

Sugar Alcohol based Materials for Seasonal Storage Applications

FP7 project - SAM.SSA

Sugar Alcohol based Materials for Seasonal Storage Applications

Workshop and Onsite Demonstration– CiCenergigune

Miñano, Alava, Spain



Session 1, Sugar Alcohol Development



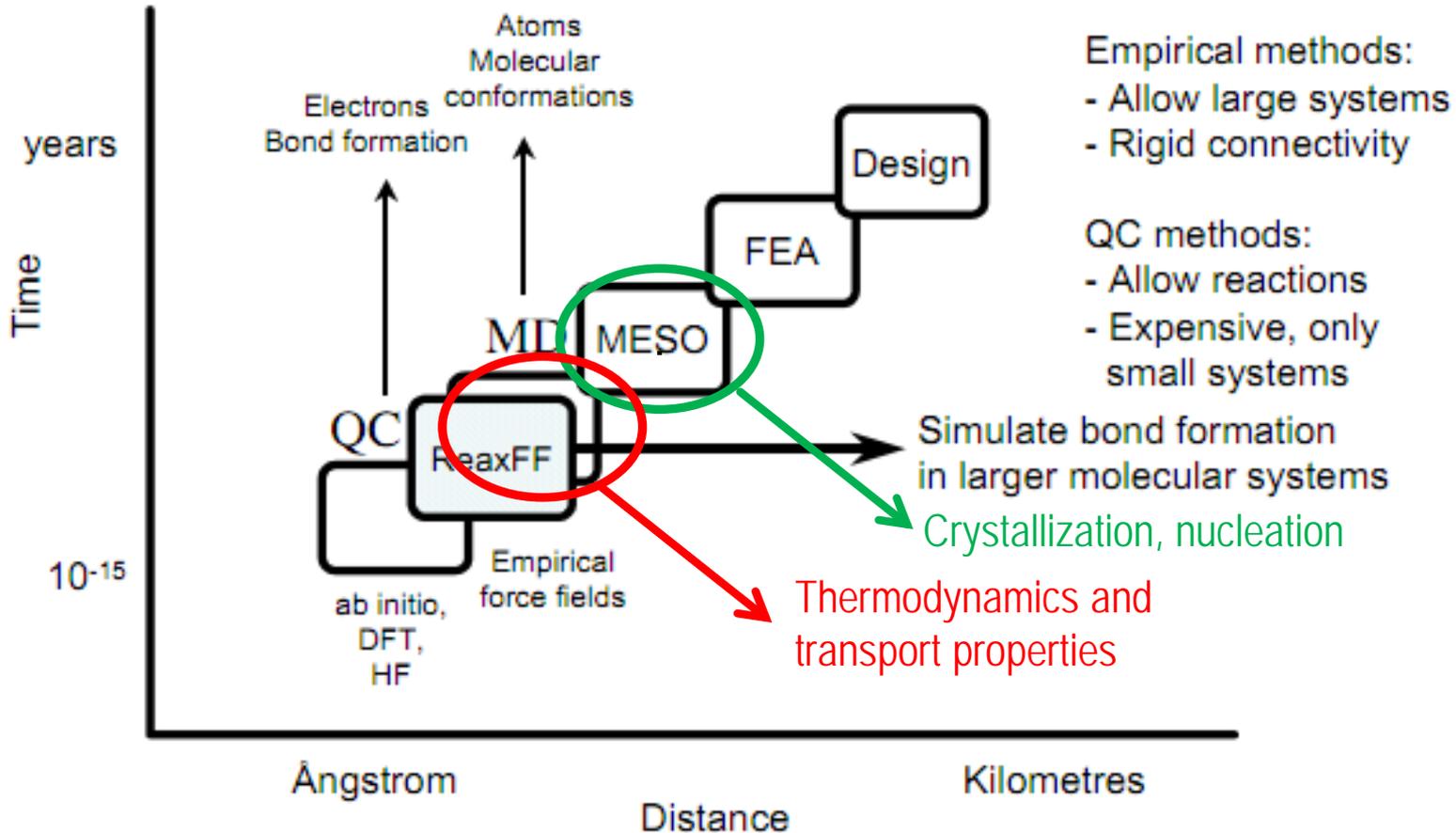
Presented by: H.Zhang
Work Package Leader: S.V.Nedea
Participants: TU/e,CNRS,Rhodia,FhG

Multi-scale modelling of SA properties and crystallization kinetics



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Hierarchy of computational chemical methods



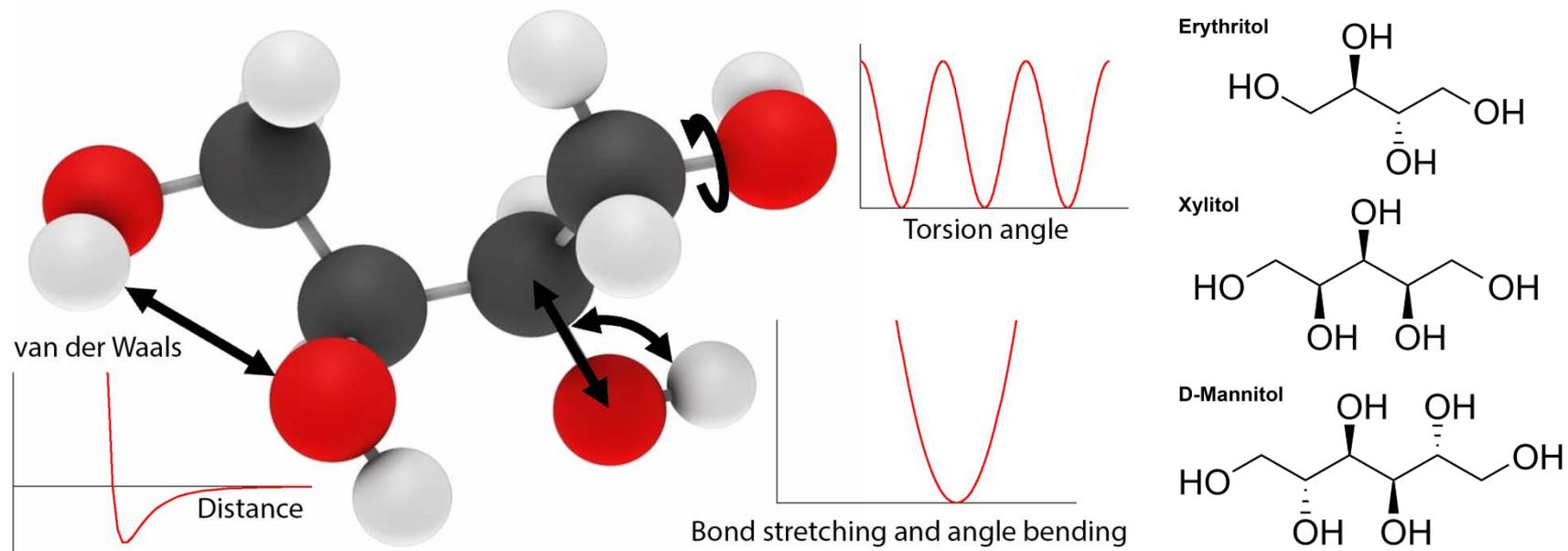
- First principle quantum mechanical (density functional theory) calculations



