

TRANSPORTPHÄNOMENE IN
FLÜSSIGKEITEN UND FESTKÖRPERN:
WIE MAN MITTELS COMPUTERSIMULATION
VERSTÄNDNIS GEWINNT

KURT BINDER, Mainz

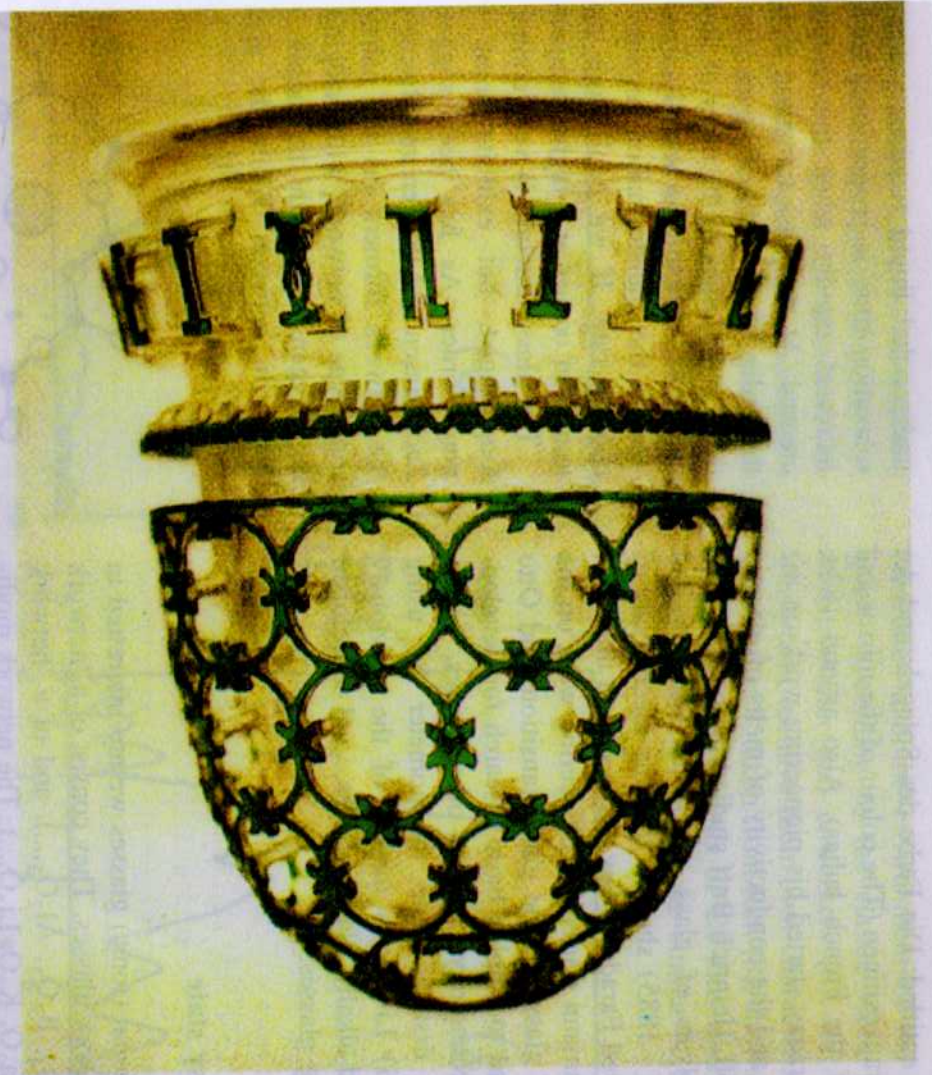
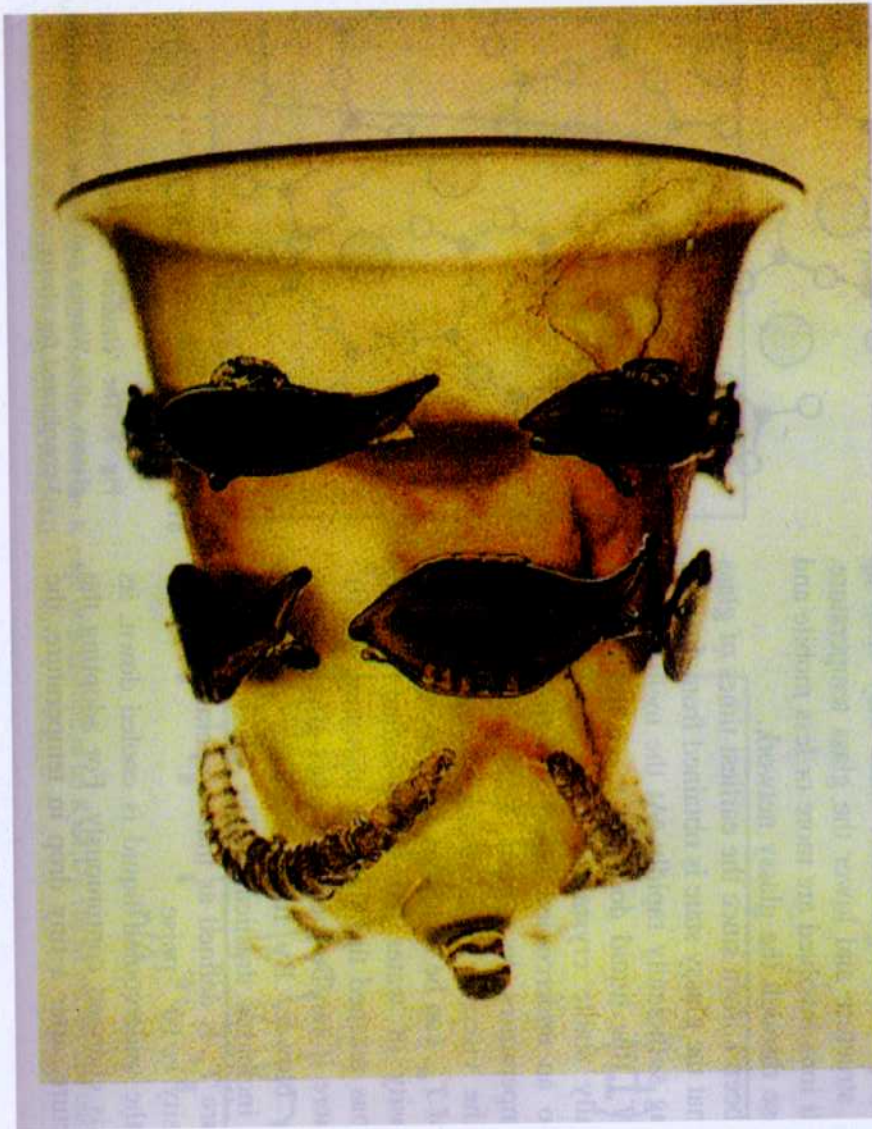
Mitarbeiter: W. KOB, J. HORBACH

