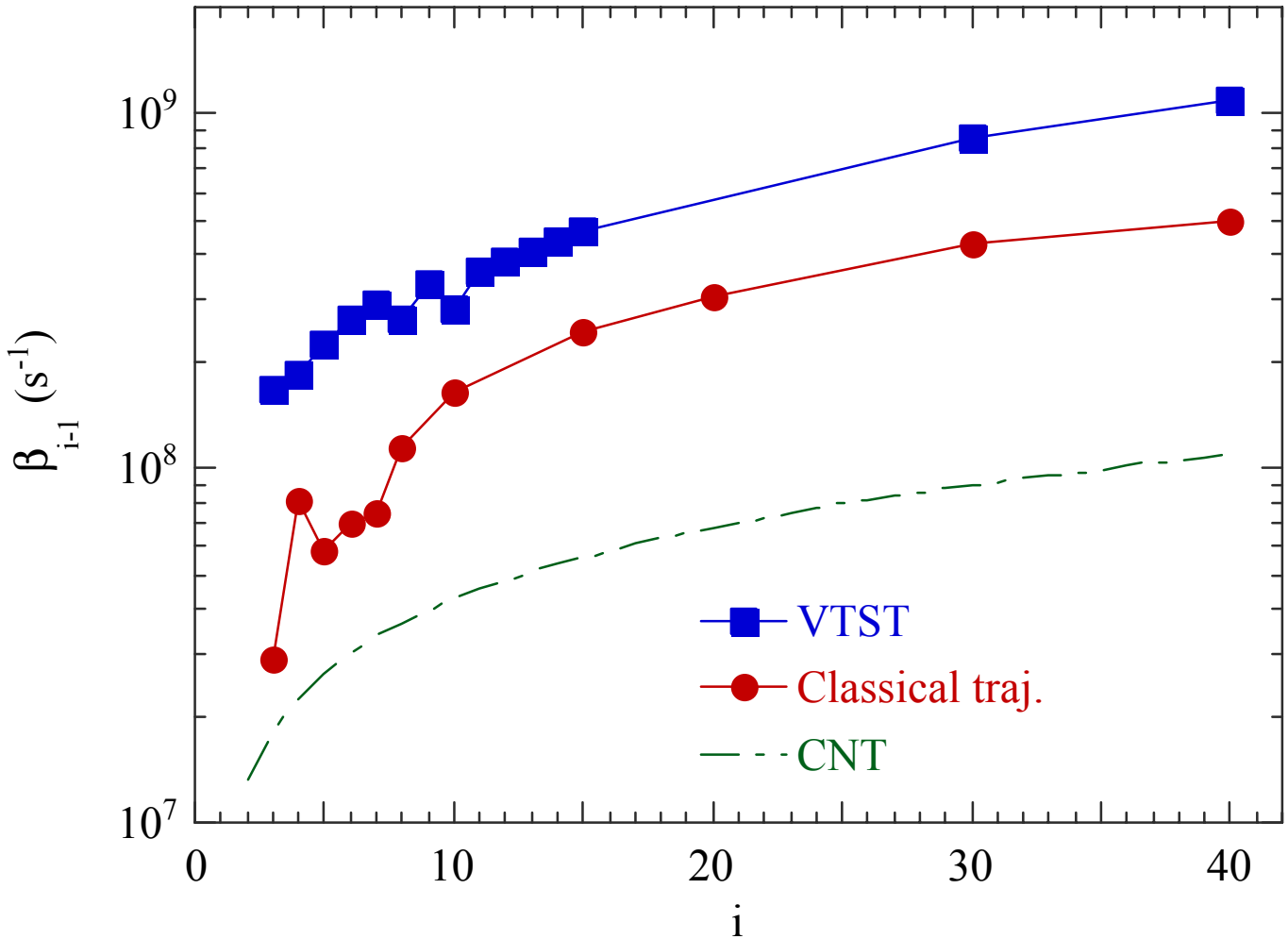


Probabilities at b=0



Condensation Rate Constants

$$\beta_i = \bar{c}\, \rho_1 \int_0^\infty db\; 2\pi b\; P_i(b)$$



Summary and Future Directions

- New molecular theory of nucleation kinetics has been developed - cluster is defined by spherical shell that minimizes flux
- New theory shows the rate of evaporation is proportional to the rate of change of the free energy with respect to shell radius (Previous molecular theories assumed free energy was insensitive to radius of shell enclosing cluster)
- Computationally tractable approach for water cluster evaporation (and condensation)
- Formalism has been extended to multicomponent systems
- Tests are being performed of sensitivity of nucleation rates to intermolecular potentials
- Nucleation rates for water nucleation are being calibrated and compared with new experimental data (Mikheev, Laulainen, Barlow)
- Extend applications to binary and ternary nucleation (sulfuric acid - water - ammonia)