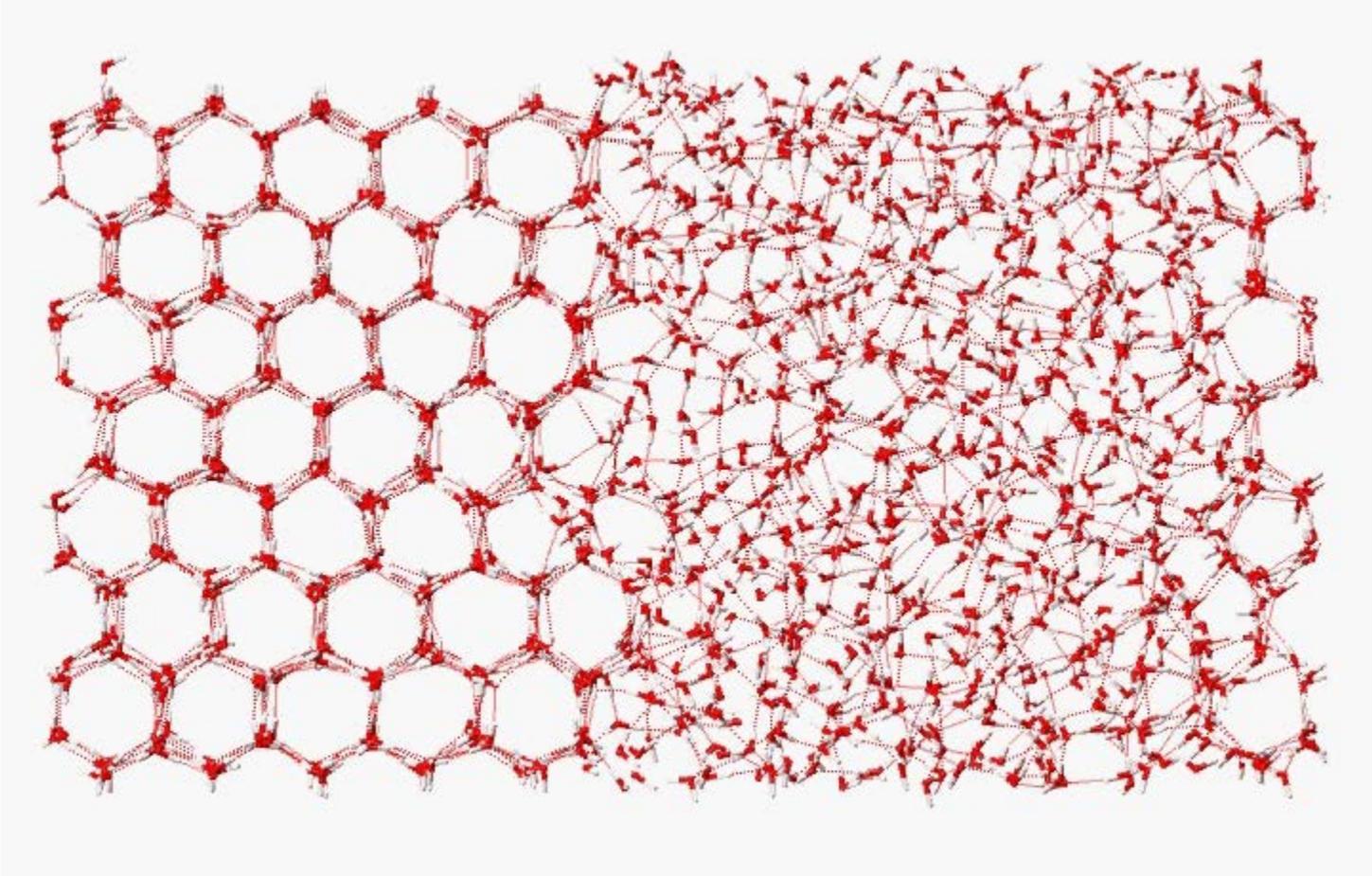
By fitting potential energies

- Force field: a set of interaction rules that governs the atomic motion

- Atoms move according to Newton's equations of motion
- Van der Waals interaction, electrostatic interaction
- Bond stretching, angle bending, dihedral torsion
- Typical time step 1fs (10^{-15} s), box size 10nm



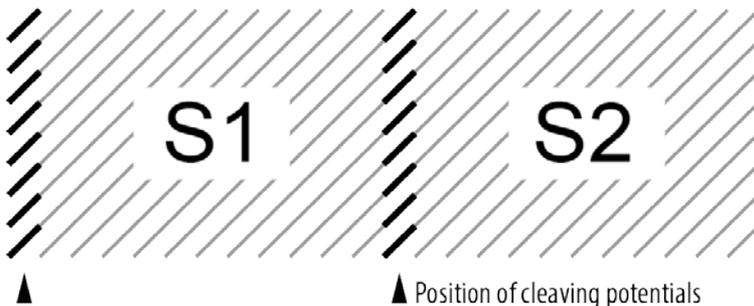
Demonstration: Water Crystal Growth



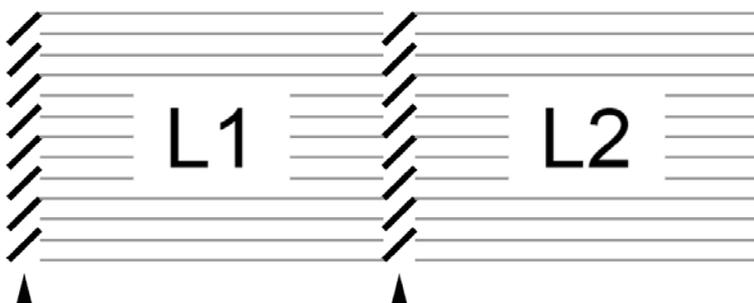
- Sugar alcohols have much lower crystallization kinetics and therefore direct simulation becomes unfeasible
- A meso-scale model is therefore needed to describe lattice growth of sugar alcohols.
- Key properties that determines nucleation and crystallization kinetics and morphology:
 - Bulk free energy of both solid and supercooled liquid state*
 - Anisotropic solid-liquid interfacial free energy*
 - Viscosity, to extract activation energy of viscous flow*
 - Lattice parameters, temperature dependent density*
 - ...
- Most properties are easily calculated using modern software packages with their built-in functions

- Interfacial free energies are calculated using a Wall Cleaving method.
- An artificial wall is generated that guides a layer of liquid molecule to form a crystalline structure
- Use transition state sampling to sum up the free energy difference between the initial and final state

