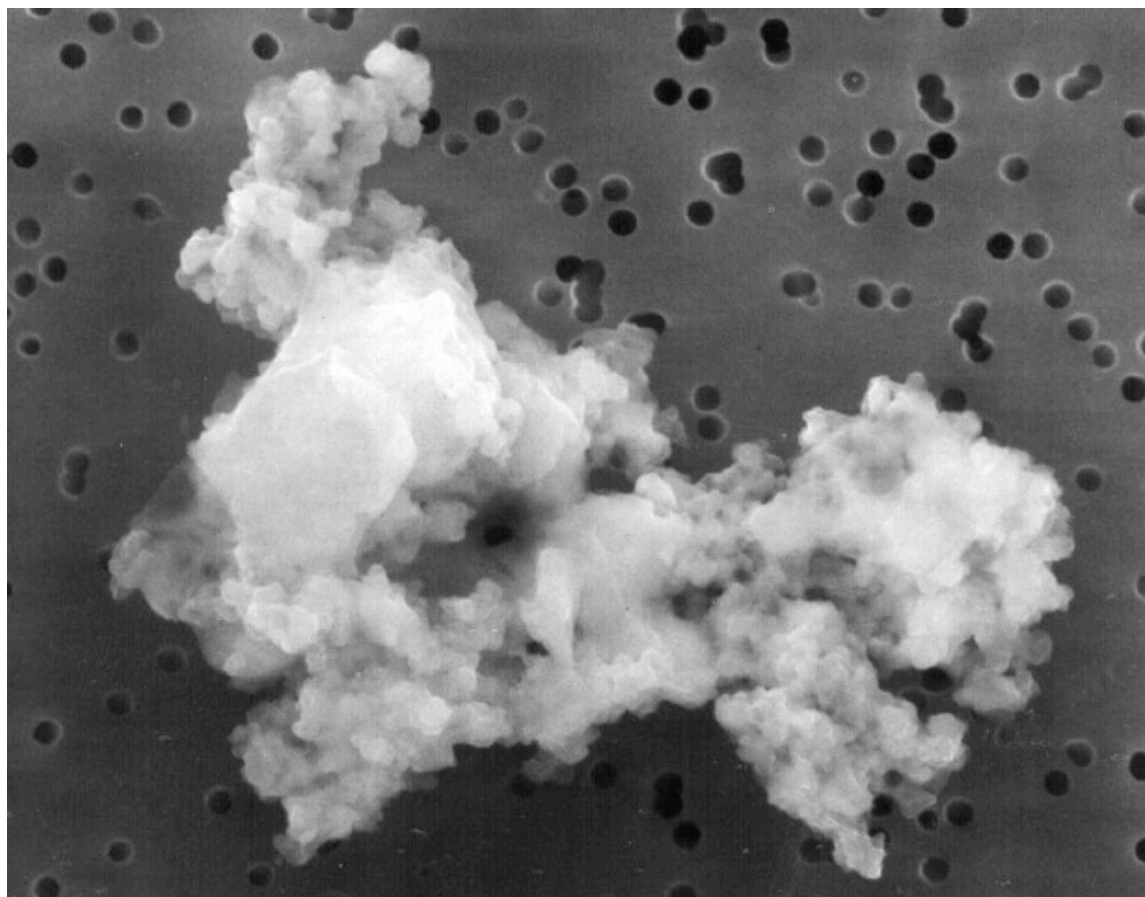


# Uncertainties in Modeling of Interstellar Surface Chemistry: too many Degrees of Freedom?



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Last refuge of a scoundrel? Any predictive power?  
Daunting but necessary.....

