Prospects of SHE Chemistry Studies Using Vacuum Thermochromatography

Ivo Zvára

Flerov Laboratory of Nuclear Reactions, Joint Institute for Nuclear Research, Dubna, Russian Federation

TAN 11 Sochi September 2011

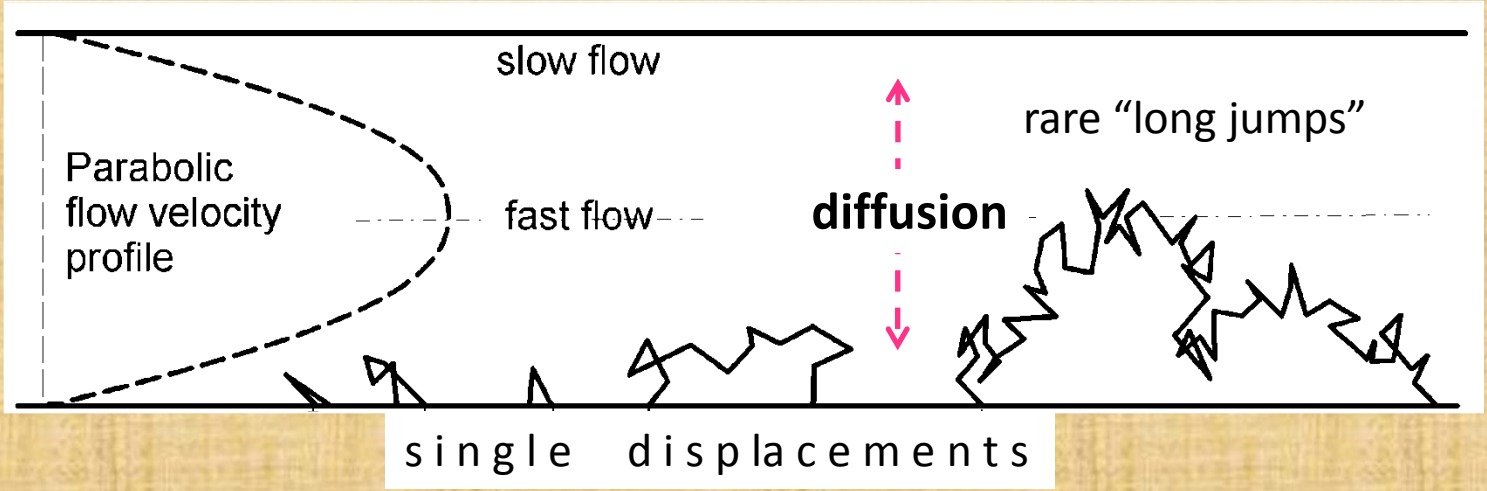
Gas-solid (thermo)chromatography

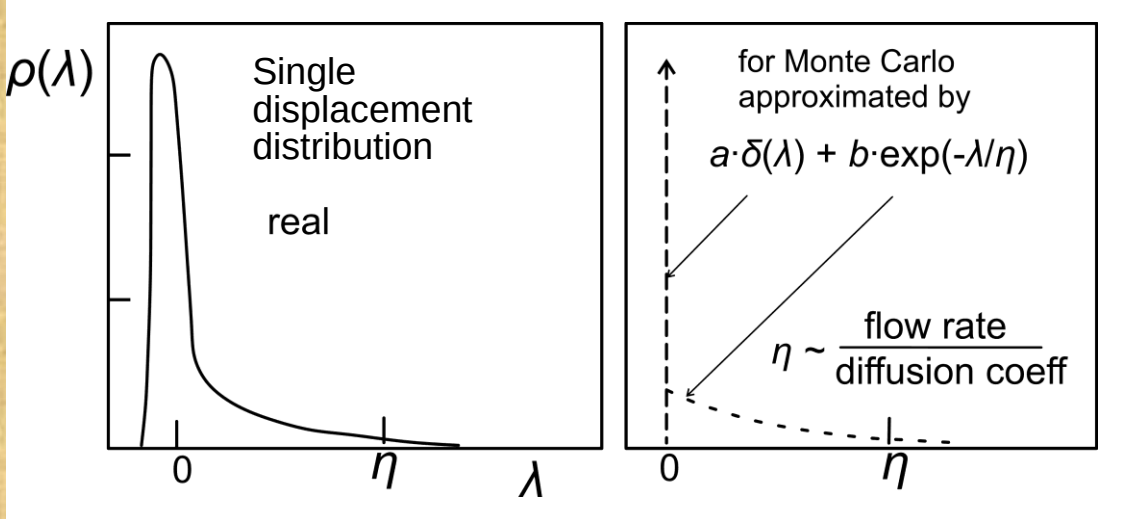
mean adsorption time

period of vibrations

desorption energy

$$\tau_a = \tau_0 e^{\varepsilon_d / kT_z}$$

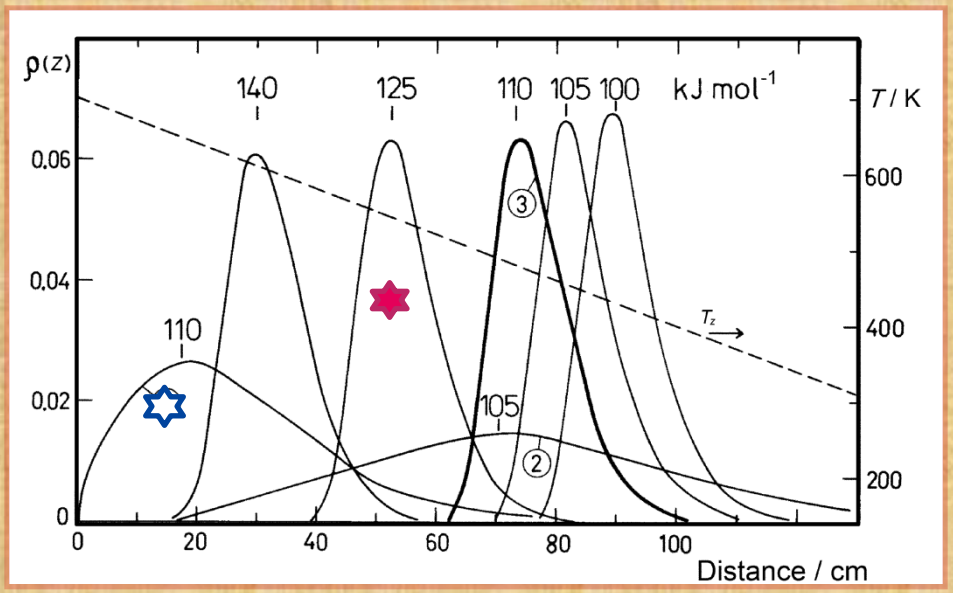




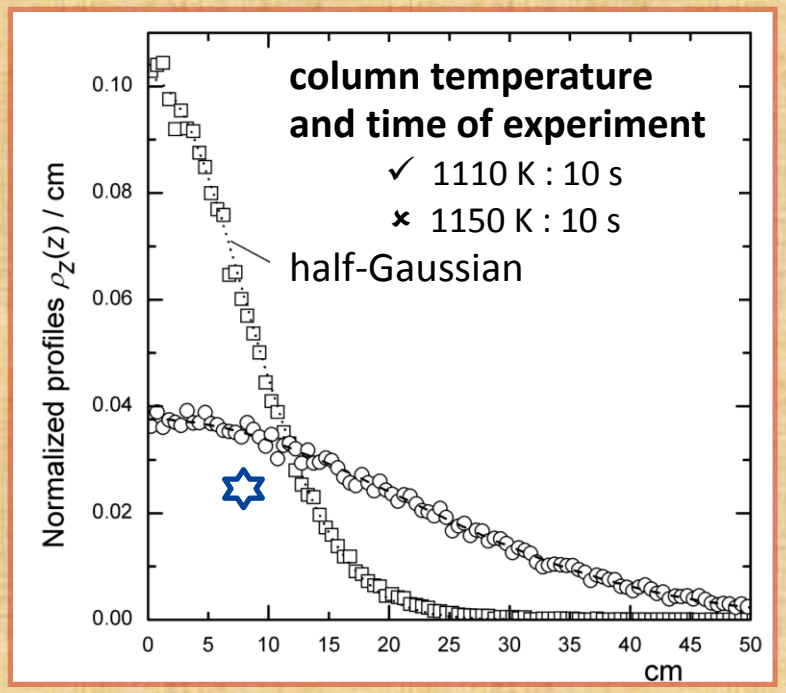
Gas-solid isothermal chromatography and thermochromatography

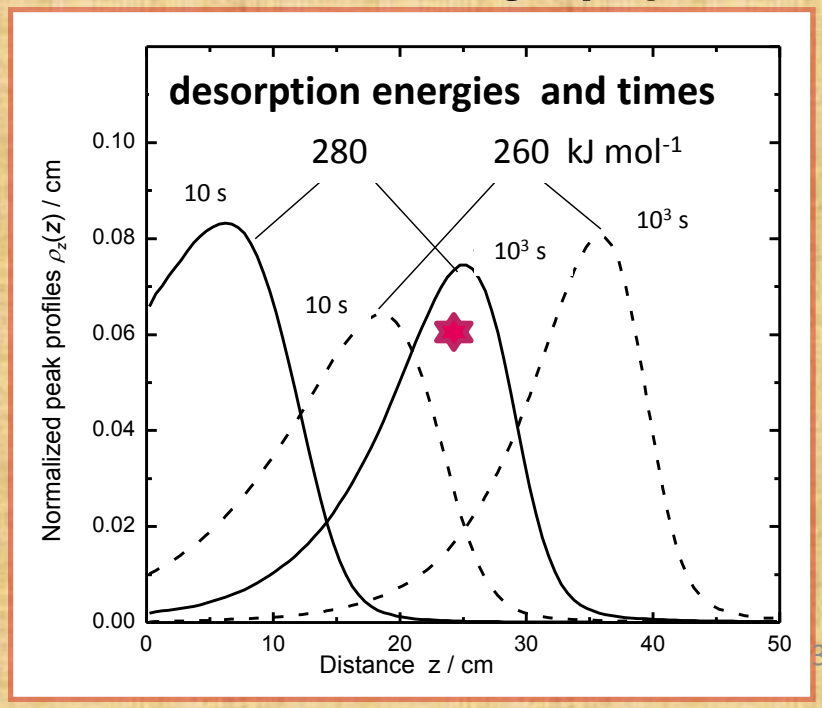
notice different shapes of peaks

- isothermal
- temperature gradient



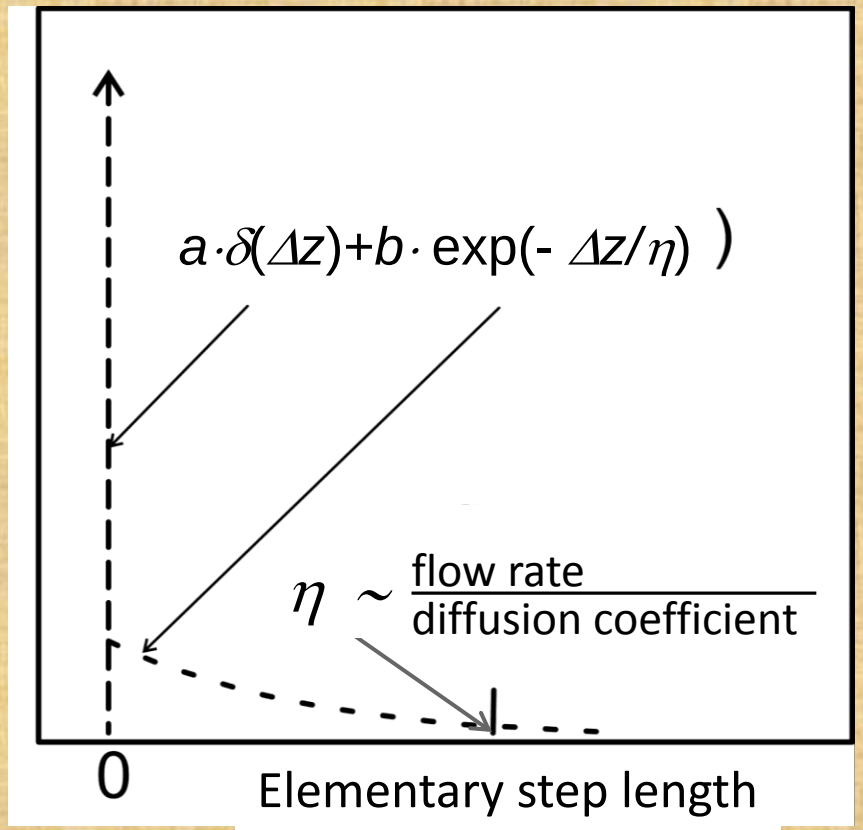
Vacuum isothermal chromatography and thermochromatography