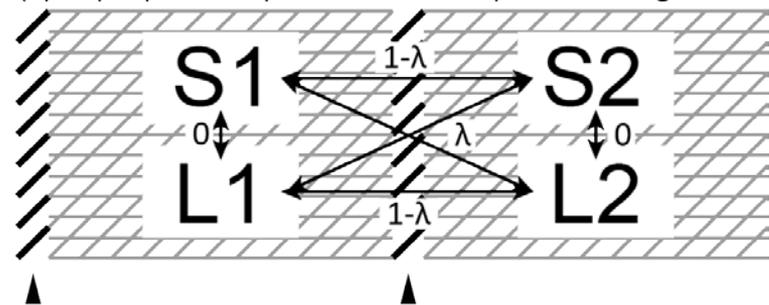
(a) Crystal (solid) with cleaving potential



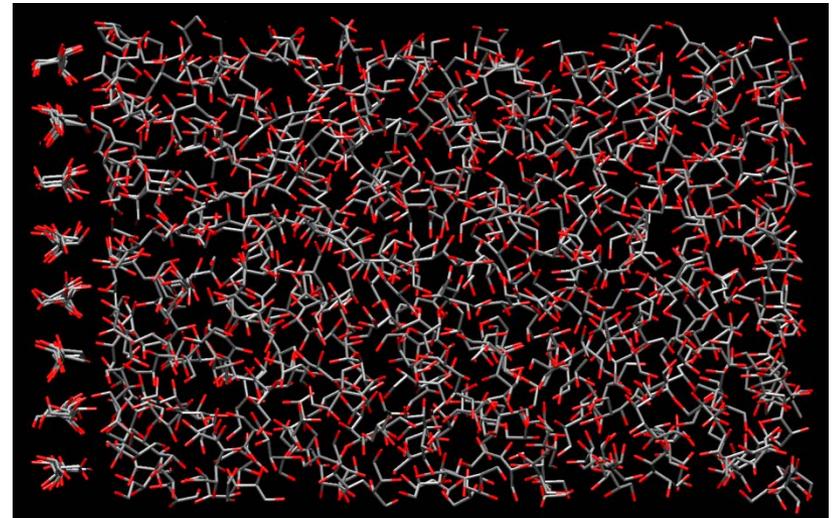
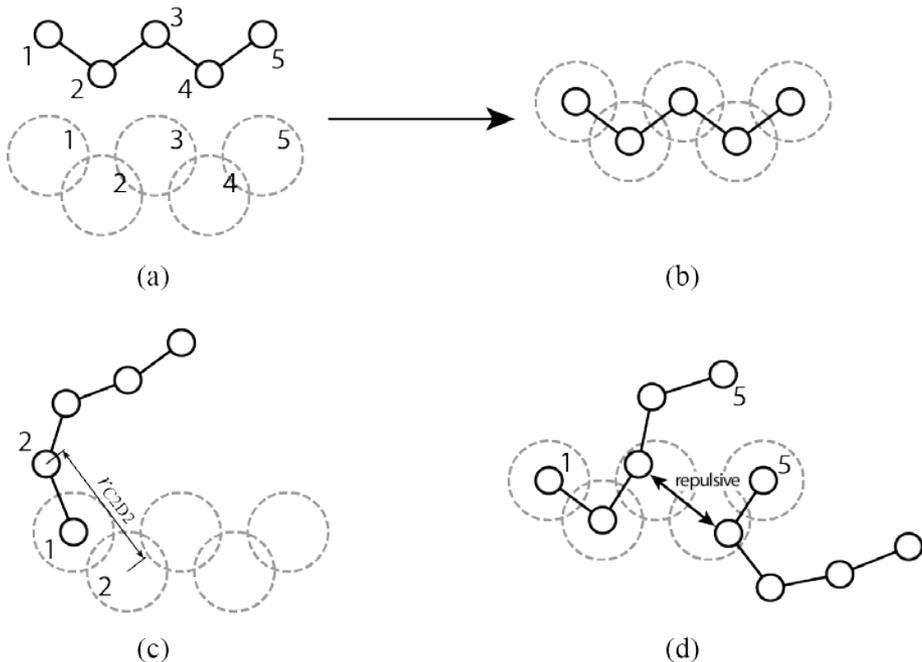
(b) Melt (liquid) with cleaving potential



(c) Superposed liquid and solid in pbc rearrangement

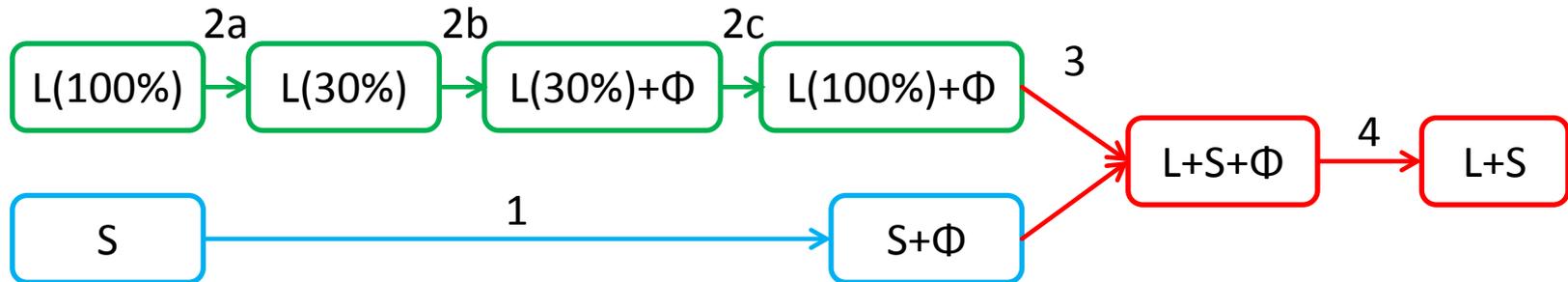


- Cleaving potential is carefully designed to trap all atoms of a molecule
- After cleaving, a layer of crystalline structure is formed



▲ Position of Cleaving Potentials

Interfacial Free Energy Calculation



	1 (kJ/mol)	2a (kJ/mol)	2b (kJ/mol)	2c (kJ/mol)	3(2x) (kJ/mol)	4 (kJ/mol)	SUM (kJ/mol)	2A (nm ²)	IFE (mJ/m ²)
Xyl (1 0 0)	-4050.9		-2605.4	-8381.2	-118.5	+7801.2	1029.7	25.9034	66.01
Xyl (0 1 0)	-4050.2	+8325.3	-2944.7	-8288.3	-143.7	+7642.4	612.7	23.8518	42.66
Xyl (0 0 1)	-4070.0		-2940.6	-8270.3	225.5	+8015.7	1172.8	24.0269	81.05
Xyl ISO	Isotropic approximation with SU hysteresis method								~58
Man (1 0 0)	-4950.4		-3676.6	-12724.5	+411.9	+9888.5	1280.6	23.6141	90.05
Man (0 1 0)	-3810.5	12537.6	-2788.7	-12686.5	+131.1	+7759.8	1077.3	22.9631	78.24
Man (0 0 1)	-3987.6		-2736.4	-12633.0	+127.6	+7533.9	778.4	23.3600	55.33
Man ISO	Isotropic approximation with SU hysteresis method								~78