L. YELASH, P. VIRNAU, W. PAUL, B. M. MOÇNETTI

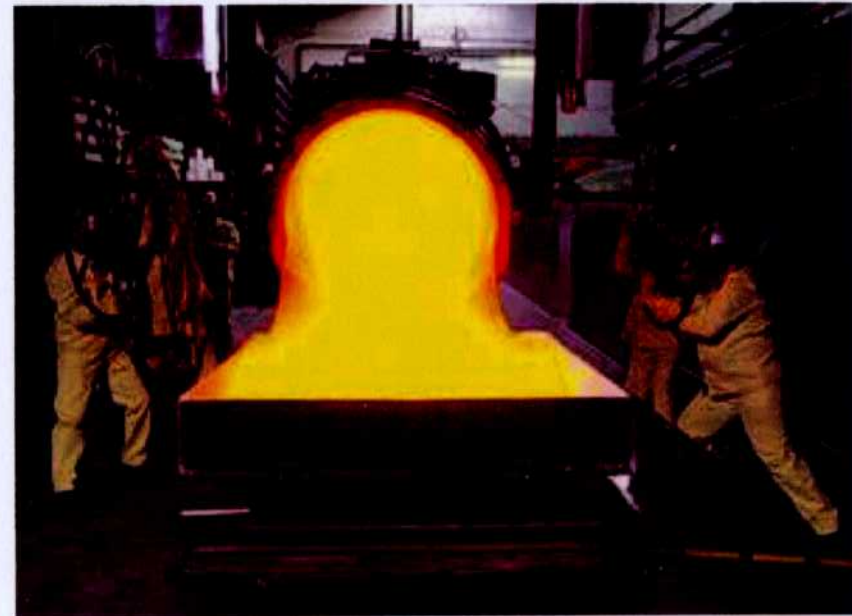
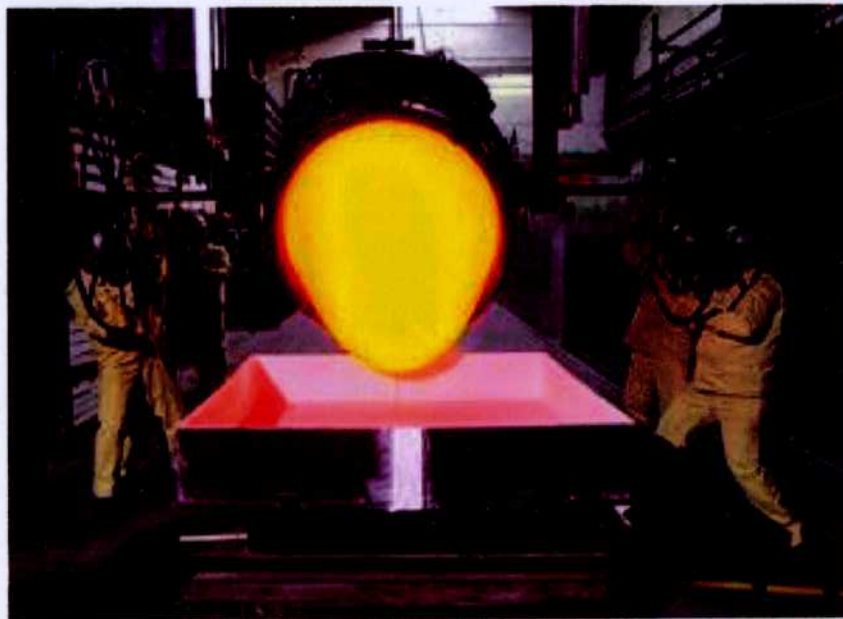