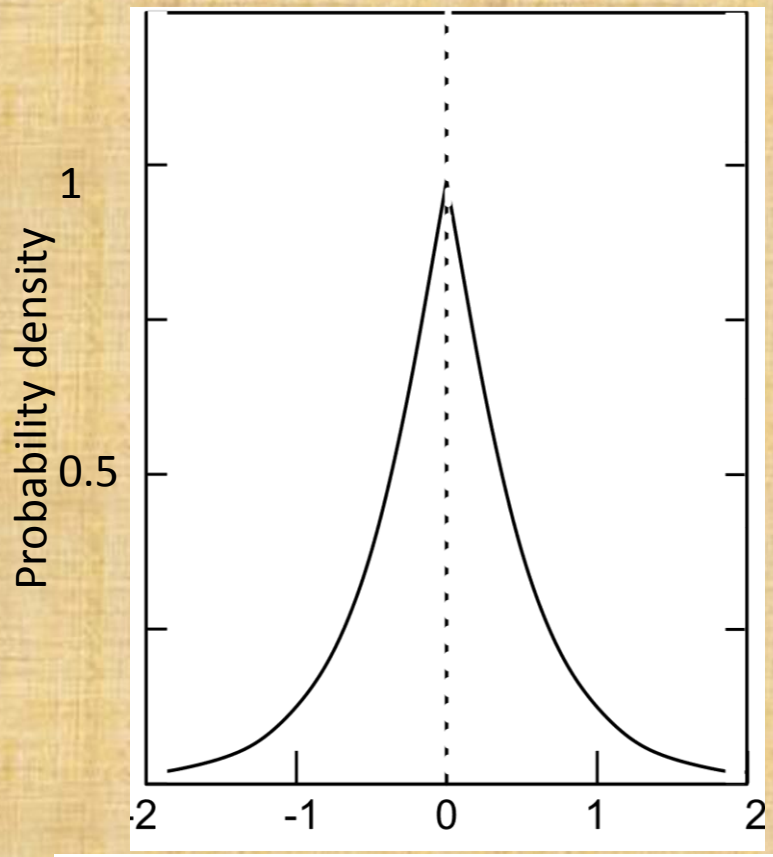


Different migration mechanisms

Gas –solid thermochromatography



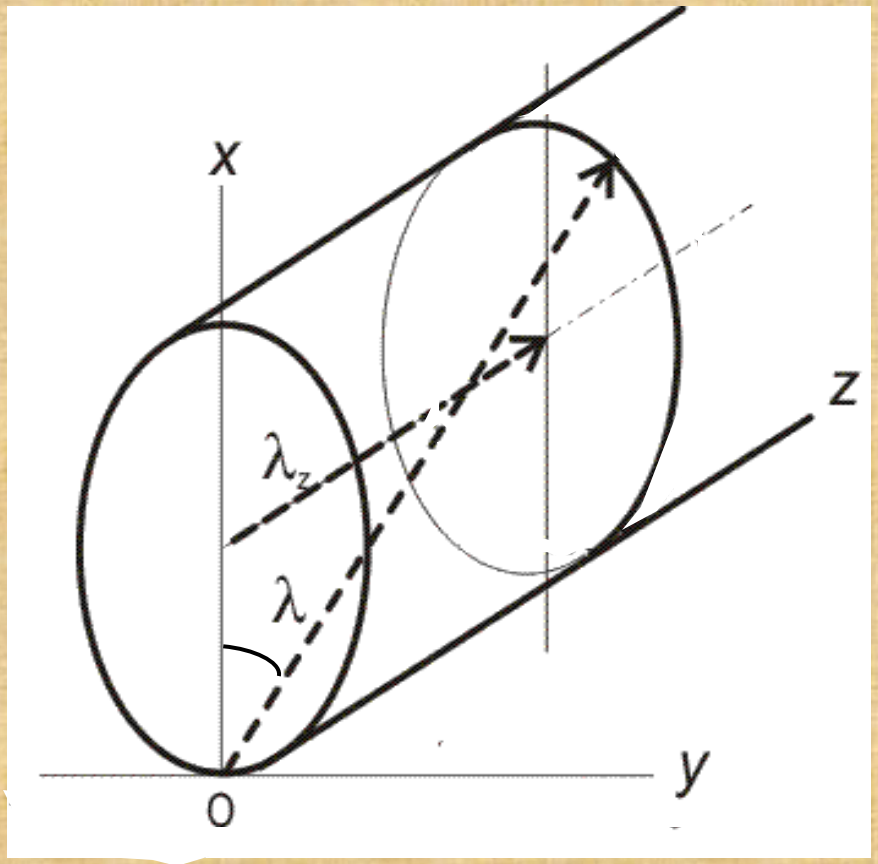
Vacuum thermochromatography



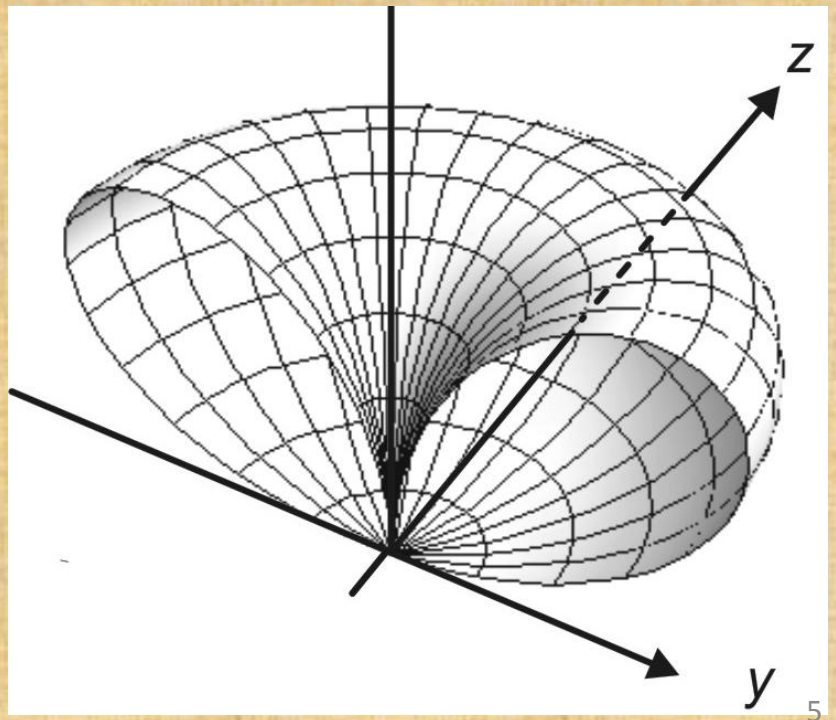
Single walk (in column diameters) off an adsorption site

Geometry of a random walk

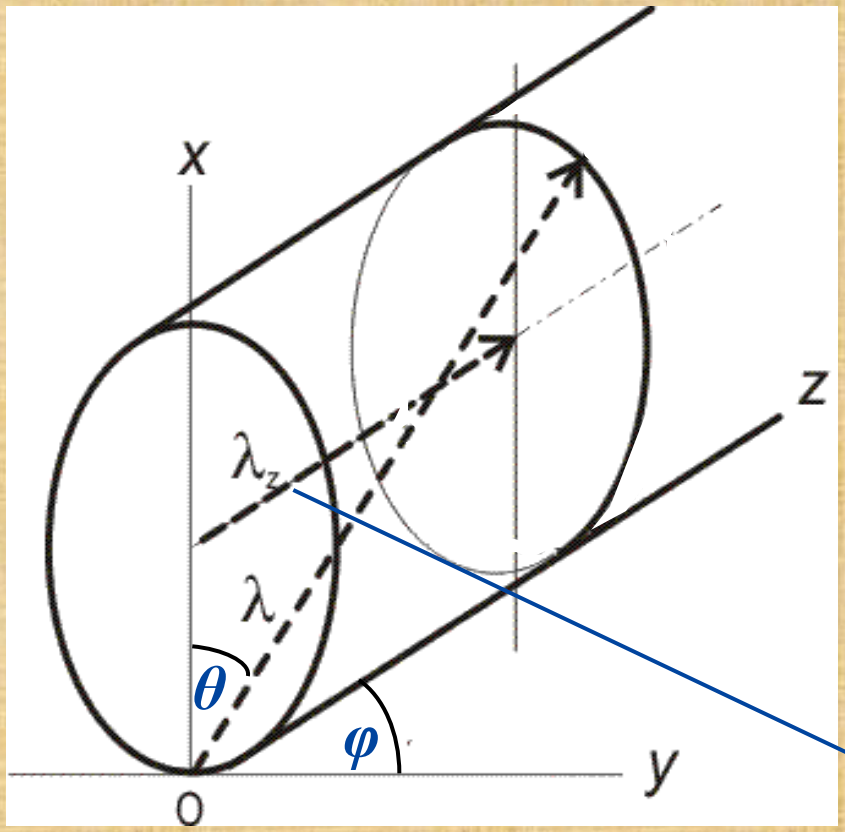
In experiment, one observes the result of a large number of successive random walks up or down the column