Two Phase Thermodynamics (2PT)

- Of all condensed phases, thermodynamic properties of (supercooled) liquid state is difficult to calculate
- 2PT assumes the vibrational density of state of liquid can be decomposed into a solid-like component and gas-like component, and so is its thermodynamics properties

- Consistent theory in all condensed phases
- Converge in 20ps

- Translational

$$D_{\text{tn}}(\nu) = \frac{2}{k_B T} \sum_{k=x,y,z} \sum_{j=1}^{N_M} \lim_{\tau \rightarrow \infty} \frac{M}{2\tau} \left| \int_{-\tau}^{\tau} v_{c,j}^k(t) e^{-i2\pi\nu t} dt \right|^2$$

- Rotational

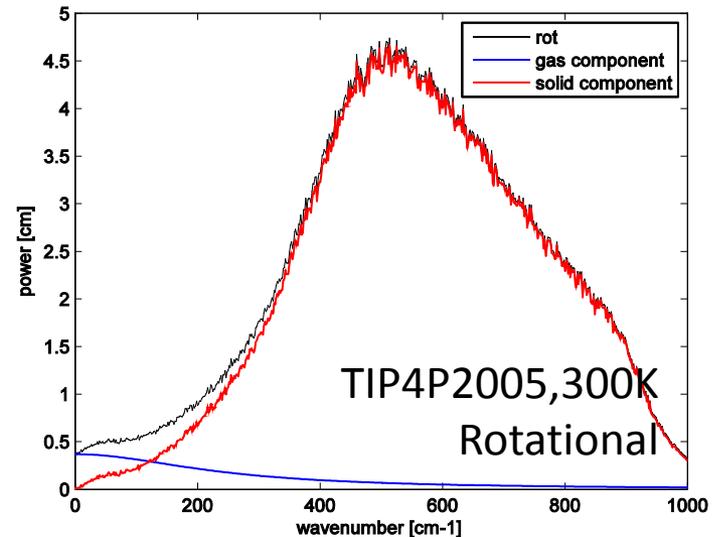
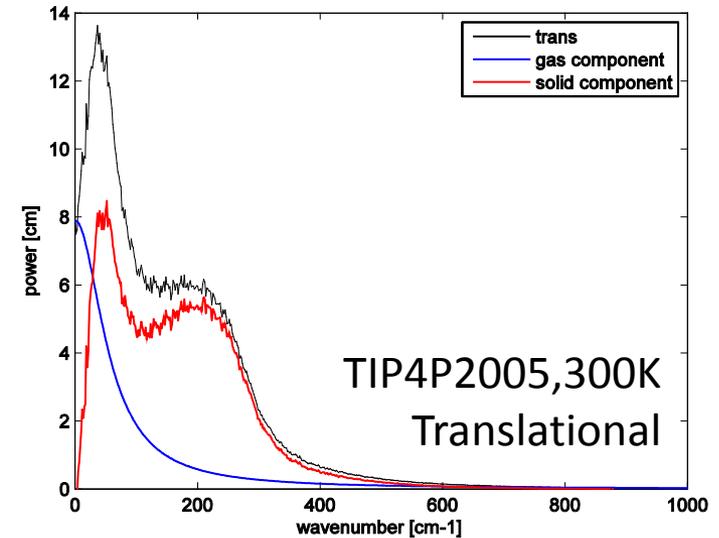
$$D_{\text{rot}}(\nu) = \frac{2}{k_B T} \sum_{k=1,2,3} \sum_{j=1}^{N_M} \lim_{\tau \rightarrow \infty} \frac{I_j^k}{2\tau} \left| \int_{-\tau}^{\tau} \omega_j^k(t) e^{-i2\pi\nu t} dt \right|^2$$

- Vibrational

$$D_{\text{vib}}(\nu) = \frac{2}{k_B T} \sum_{k=x,y,z} \sum_{j=1}^{N_m} \sum_{l=1}^N \lim_{\tau \rightarrow \infty} \frac{m_j}{2\tau} \left| \int_{-\tau}^{\tau} v_{\text{vib},j,l}^k(t) e^{-i2\pi\nu t} dt \right|^2$$

- Gas-like component

$$D_{\text{tn}}^G(\nu) = D_{\text{tn}}(0) \left[1 + \left(\frac{\pi D_{\text{tn}}(0) \nu}{6 f_{\text{tn}} N_m} \right)^2 \right]^{-1}$$



- **Harmonic Oscillator:**
each vib. mode is treated as Quantum HO

$$\varepsilon_n = \left(n + \frac{1}{2}\right)h\nu$$

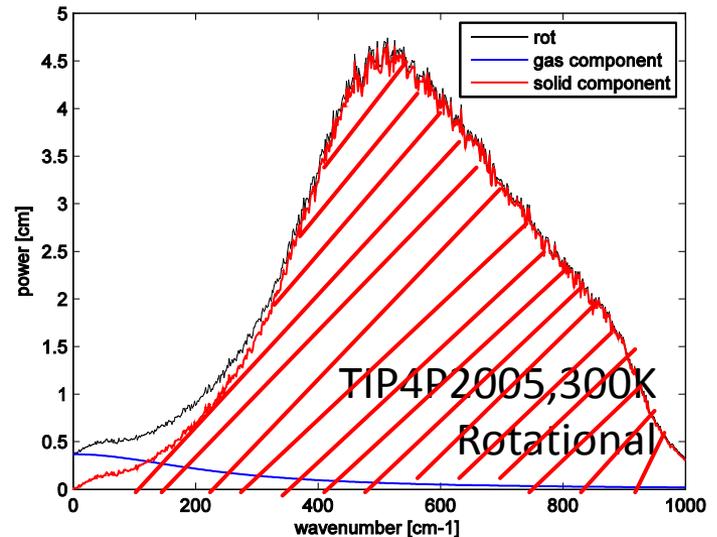
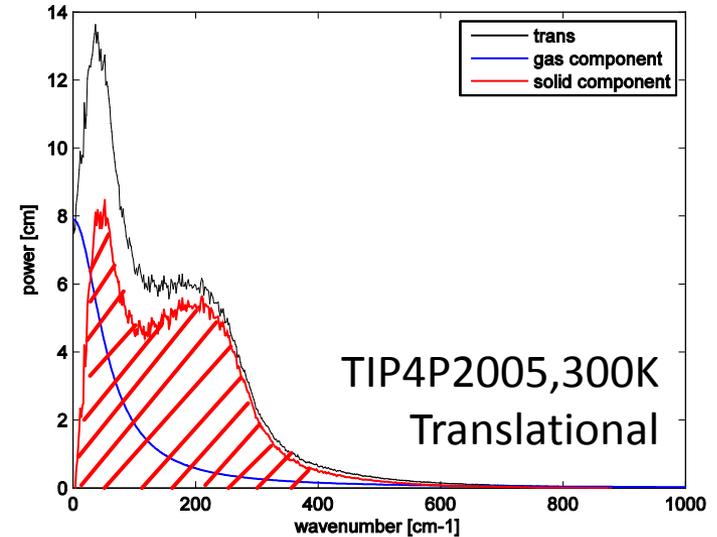
$$q_{HO}^Q(\nu) = \sum_n \exp(-\beta\varepsilon_n) = \frac{\exp(-\beta h\nu/2)}{1 - \exp(-\beta h\nu/2)}$$