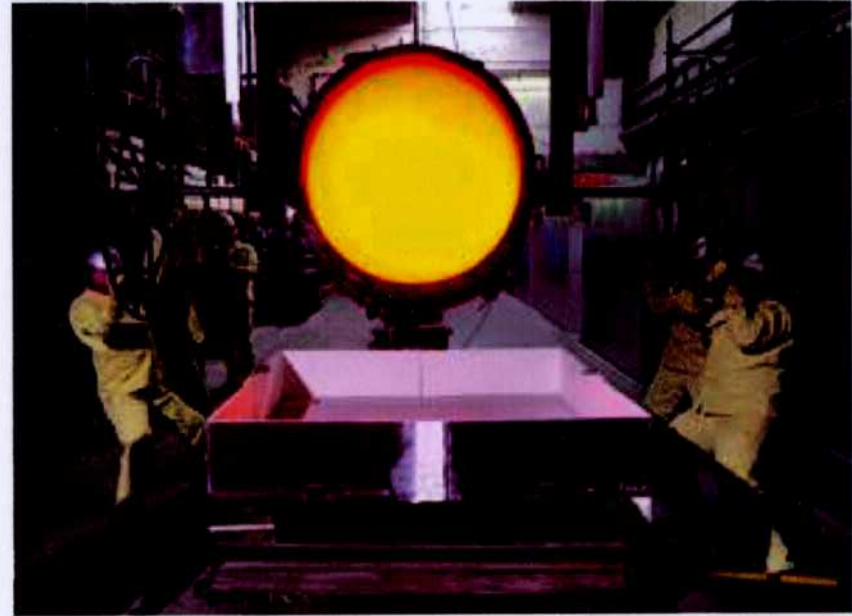
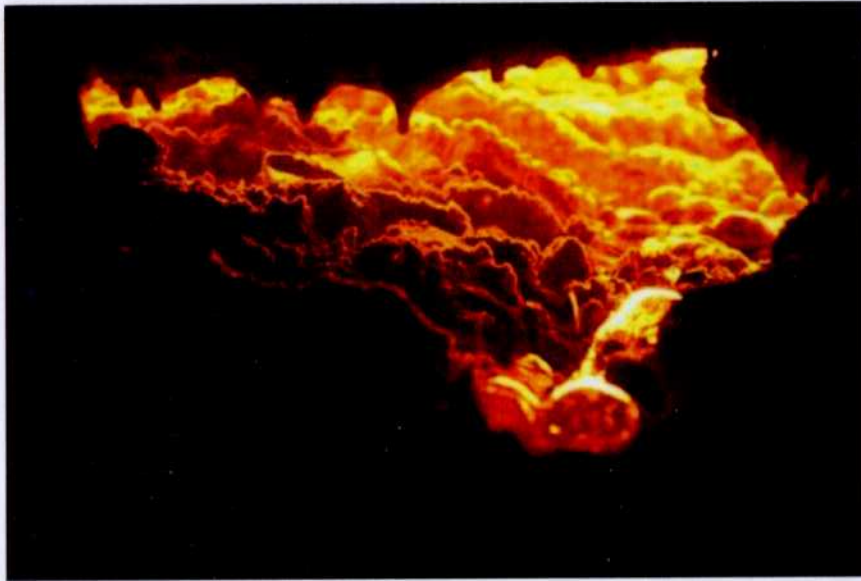
finanzielle Förderung:

SCHOTT AG, BASF SE, BMBF, DFG, NIC

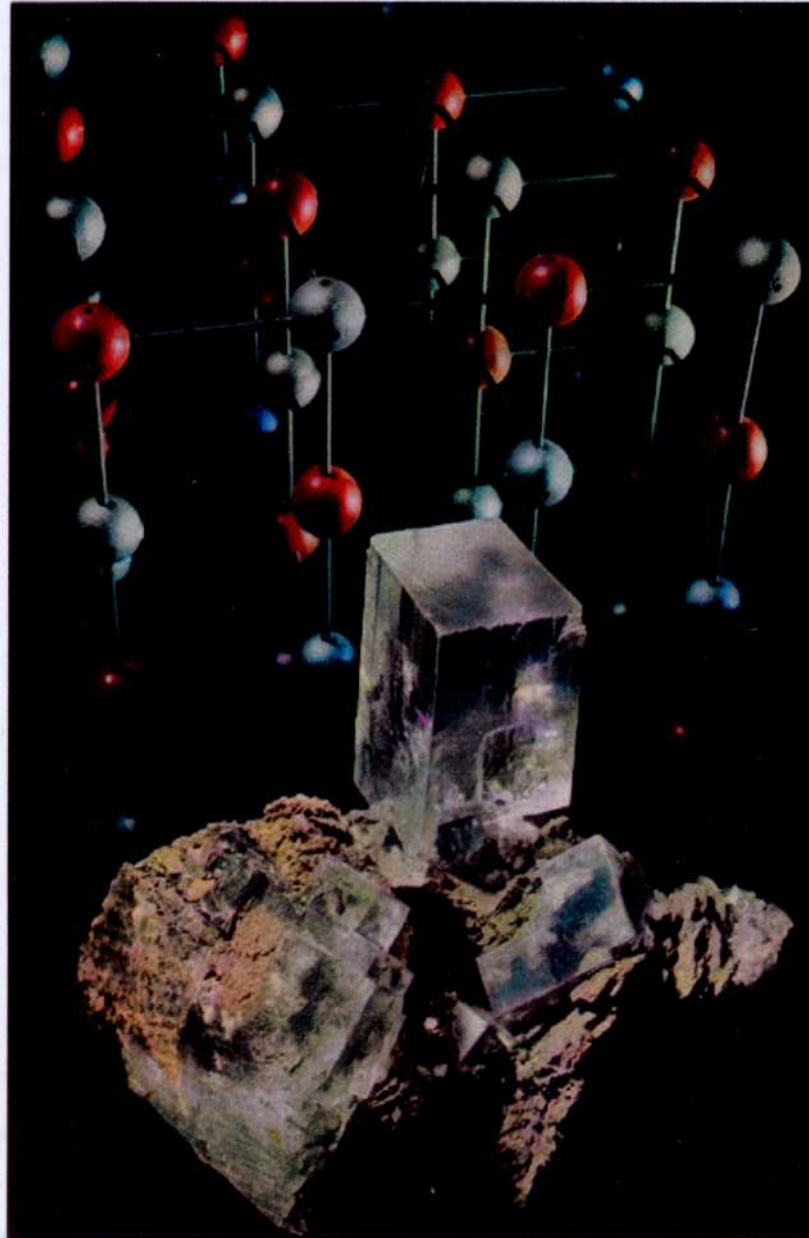
Röm. Glasbehälter 3./4. Jh.