# Physisorption vs Chemisorption

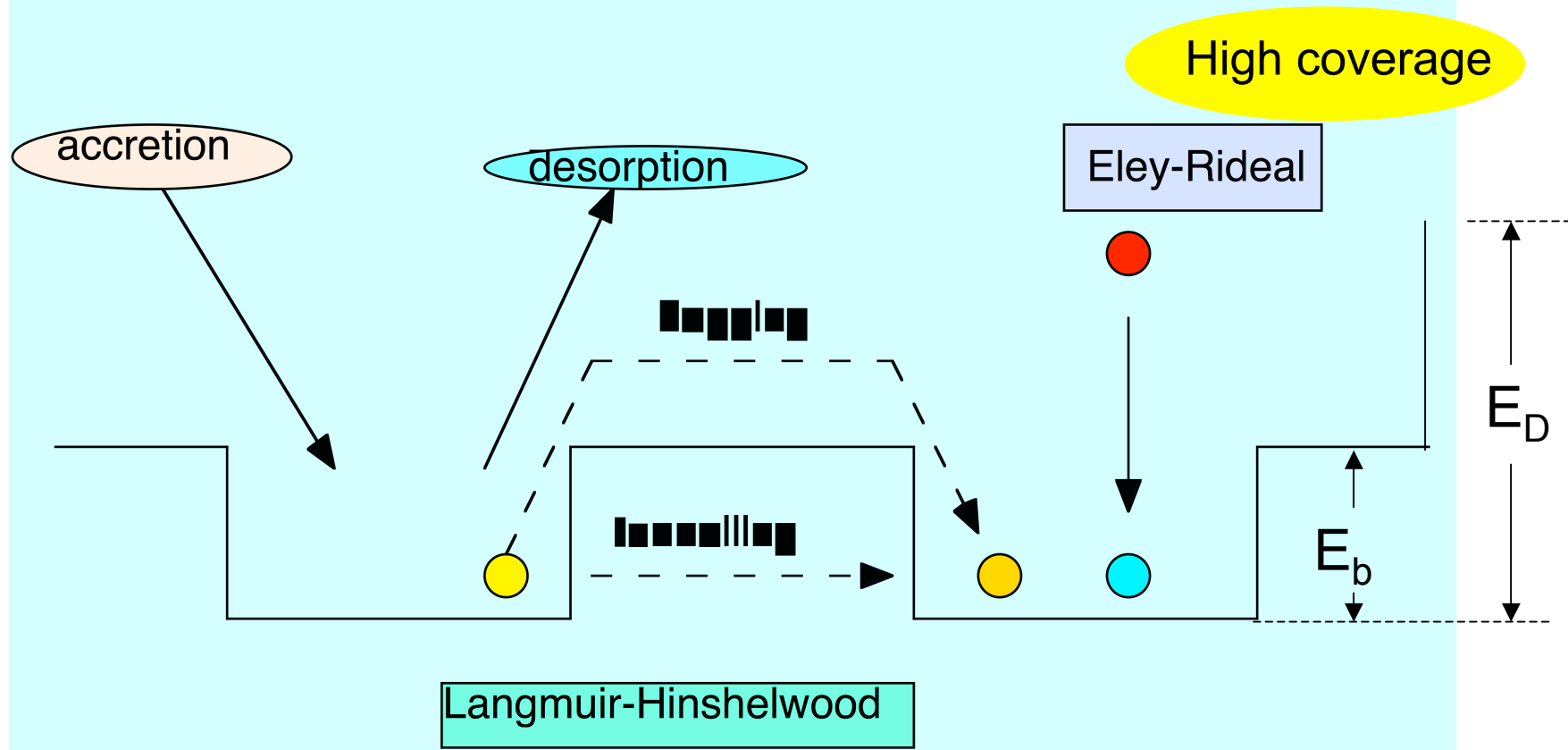


no barrier; weak binding allows diffusion at low temperatures

Possible barrier; diffusion at higher temperatures

*Next, types of surfaces and mechanisms.....*

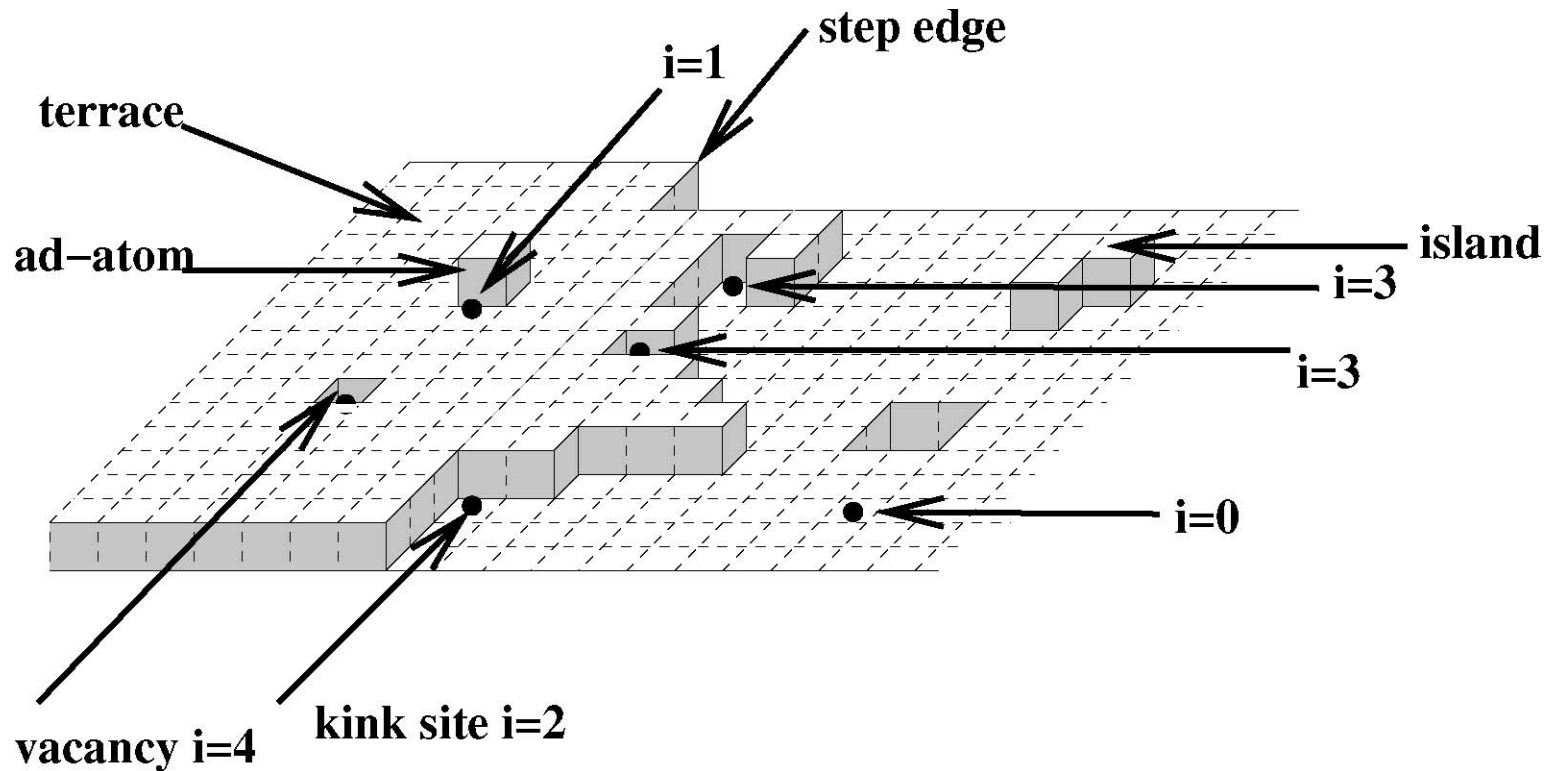
# GRAIN SURFACE PROCESSES



"flat" surface

Low coverage + diffusion

# Irregularities on rough surface

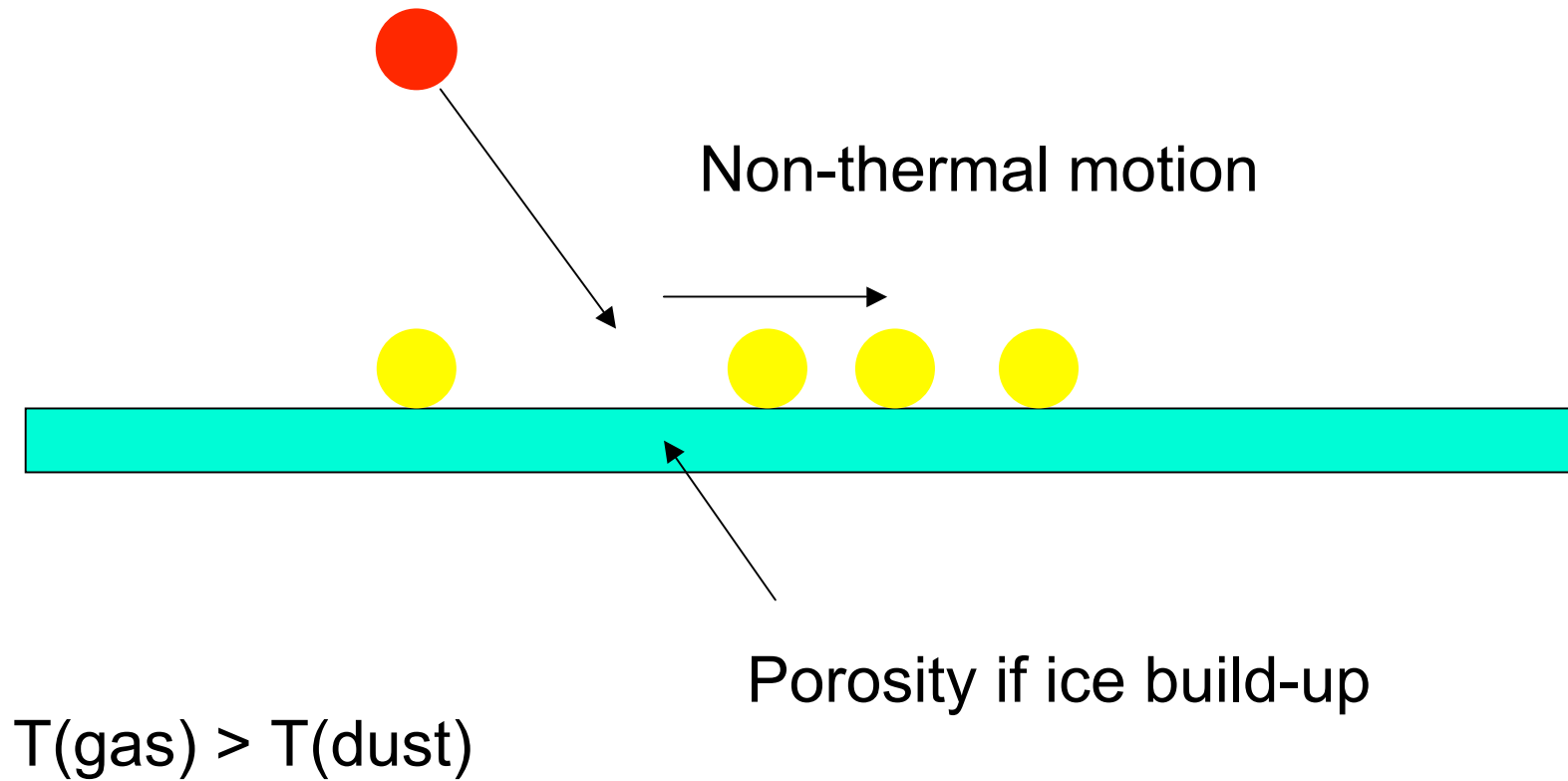