$$\ln Q = \int_0^\infty d\nu S(\nu) \ln q_{HO}(\nu)$$

$$E = V_0 + T\beta^{-1} \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V}$$

$$A = V_0 - \beta^{-1} \ln Q = V_0 + \beta^{-1} \int_0^\infty d\nu S(\nu) W_A(\nu)$$

$$S = k \ln Q + \beta^{-1} \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V}$$



- **Hard Sphere Gas:**
each vib. Mode is treated as Quantum HO

$$S^{HS} = \frac{1}{3} k_B \int_0^\infty \left[\frac{5}{2} + \frac{3}{2} \ln \frac{2\pi m k_B T}{h^2} + \ln \frac{V(1+y+y^2-y^3)}{f_i N (1-y)^3} + \frac{y(3y-4)}{(1-y)^2} \right] D^{HS}(\nu) d\nu$$

$$E^{HS} = \frac{1}{3} k_B T \int_0^\infty \frac{3}{2} D^{HS}(\nu) d\nu = \frac{3}{2} f_{\text{tm}} N_m k_B T$$

$$c_V^{HS} = \frac{1}{3} k_B \int_0^\infty \frac{3}{2} D^{HS}(\nu) d\nu = \frac{3}{2} f_{\text{tm}} N_m k_B$$

$$A^{HS} = E^{HS} - TS^{HS}$$

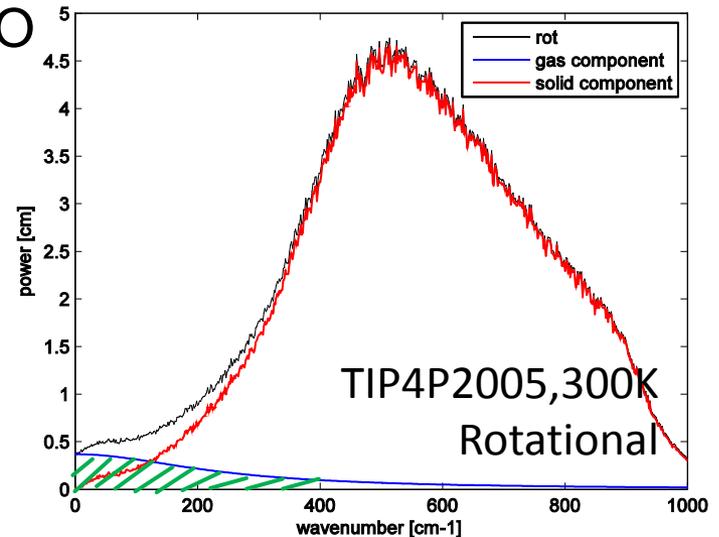
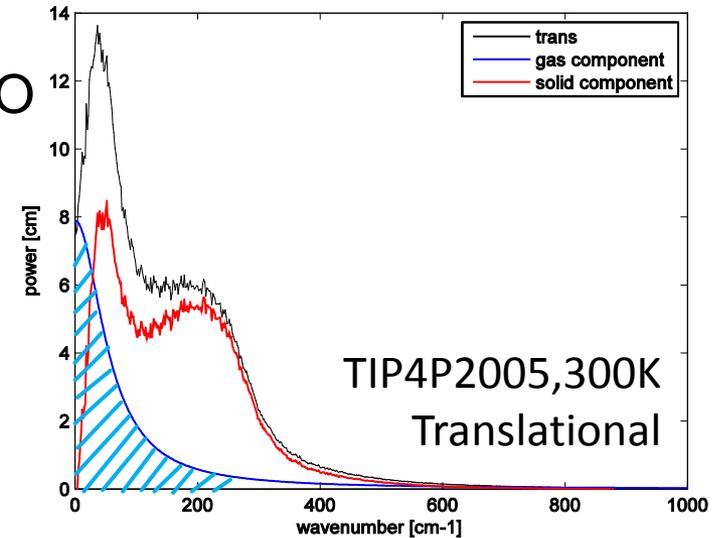
- **Rigid Rotor:**
each vib. Mode is treated as Quantum HO

$$S^{RR} = \frac{1}{3} k_B \int_0^\infty \frac{1}{2} \left[3 + \ln \frac{\pi}{\sigma^2} + \ln \frac{T^3}{\Theta_1 \Theta_2 \Theta_3} \right] D^{RR}(\nu) d\nu, \Theta_i = \frac{h^2}{8\pi k I_i}$$

$$E^{RR} = \frac{1}{3} k_B T \int_0^\infty \frac{3}{2} D^{RR}(\nu) d\nu = \frac{3}{2} f_{\text{rot}} N_m k_B T$$

$$c_V^{RR} = \frac{1}{3} k_B \int_0^\infty \frac{3}{2} D^{RR}(\nu) d\nu = \frac{3}{2} f_{\text{rot}} N_m k_B$$