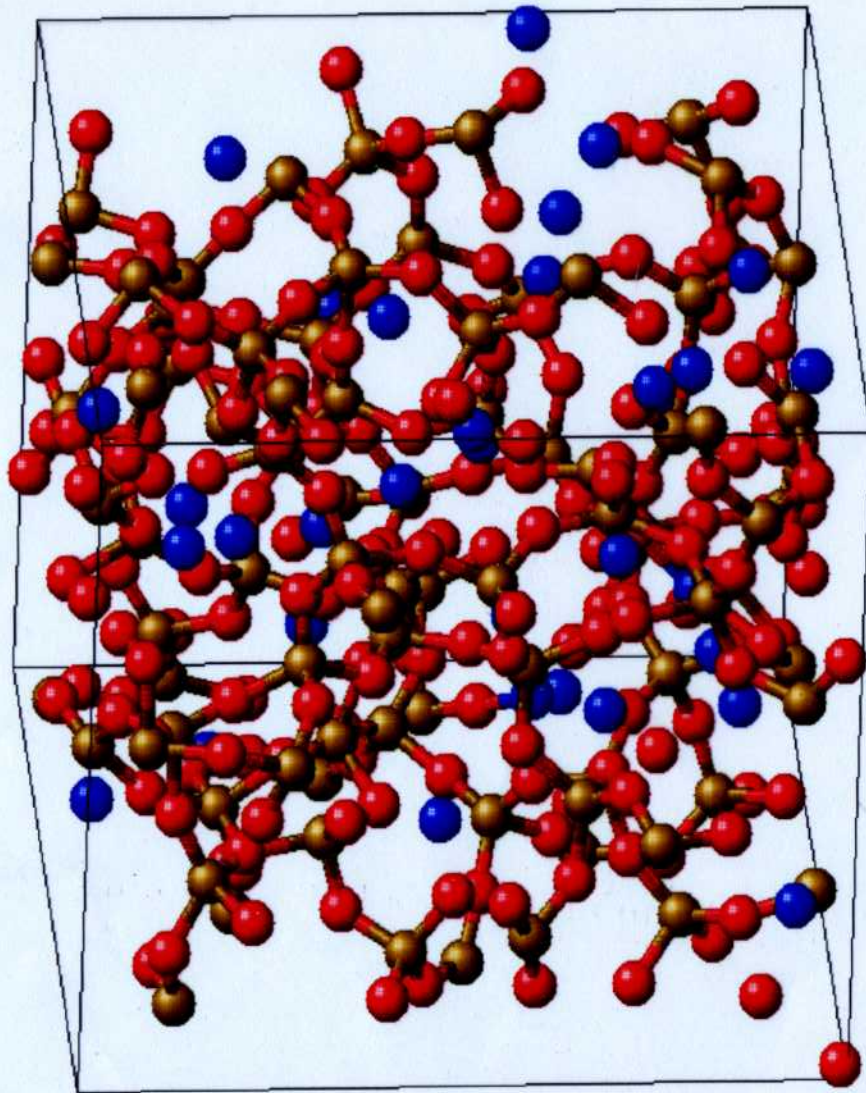


Glasproduktion bei Schott

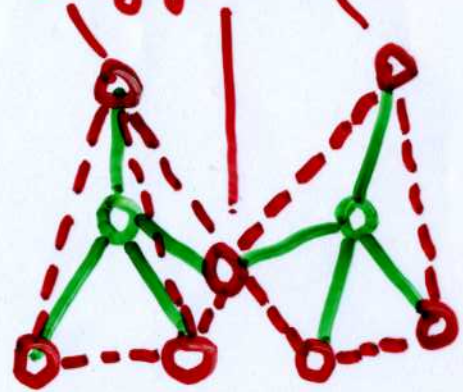


Kristalline Struktur





oxygen atoms