Binding energy affected by environment; picture may be more applicable to chemisorption and directed bonds.

# Amorphous Material

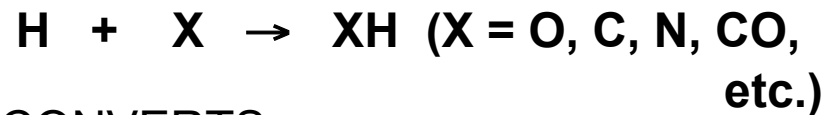
- Gaussian distribution of desorption energies and diffusion barriers

# HOT-ATOM MECHANISM

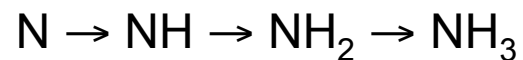
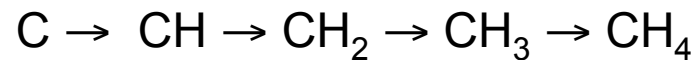
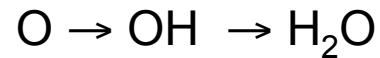


# TYPES OF SURFACE REACTIONS: Low T

REACTANTS: MAINLY MOBILE  
ATOMS AND RADICALS



WHICH CONVERTS





# Higher Temperatures (>30 K)

- Heavier species, such as atoms or radicals formed by photodissociation, can diffuse and react:
- e.g.  $\text{HCO} + \text{CH}_3\text{O} \rightarrow \text{HCOOCH}_3$
- Garrod & Herbst (2006) Widicus-Weaver, Garrod, Herbst, in prep., Charnley and co-workers

Now thought to be important in hot cores and corinos...