Flux density of desorbing molecules
"cosine-law" reemission



Monte Carlo simulation of random walks 1



Let ξ be random variable with standard uniform distribution

random polar angle

$$\theta^* = \arcsin\sqrt{\xi}$$

random azimuthal angle

$$\varphi^* = \frac{\pi}{2}\xi$$

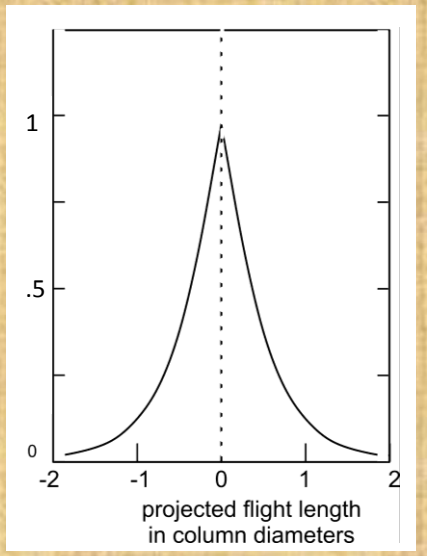
random projected walk

$$\lambda_z^* = \frac{\cos\theta^* \sin\theta^* \sin\varphi^*}{1-\sin^2\theta^* \sin^2\varphi^*}$$

Monte Carlo simulation of random walks 2

Alternatively:
Probability density function of projected walk is

$$\rho(\lambda_z) = 2 - \frac{3\lambda_z + 2\lambda_z^3}{\left(1+\lambda_z^2\right)^{3/2}}$$



A random projected walk results from solving

$$\xi = \int_0^{\lambda_z^*} \rho(\lambda_z)\, d\lambda_z \quad \text{for} \quad \lambda_z^*$$

$$\lambda_z^* = \frac{1}{12(\xi-1)}\left[1 - 2\xi + \xi^2 + \frac{(\xi-1)^2\left(-47 - 2\xi + \xi^2\right)}{\psi(\xi)} + \psi(\xi)\right]$$

where

$$\psi(\xi) = \left[-71 - 150\xi + 663\xi^2 - 596\xi^3 + 159\xi^4 - 6\xi^5 + \xi^6 + 12\sqrt{3}\sqrt{(-1+\xi)^4\left(3 - 2\xi + \xi^2\right)^2\left(28 - 2\xi + \xi^2\right)}\right]^{\frac{1}{3}}$$

Monte Carlo simulation of peak profiles 1

Set experimental conditions and analyte properties

start migration:
zero sojourn and distance

take random
projected walk

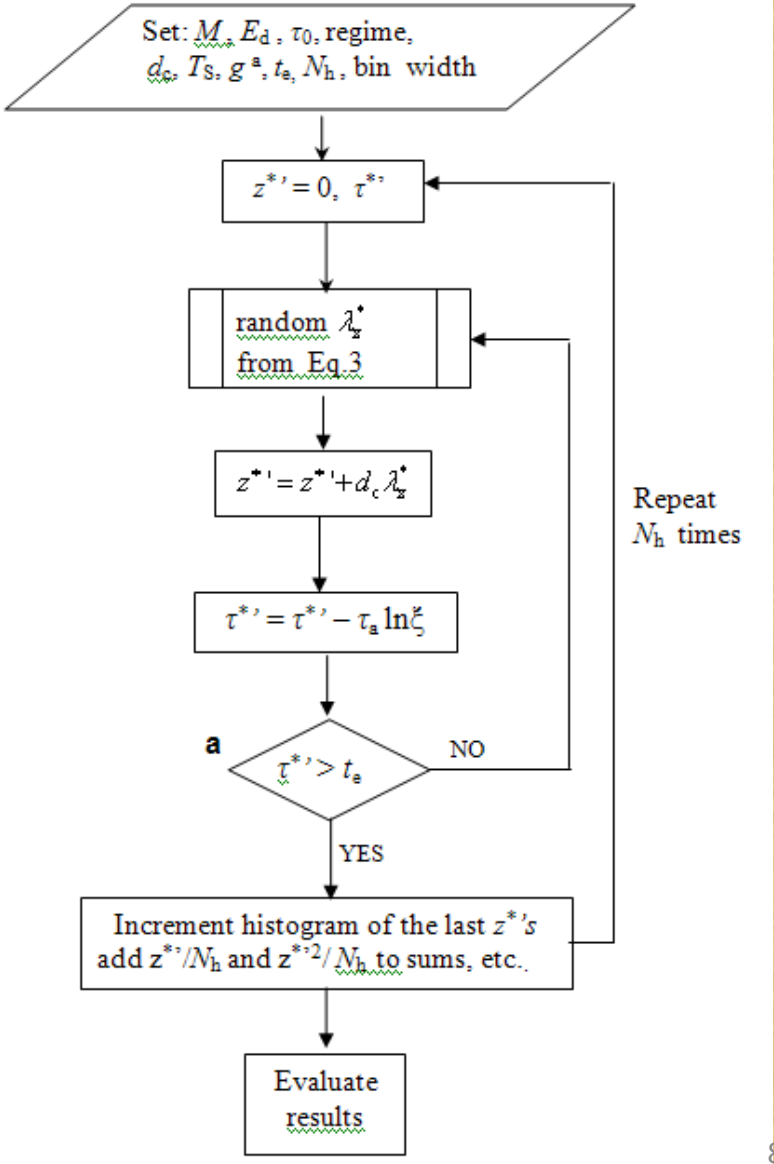
add it to running
distance

$$\tau_a = \tau_0 e^{\varepsilon_d / kT_z}$$

add random adsorption
time to running sojourn

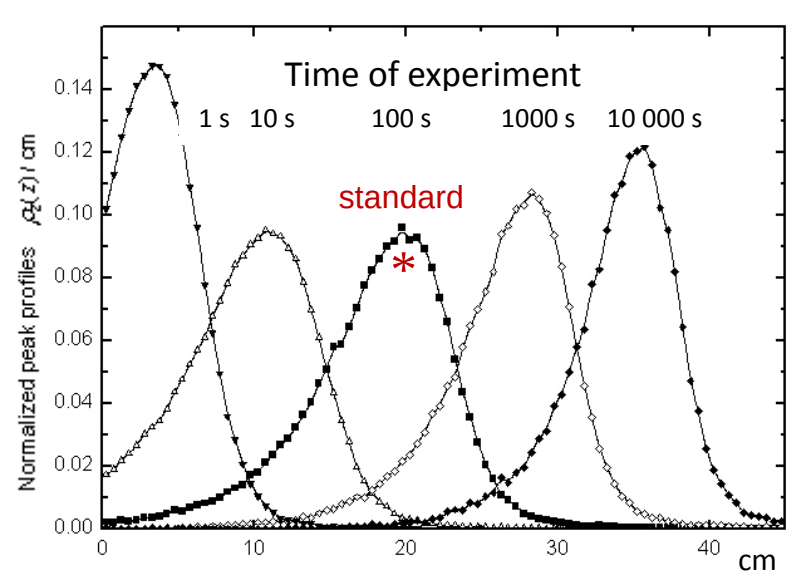
is running sojourn
longer than time
of experiment ??