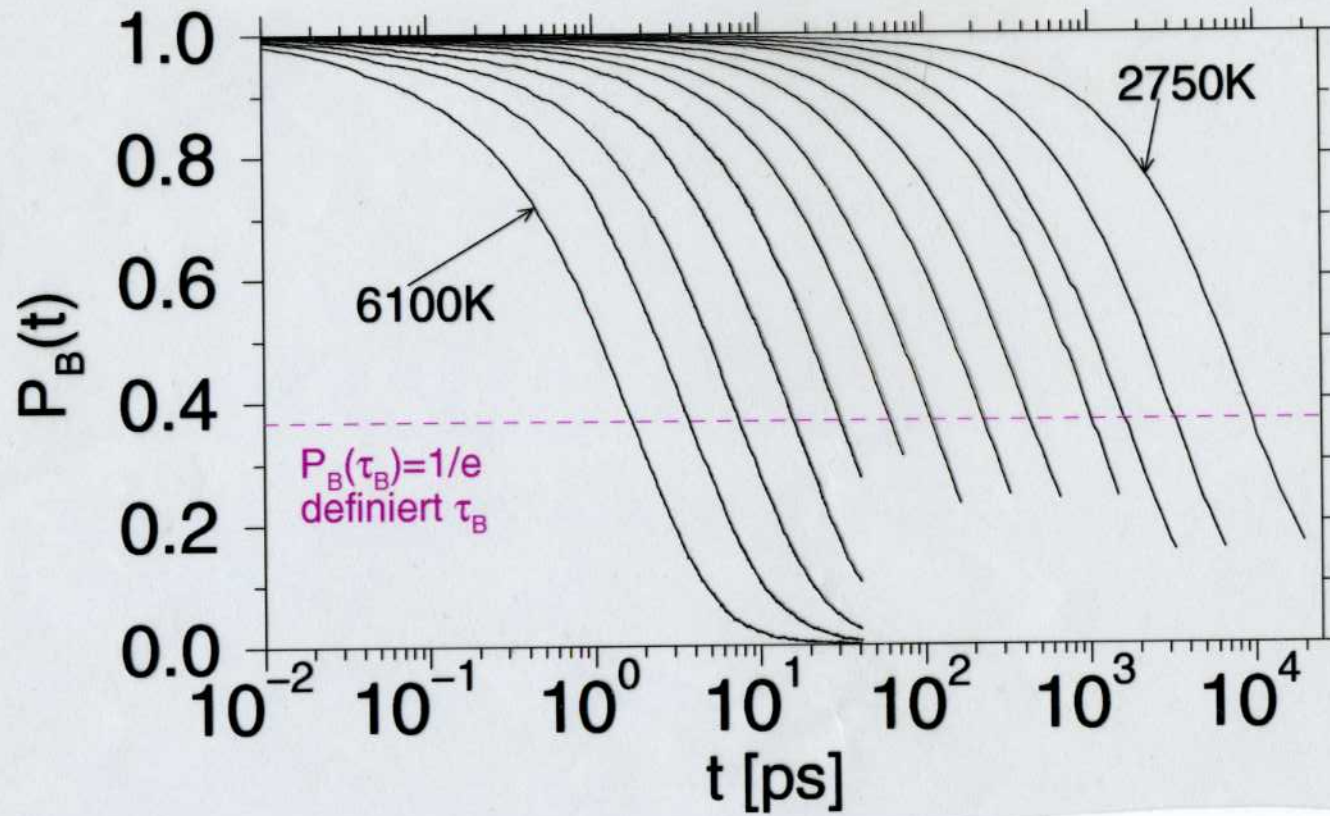


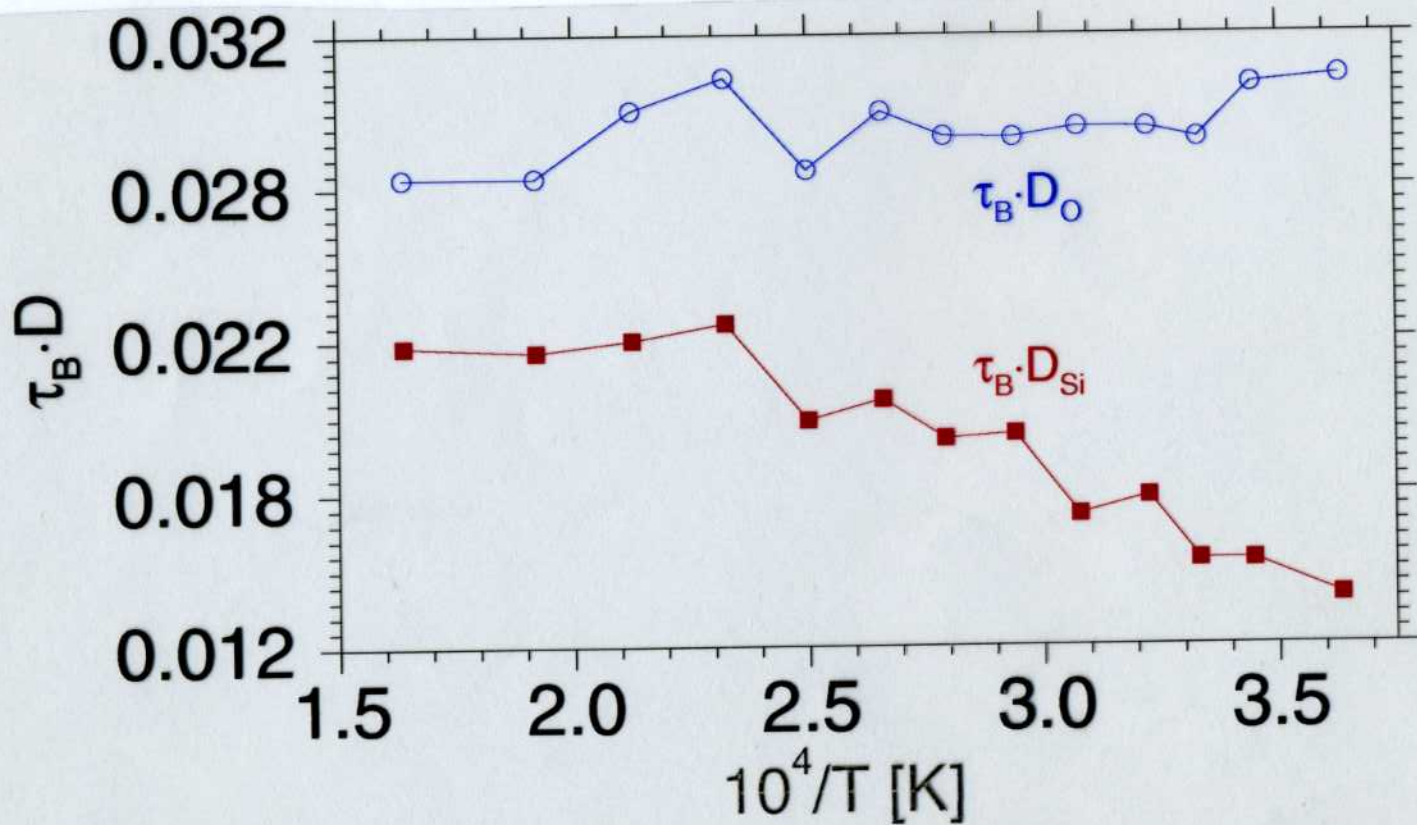
silicon atoms: in
the centers of
(distorted) tetrahedra