# Methods of Modeling Surface Reactions

- Chemical dynamics vs kinetics
- Rate equations (diffusion mainly); best for table-tops.
- Stochastic approaches: macroscopic vs microscopic

# Desorption Mechanisms

- **Thermal**, as temperature rises
- **Non-thermal at low temperature**, includes reactive desorption, cosmic ray bombardment (inefficient)
- **Shock-wave sputtering**, may be needed in galactic center
- **Photodesorption**, seems to be very specific

# Standard Gas-Grain Model

- Gas and grain chemistries coupled by accretion and desorption, both thermal and non-thermal, including reactive desorption (Garrod, Wakelam, Herbst 2007)
- Diffusive (LH) mechanism treated by **rate equations**. Uses one set of appropriate energy parameters per adsorbate/surface pair. 550 reactions
- **One size** dust particle utilized

# Modelling Diffusive Surface Chemistry I

Consider a species A that hops to the next site to find and react with a species B:

$$\text{Rate} = k_{hop}(A)N(B)/N = k_{diff}(A)N(B)$$

where

$$k_{diff}(A) = k_{hop}(A)/N$$

Now consider a number of moving species A:

$$dN(A)/dt = -(k_{diff}(A) + k_{diff}(B))N(A)N(B) = -KN(A)N(B)$$

# Thermal Desorption & Diffusion

$$k_{des} (s^{-1}) = \nu \exp(-E_D / k_B T) \approx 0 \quad \text{for heavies at 10 K}$$

$$k_{hop} (s^{-1}) = \nu \exp(-E_b / k_B T); E_b \approx 0.30 E_D$$

(in the absence of tunneling....)

# Energy Parameters

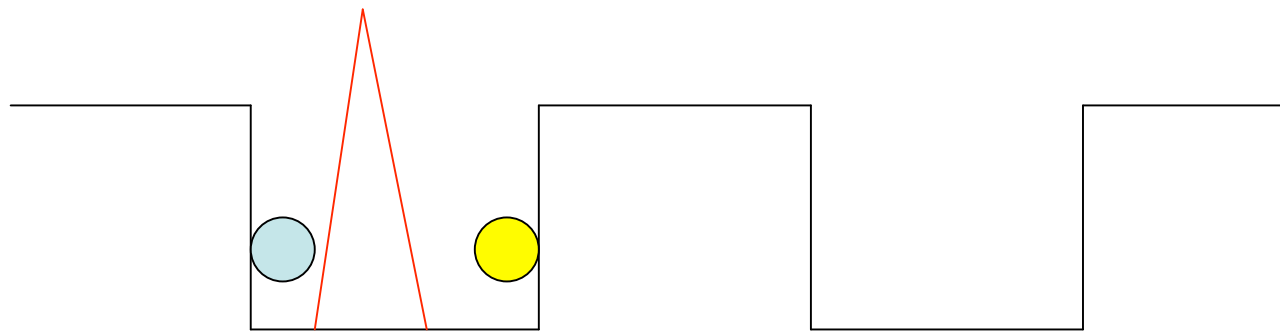
- Binding (desorption) energies obtainable by a variety of techniques including TPD
- Barriers against diffusion much harder to obtain.

# Chemical Activation Energy

- How handle, e.g.,  $\text{H} + \text{CO} \rightarrow \text{HCO}$ ?
- Method I: Just multiply  $K$  by tunneling or hopping rate over chemical barrier
- Method II: consider competition between diffusion and tunneling/hopping through/over chemical barrier.
- Method II minimizes effect of small activation energy barrier.



# Model of Competition



# Problems with Rate Equations

- a) inaccurate treatment of random walk; problem known as “back diffusion”
- b) overestimate of rate in “accretion limit” where average number of reactive particles less than unity and discreteness and fluctuations important (Tielens)
- c) cannot completely take into account microscopic structure of surface (e.g. roughness)

# MACROSCOPIC STOCHASTIC METHODS

Idea is to follow **probabilities** that a certain number of atoms/molecules of a species are present on a particular grain as a function of time. Directed at **accretion limit** problem. So far used only for LH mechanism.