$$A^{RR} = E^{RR} - TS^{RR}$$



An Example of Xylitol

Entropy of xylito

$$\Delta S(500K) = 112J/mol/K$$

$$\Delta S(382K) = 82J/mol/K$$

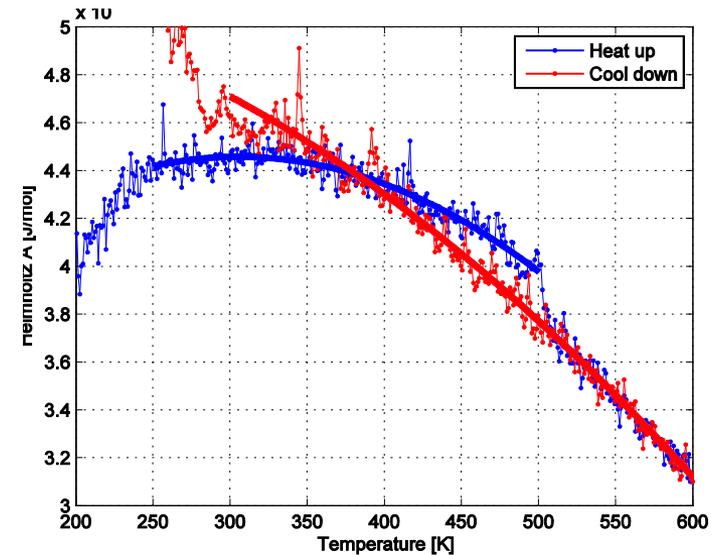
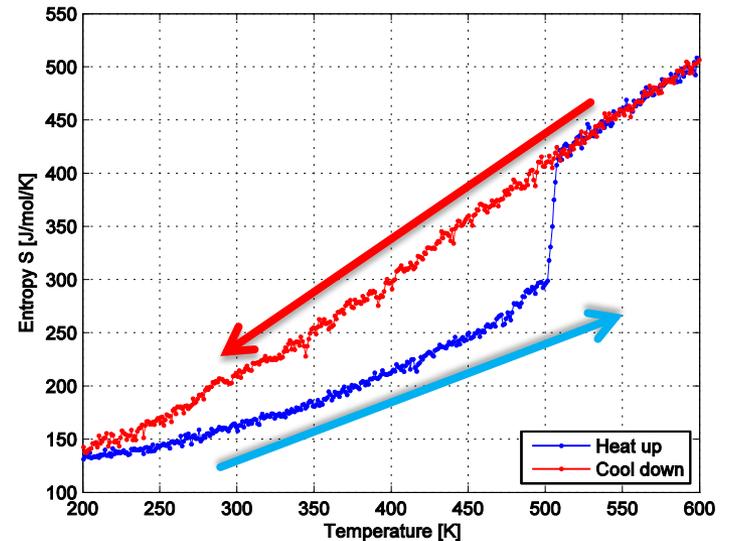
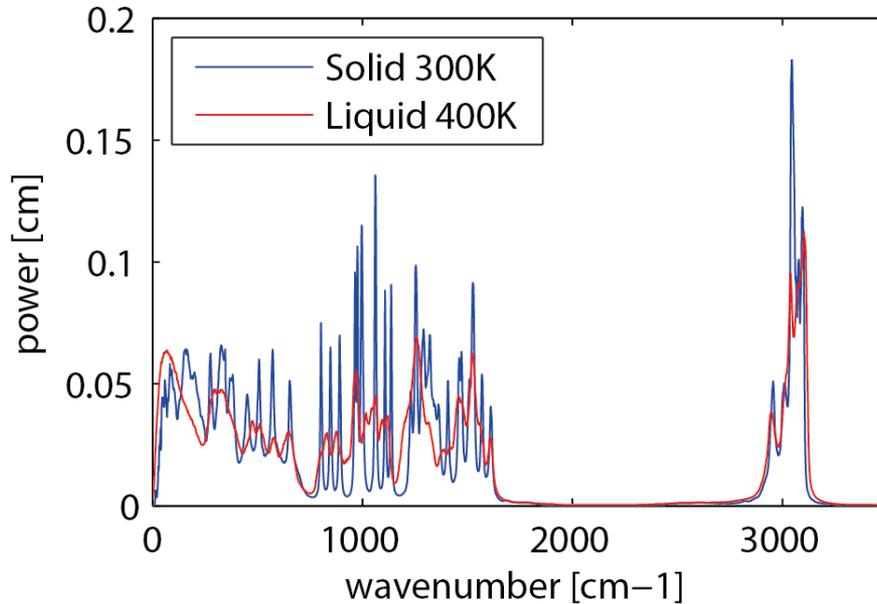
$$\Delta S(368K) = 81J/mol/K$$

$$\Delta S_{exp}(367.52K) = 91.64 J/mol/K$$

Free energy of xylitol

Intersection at $382 \pm 5K$. Exp. value 367.52

Phonon density of state (DoS) of xylitol

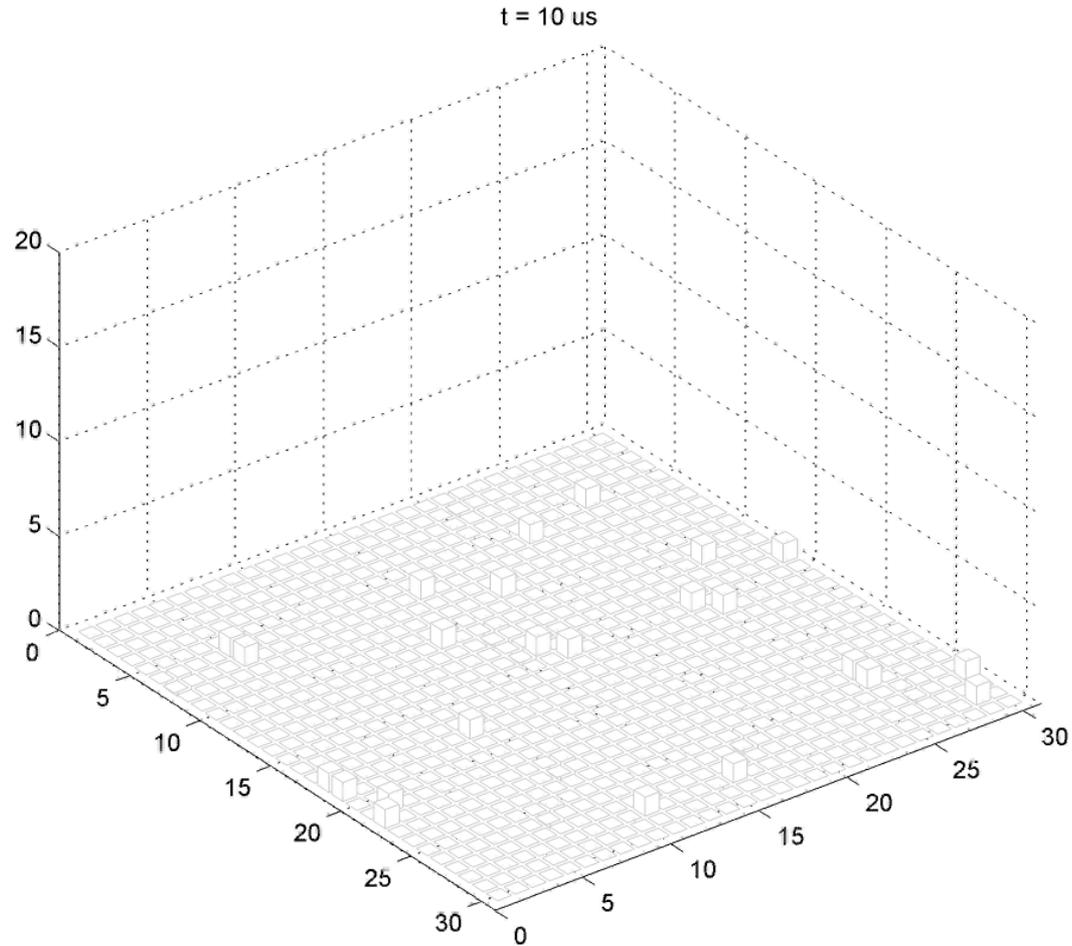


- Gilmer's model points out the crystal growth is a stochastic process of three basic events competing.
- Creation, Annihilation, Surface diffusion