ideal network:
every oxygen is SHARED
by two neighboring
tetrahedra

Das Brechen von Bindungen

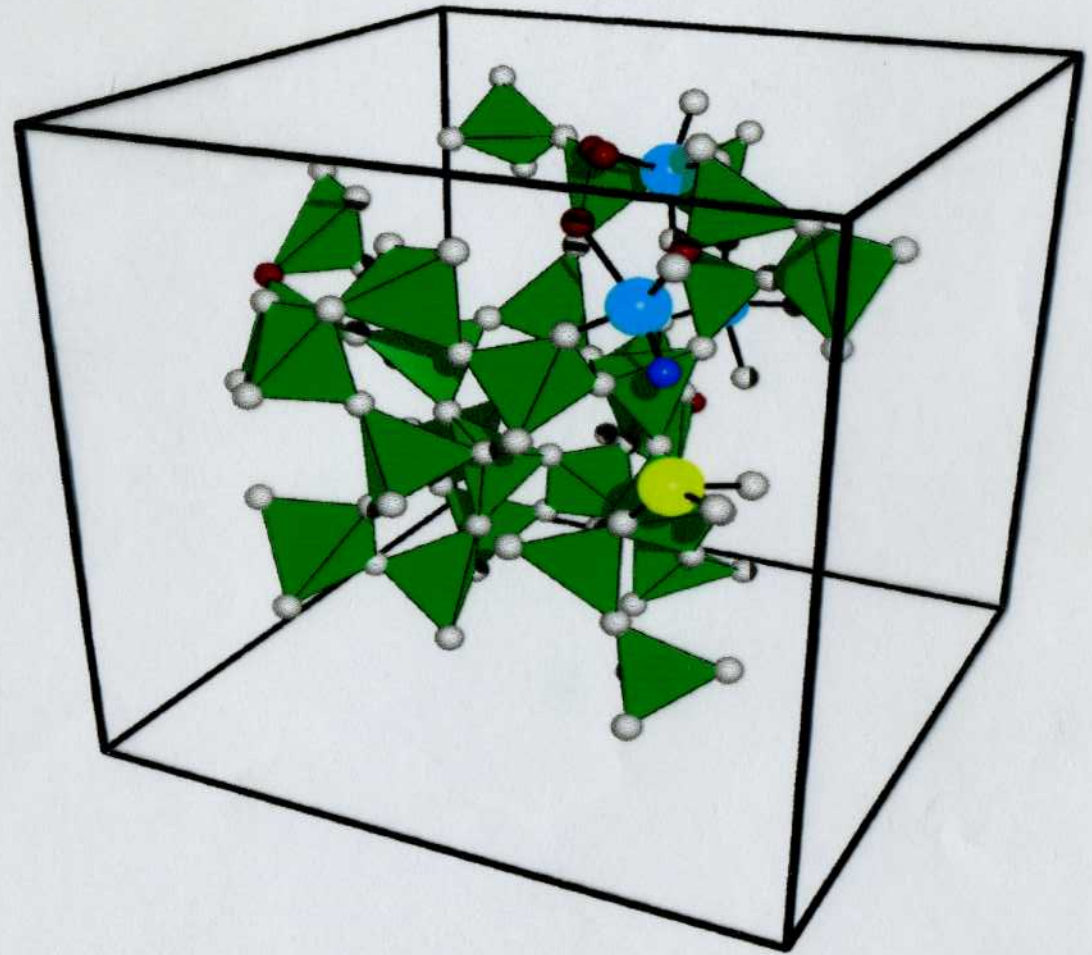
- $P_B(t)$: Wahrscheinlichkeit, daß eine Si-O-Bindung, die zur Zeit $t = 0$ bestanden hat, auch noch zur Zeit $t \neq 0$ besteht.