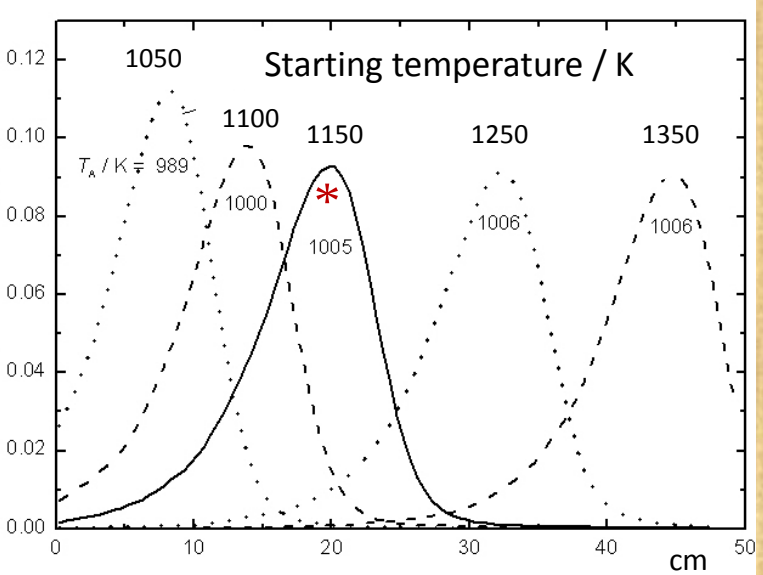
increment bins of
histograms of
various quantities

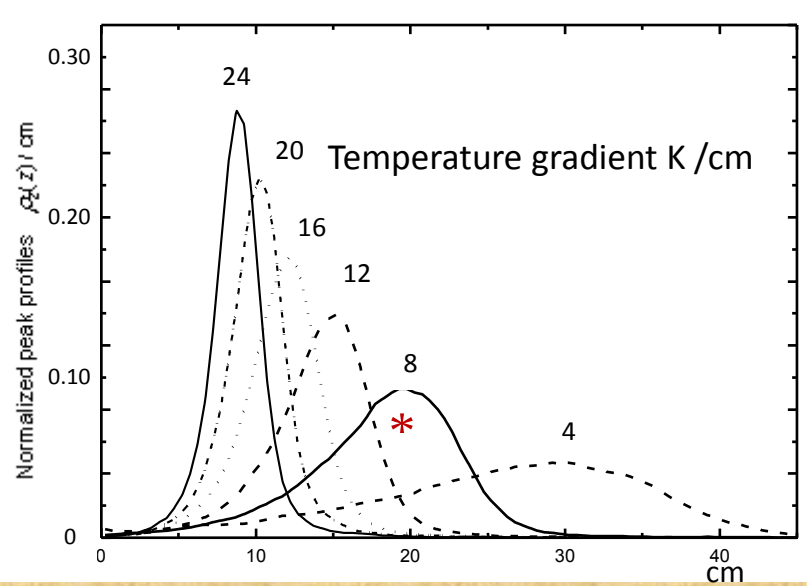


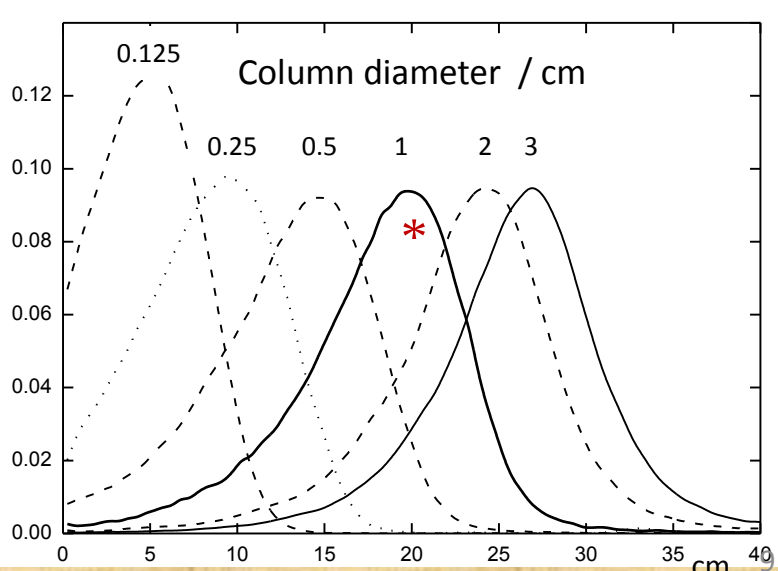
Monte Carlo simulation of peak profiles 2

Standard conditions : desorption energy – 280 kJ / mol, time of experiment – 100 s, starting temperature – 1150K, temperature gradient – 8 K / cm, column diameter – 1 cm









VTC peak profiles from mass diffusion equation 1

Frequent short random walks result in a diffusion picture

Diffusion coefficient ~ walk frequency × mean squared walk length

mean adsorption time is $\tau_a = \tau_0 e^{\varepsilon_d / kT_z}$

mean molecular velocity is $u_m = 1.5 \cdot 10^4 \sqrt{T/M}\ \text{cm s}^{-1}$

For column diameter equal 1 cm :

$$D = \frac{u_m}{3(1 + u_m \tau_a)}$$

for very long τ_a : $D \to \frac{1}{3\tau_a}$

for very short τ_a : $D \to \frac{u_m}{3}$, which is $\approx 10000\ \text{cm}^2 / \text{s}$

VTC peak profile from mass diffusion equation 2

$$\frac{\partial U(t,z)}{\partial t} = D\frac{\partial^2 U(t,z)}{\partial z^2}$$

$$D = \frac{u_m}{3(1+u_m\tau_a)}$$

?U

$U(t,z)$ is the ratio of the volume and surface concentrations of molecules at a particular temperature