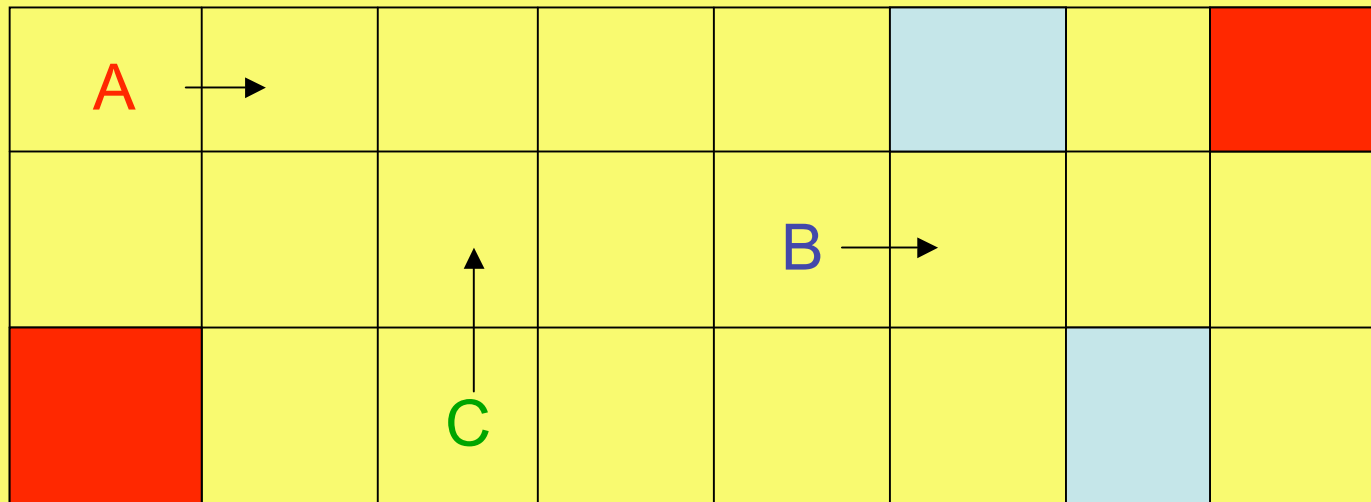
**MONTE CARLO METHOD**: use random numbers (Charnley)

**MASTER EQUATION METHOD**: propagate probabilities forward via differential equations (Biham et al.; Green et al.); more easily coupled to gas-phase rate equations (Stantcheva et al.); approximations still necessary. Method of moments most useful (Biham).

# CTRW (MICROSCOPIC) APPROACH

Chang, Cuppen & Herbst (2005)

- A Monte Carlo approach in which the actual positions of individual species on a lattice are followed with time. Can use to follow reactions (LH,ER) and mantle build-up.



# Some CTRW Studies

- **H<sub>2</sub> formation on amorphous and rough** silicate and carbon grains of different sizes in diffuse clouds. Results fit to effective rate coefficients. (Cuppen & Herbst 2005; Chang et al. 2006) Can include stochastic heating by cosmic rays and photons (Cuppen et al. 2006).
- **Formation & morphology of ice mantles in cold dense sources starting with deposition of H and O atoms** (Cuppen & Herbst 2007).
- **Gas-grain model of cold cores** of moderate size with rough surface and mantle build-up (Chang, Cuppen & Herbst 2007). Severe approximations needed.

# The Future

- Better integration of gas-phase network and master equation surface network (Biham)
- Closer relation between lab work and modeling of surface reaction rates (Leiden meeting)
- Inclusion of three grain sizes in standard model
- Inclusion of chemisorption & ER, HA
- More detailed gas-grain models of hot cores, protoplanetary disks, shocked regions, PDR's
- Better appreciation of role of PAHs
- More dynamics, heterogeneity, and radiative transfer in all models in the ALMA era