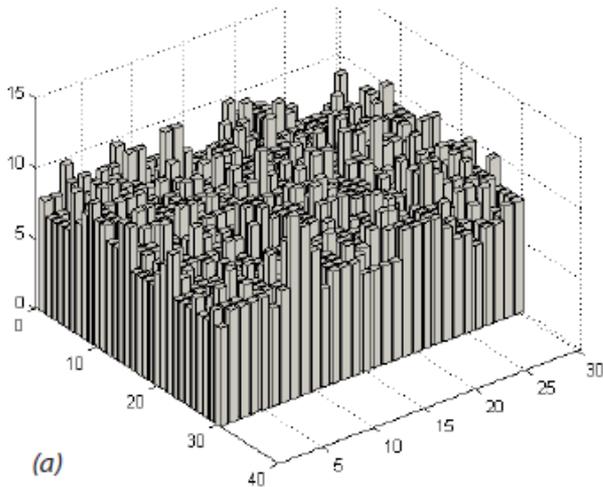
Event	Frequency[Hz]
Creation 	$k_p^+ = f_t \exp\left[-\frac{A\gamma}{kT}(2 - j_p) + \frac{\Delta G}{2kT}\right]$
Annihilation 	$k_p^- = f_t \exp\left[+\frac{A\gamma}{kT}(2 - i_p) - \frac{\Delta G}{2kT}\right]$
Diffusion 	$k_{pq} = f_t \left(\frac{X}{a}\right)^2 \exp\left[+\frac{A\gamma}{kT}(2 + j_q - i_p) - \frac{\Delta G}{2kT}\right]$

*base frequency: $f_t = \frac{kT}{h} \exp\left(-\frac{\Delta G_\eta}{kT}\right)$

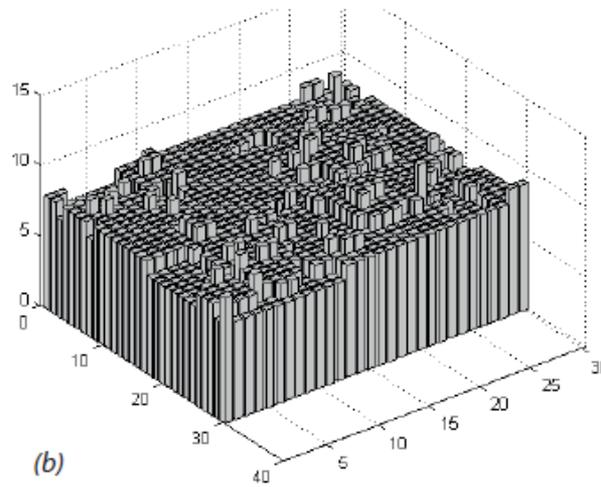
Demonstration: Lattice Growth



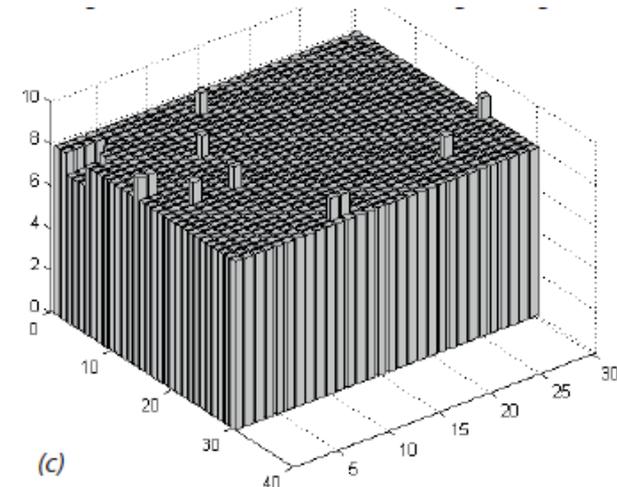
- Surface roughening parameter α (related to interfacial FE)
- Supersaturation β (related to bulk solid liquid FE difference)



$$\beta/\alpha = 0.30$$

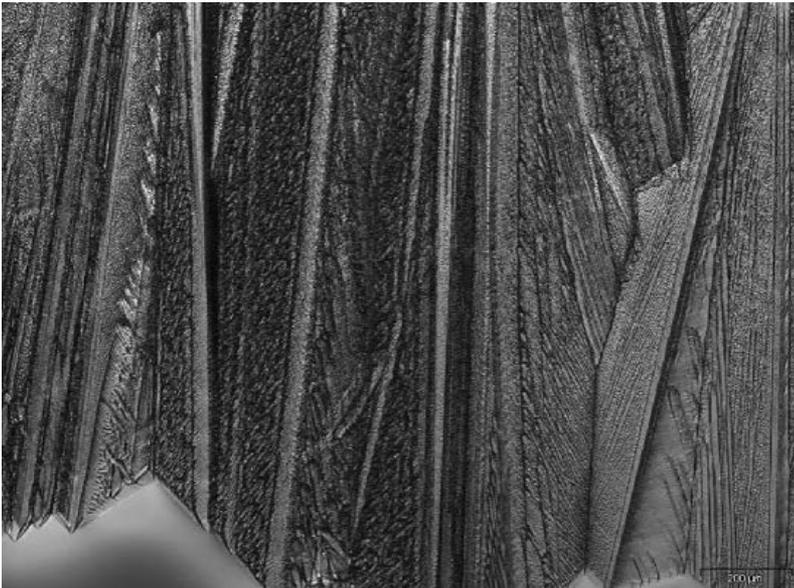


$$\beta/\alpha = 0.15$$

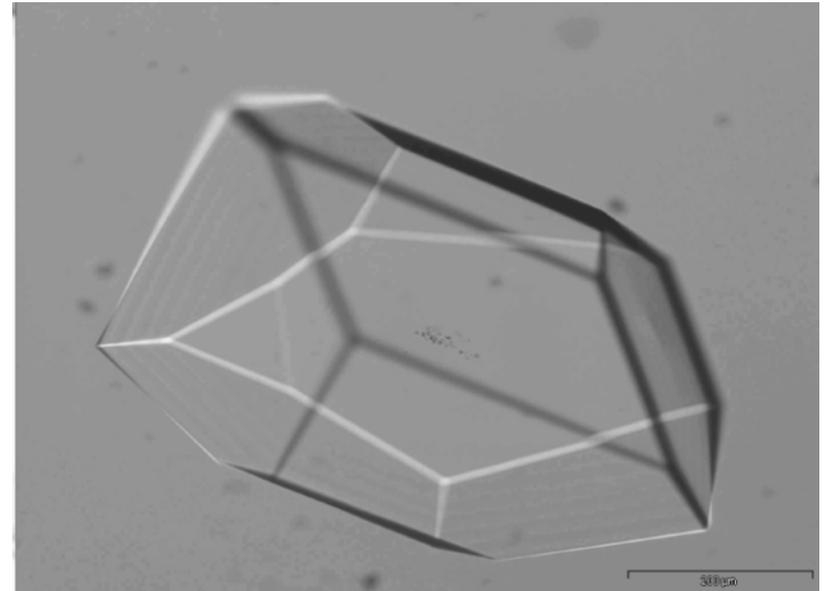


$$\beta/\alpha = 0.10$$

- The key parameter β/α determines the growth pattern which sugar alcohols follows