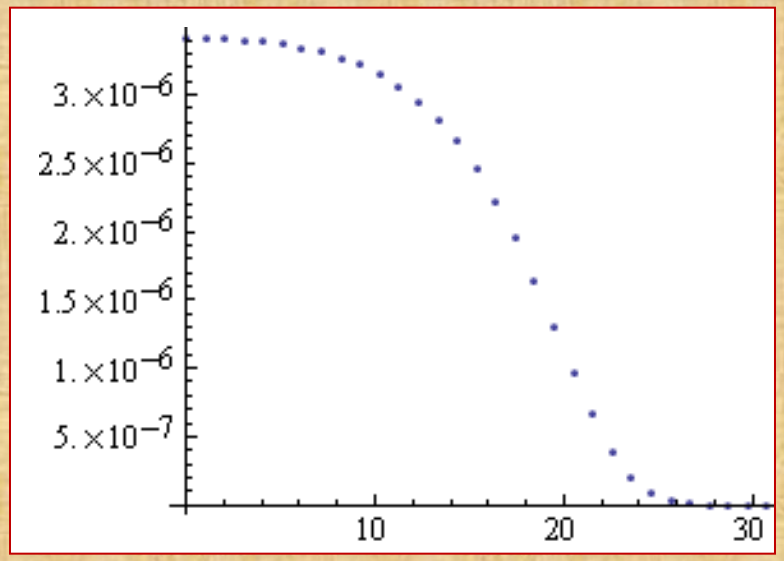
At a fixed time of experiment, t_e,

peak profile $$\rho(z) = (1+u_m\tau_a)\cdot U(t_e,z)$$

NUMERICAL SOLUTION

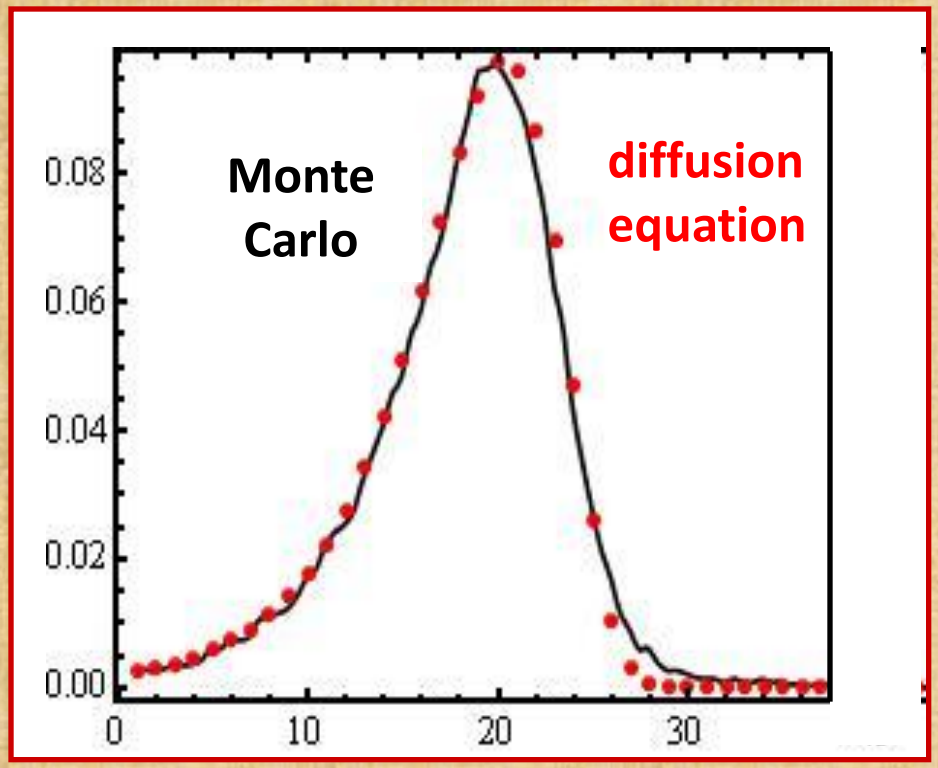
VTC peak profile from mass diffusion equation 3