# MODELLING DIFFUSIVE SURFACE CHEMISTRY II

## Rate Equations

$$\frac{dN(H)}{dt} = k_{acc}n(H) - k_{des}N(H) - K_{H-H}N(H)N(H)$$

where

$$K_{H-H} = k_{diff}(H) + k_{diff}(H)$$

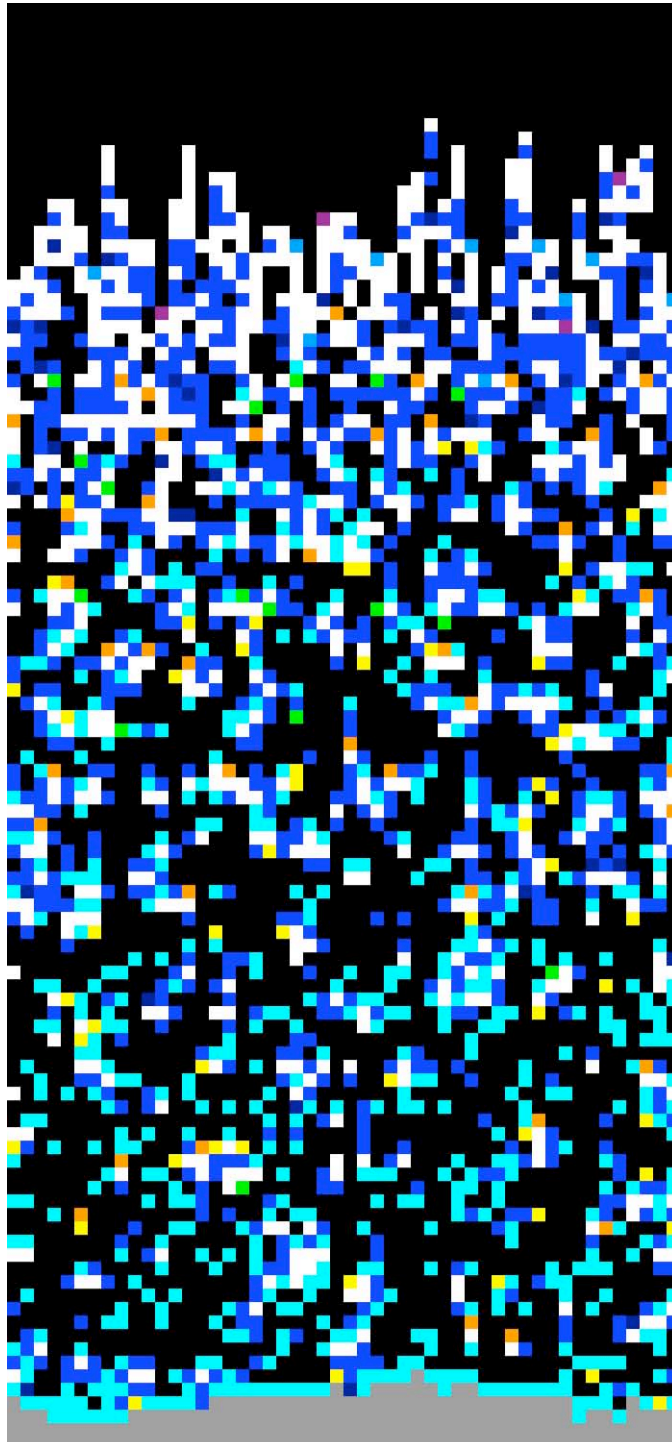
$$k_{acc} = \sigma_{grain}v(H)S$$

Pickles & Williams 1977



Development of  
ice mantle in  
cold interstellar  
core

Cuppen &  
Herbst, ApJ,  
2007



Grown on  
rough  
surface of  
amorphous  
carbon

# Interstellar Regimes

- *Diffuse clouds*: possibly bare silicates or carbonaceous material: H<sub>2</sub> formation dominant; low H coverage; LH, physisorption
- *Dense cold clouds*: build-up of possibly amorphous and porous ice layers mainly by reaction; LH, ER, porosity, physisorption
- *Hot Cores*: temperature ramp up from 10 K to 300 K; LH, ER, porosity, HA, physi- and chemisorption?
- *PDR's*: high kinetic temperatures; high temperature pulses; ER, HA, chemisorption

# MASTER EQUATION

$$\frac{dN(H)}{dt} = k_{acc}n(H) - k_{des}N(H) - K_{H-H}N(H)N(H)$$

replaced when  $N(H) \ll 1$  by a series of coupled equations for  $P_n(H)$ :

$$\langle N(H) \rangle = \sum n P_n(H)$$

$$dP_0(H)/dt = \dots\dots\dots$$