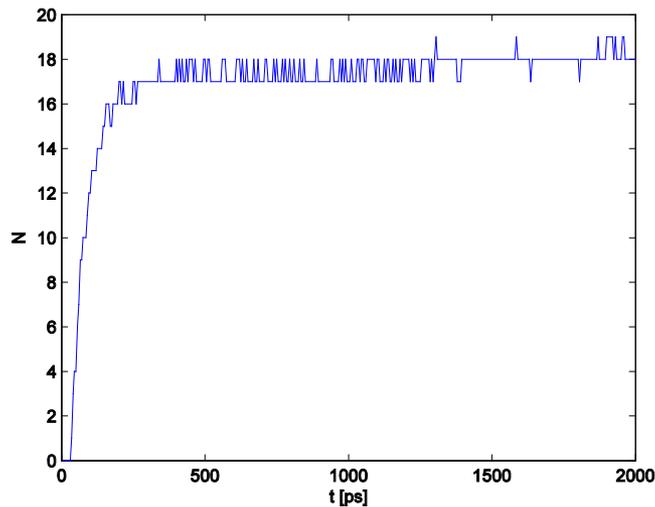


Erythritol at Tm-90K, $\beta/\alpha = 0.23$, dense branching

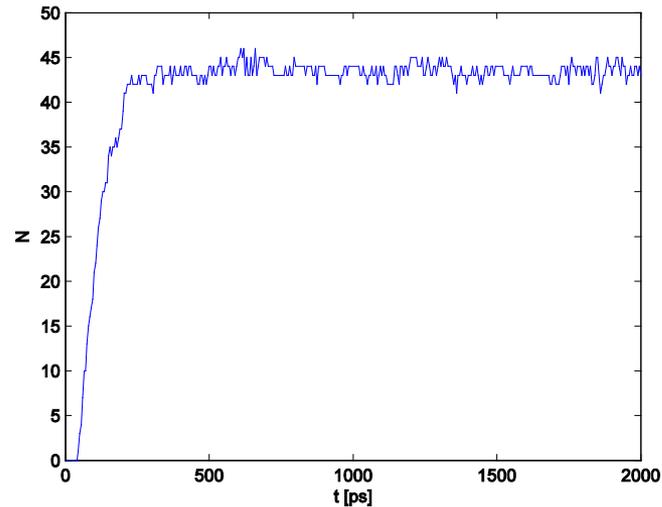


Xylitol at Tm-10K, $\beta/\alpha = 0.10$, faceted growth

- Carbon foams, aerogels, nanotubes, nanoplatelets, ...
- Confinement effects, interfacial effects, doping effects, ...
- Material property modification/ strengthening
- Solvate open-ended 5nm long CNT in xylitol: filling is spontaneous

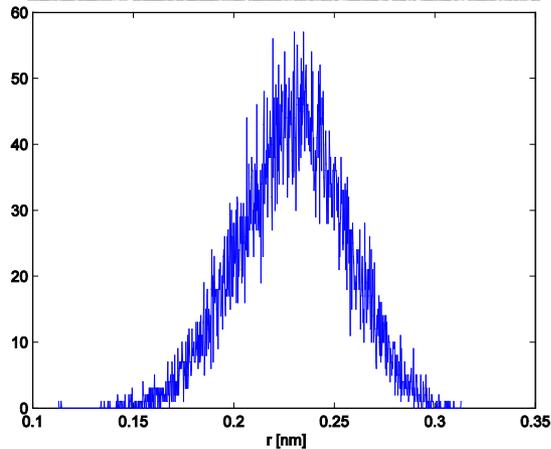
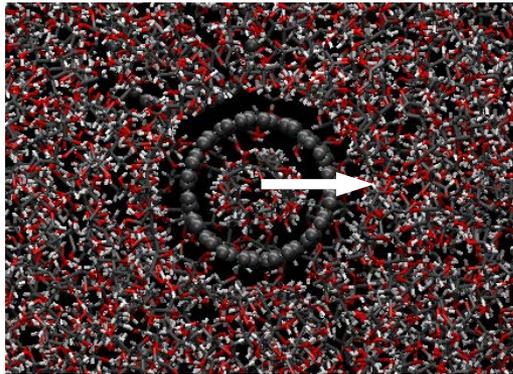


CNT(10,10), $N=3.6/\text{nm}$

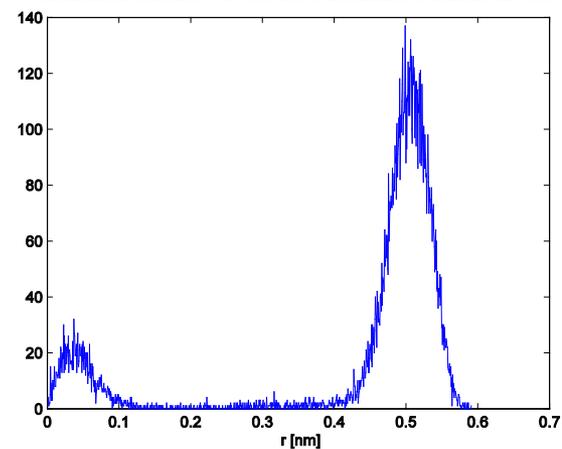
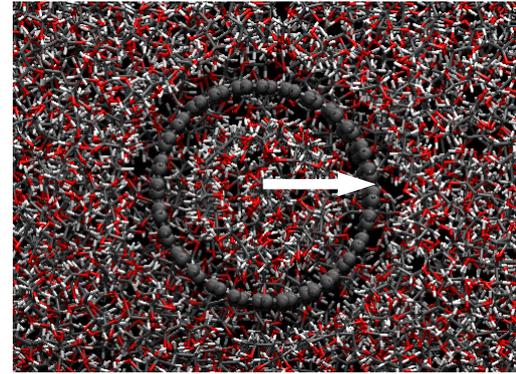


CNT(14,14), $N=8.8/\text{nm}$

- Number density distribution along the tube's radial direction



CNT(10,10), $L = 5$ nm, $d = 1.36$ nm



CNT(14,14), $L = 5$ nm, $d = 1.90$ nm

- A multiscale model is built up following a hierarchical approach
- The models are well validated in multiple conditions
- We look forward to research more on carbon-MASA systems