$U(\text{standard conditions},\ z)$



Distance / cm

$\rho(z)$



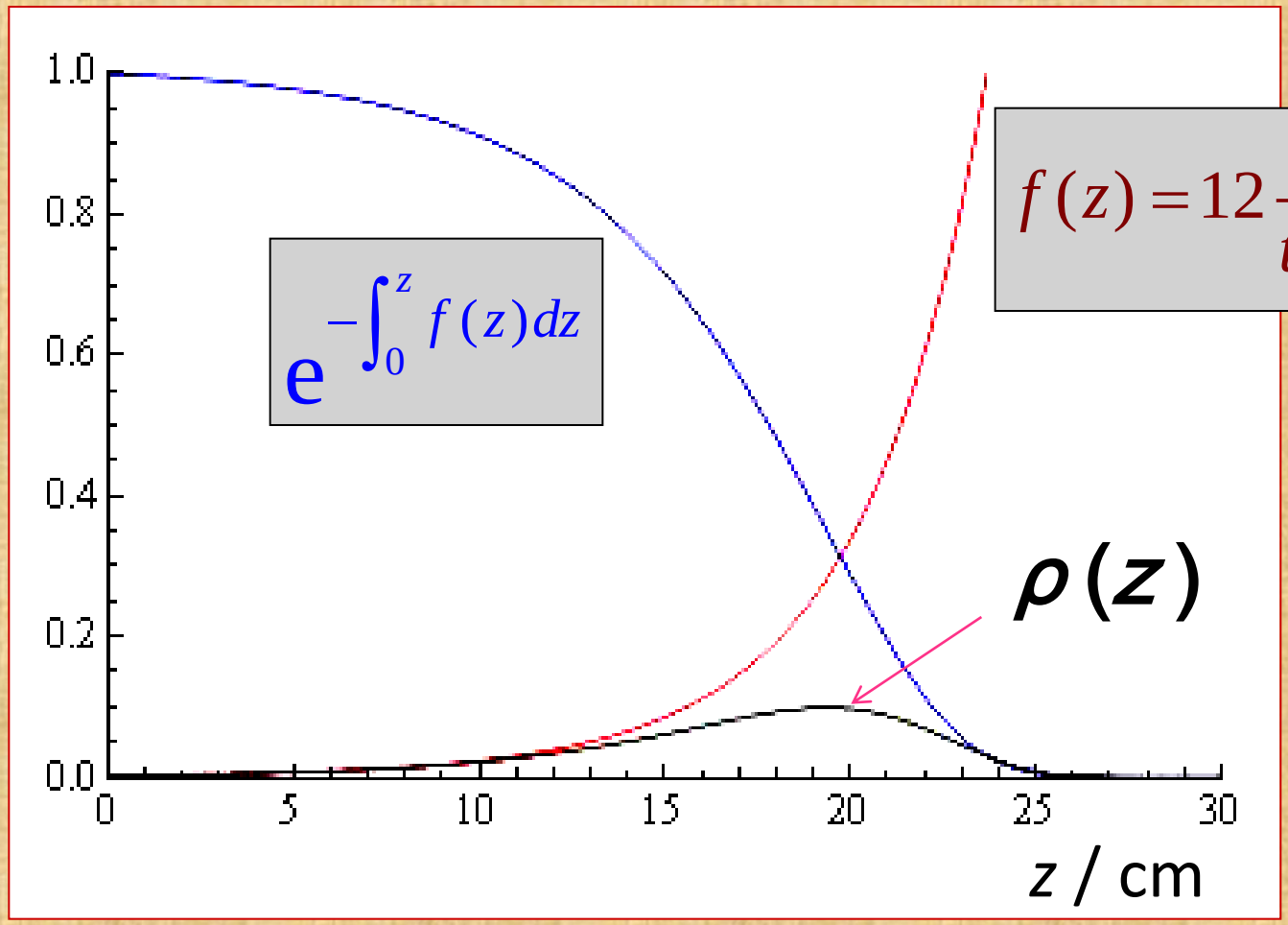
Distance / cm

Analytical formula for peak profile 1

$$\rho_z(z) = (1 + u_m \tau_a) \cdot U(t_e, z)$$

product of two factors

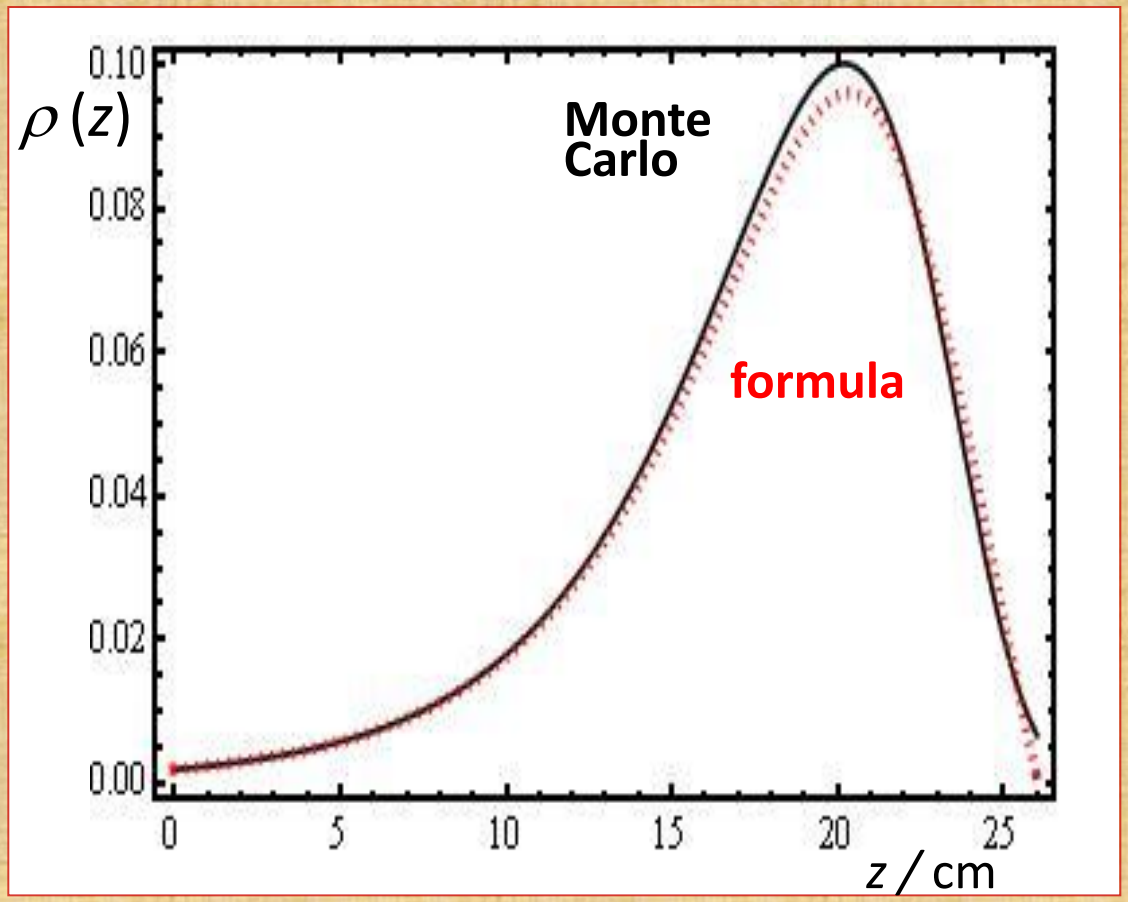
$$\rho(z) \approx f(z) \times e^{-\int_0^z f(z)dz}$$

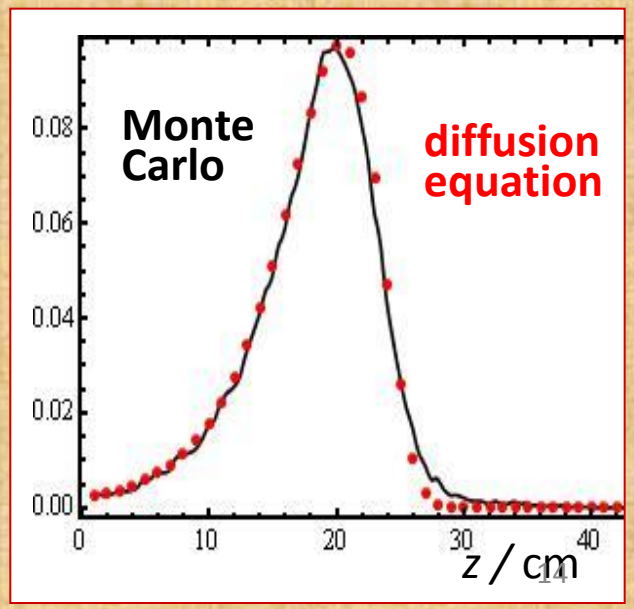


Analytical formula for peak profile 2

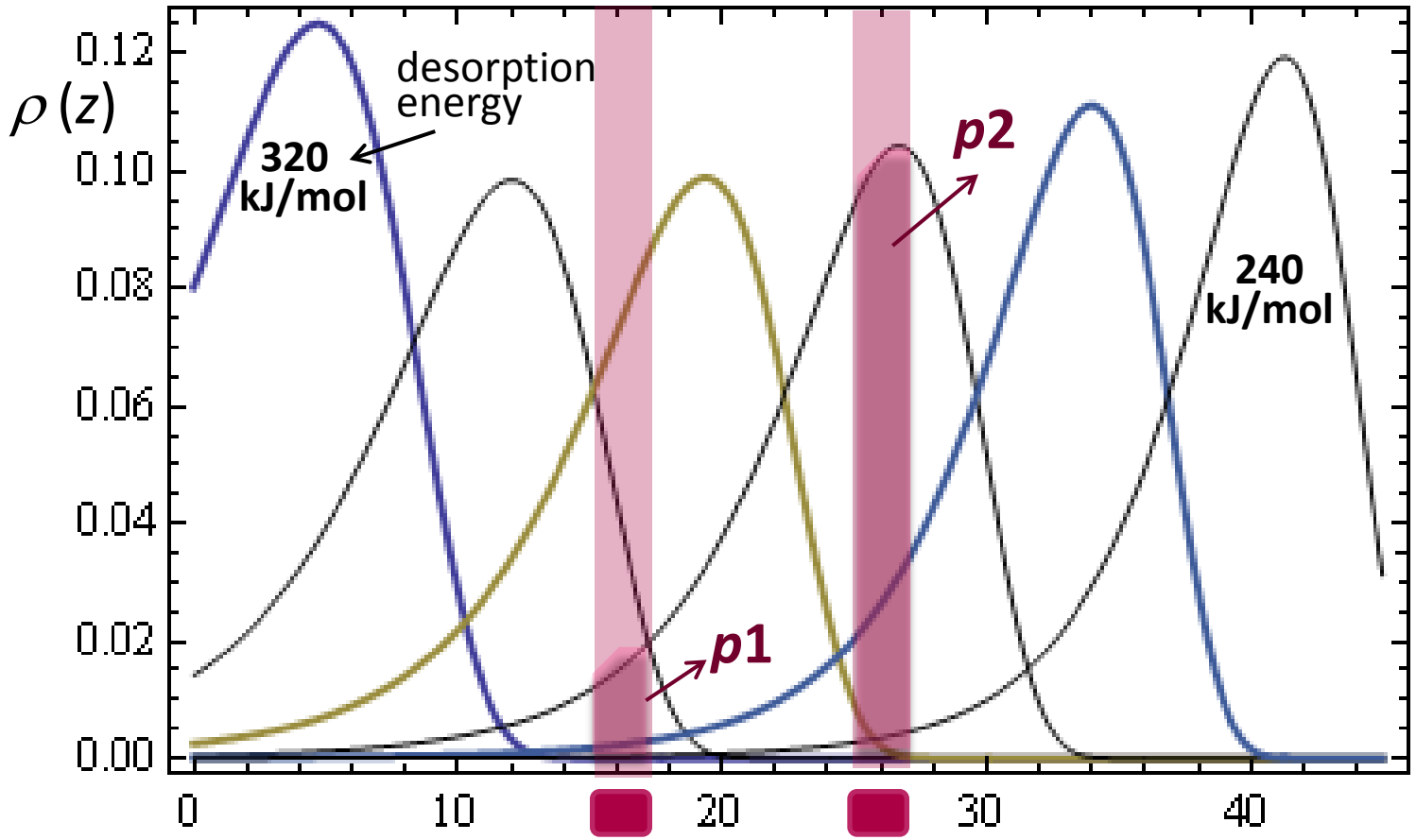
$$\rho(z) \approx 12 \frac{\tau_0}{t_e} \exp \frac{\varepsilon_d}{kT} \times \exp\left\{ -\frac{12}{g} \frac{\tau_0}{t_e} \frac{k}{\varepsilon_d} \left[T^2 \cdot e^{\frac{\varepsilon_d}{kT}} \left(1 + 2\frac{kT}{\varepsilon_d} \right) - T_S^2 e^{\frac{\varepsilon_d}{kT_S}} \left(1 + 2\frac{kT_S}{\varepsilon_d} \right) \right] \right\}$$

$$T = T_S - gz$$





Bayesian treatment of poor statistics data 1



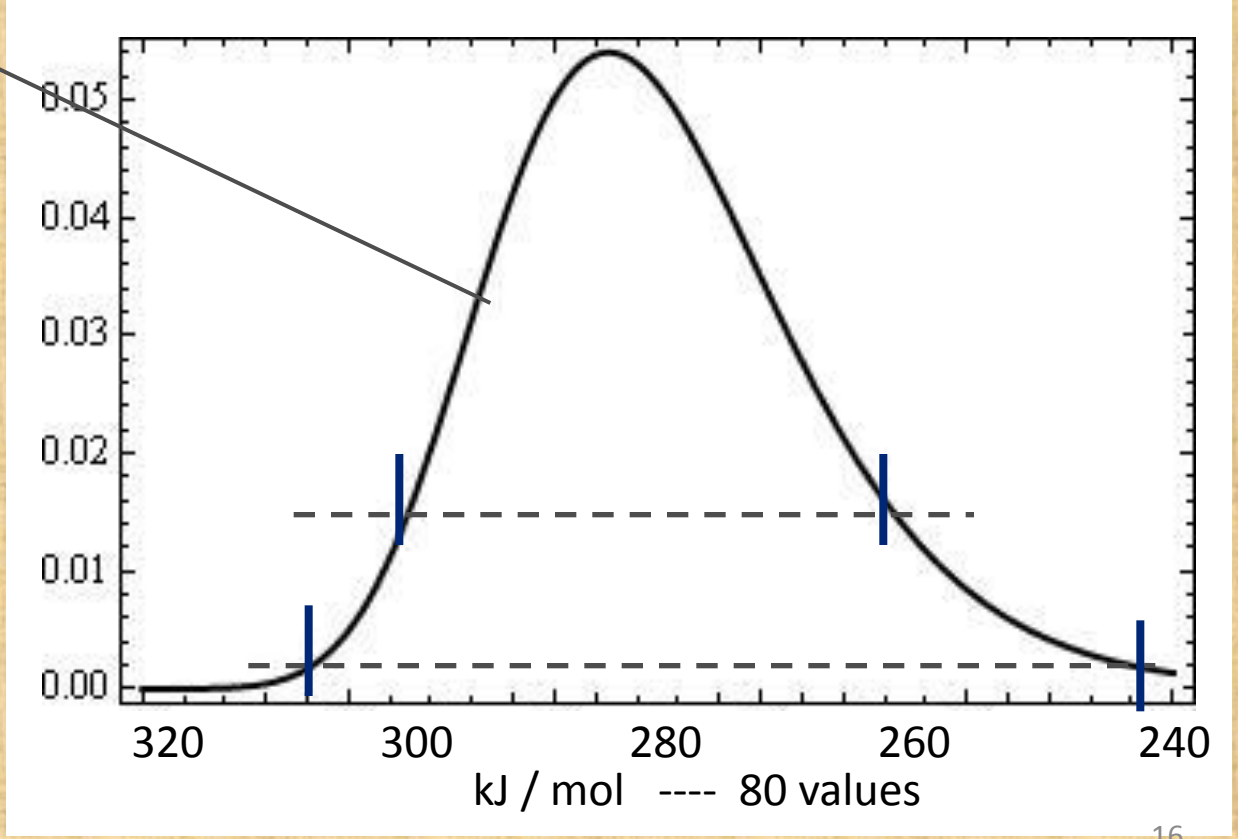
For many desorption energies in a reasonable range calculate the peak profile and probability of such observation : $p1 \times p2$

Bayesian treatment of poor statistics data 2

$p1 \times p2$ is the **likelihood** of observation two decays by the particular detectors at given desorption energy

$$\frac{p_1 p_2}{\int p_1 p_2 \cdot d\varepsilon_d}$$

is the **Bayes (normalized) posterior function** (at "complete prior ignorance")



One gets 63 / 98 / … % confidence that the true value is within the indicated interval

Prospects of using vacuum thermochromatography in transactinoid studies

Advantages of VTC compared with GTC

- Very simple fundamental molecular picture of the processing, easy to simulate by Monte Carlo for any real conditions; fewer assumptions necessary.
- Description of peak shapes by an analytical function of the experimental parameters and properties of the molecules. It much enables (Bayesian) evaluation of uncertainty of the “experimental “ desorption energies.
- Unique possibility to realize and maintain really clean, well defined surface of the column.
- Fast diffusional transportation from the outlet of a gas-filled mass separator to some 1 meter.
- Allowed are square section columns (especially with position – sensitive detectors) . It obeys better detection efficiency and easier data evaluation.

Disadvantages of VCT compared with GTC

- Fewer ways to affect the shape of peaks and so the degree of separation.
- No porous filters possible.
- Smaller variety of chemical compounds be handled ???
- Non-trivial problems with introducing molecules into the column.

First choice studies with SHE and expected experimental problems

- Adsorption of SHE atoms on metallic and other surfaces
- Introducing the SHE atoms into the column -- possible solution: recoils from gas-filled separator are stopped in a liquid catcher and isolated by evaporation (continuously)

CAVEAT: Only some ten detectable atoms allow quantitative conclusions; the same holds for conclusiveness of zero counts in NO / YES experiments.

Future:

Surfaces thermally stable but chemically active towards the atoms under study


THE END IS
JUST THE BEGINNING...