- \Rightarrow Sauerstoffdiffusion ist mit dem Bruch einer Si-O-Bindung verknüpft.

Schnappschuß bei $T=3580\text{K}$



- Koordinationszahlverteilung:

$$Z_{\text{Si-O}} = 3: 1\%$$

$$Z_{\text{Si-O}} = 4: 95.2\%$$

$$Z_{\text{Si-O}} = 5: 3.8\%$$

$$Z_{\text{O-Si}} = 1: 0.9\%$$

$$Z_{\text{O-Si}} = 2: 96.8\%$$

$$Z_{\text{O-Si}} = 3: 2.3\%$$

- α -Relaxationszeit ist in der Größenordnung von 100ps bei 3580K .

Molekulardynamik - Methode

Integration der Newton'schen Bewegungsgleichungen der klassischen Mechanik:

$$m_i \frac{d^2 \vec{r}_i}{dt^2} = \vec{F}_i = - \frac{\partial U(\vec{r}_1, \dots, \vec{r}_N)}{\partial \vec{r}_i}$$

Masse mal Beschleunigung = Kraft = negativer Gradient der potentiellen Energie

Aber: Atome = Kerne + Elektronen \Rightarrow QUANTENMECHANIK erforderlich!

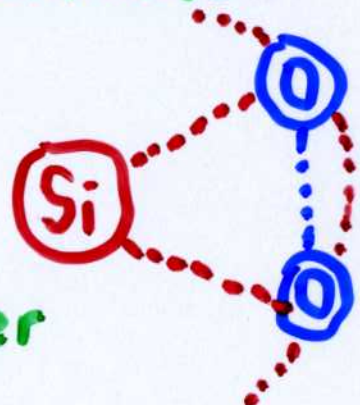
$$U = \frac{1}{2} \sum_i \sum_j \phi(r_{ij})$$

\hookrightarrow "ab initio" Quantenchemie \Rightarrow effektive Potentiale
van Beest, Kramer, van Santen (1990)

$$\phi(r_{ij}) = \frac{1}{r_{ij}} q_i q_j + A_{ij} \exp(-B_{ij} r_{ij}) - C_{ij} / r_{ij}^6$$

$i, j \in [\text{Si}, \text{O}, \text{Na}]$

"Simulation" gerichteter kovalenter Bindungen mit Paarpotentialen



Molekulardynamik - Methode

Näherungen: 1. KLASSISCHE MECHANIK statt QUANTENMECHANIK

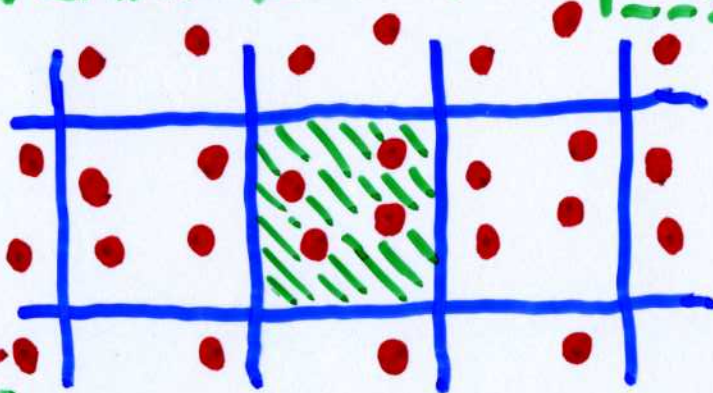
2. Nur WINZIGKLEINER AUSSCHNITT aus System wird SIMULIERT!

$1 \text{ cm}^3 \text{ Material} \cong 10^{22} \text{ Atome} \Rightarrow \text{Rechner hoffnungslos überfordert!}$

\Rightarrow kubische Box, KANTENLÄNGE z.B. 48.73 \AA , enthält nur 8016 Atome (Dichte = 2.37 g/cm^3 vorgegeben)

Oberflächen-effekte VERMIEDEN durch periodische Randbedingungen

ganzer Raum wird periodisch „ausgefüllt“ mit identischen Bildern der zentralen Simulation



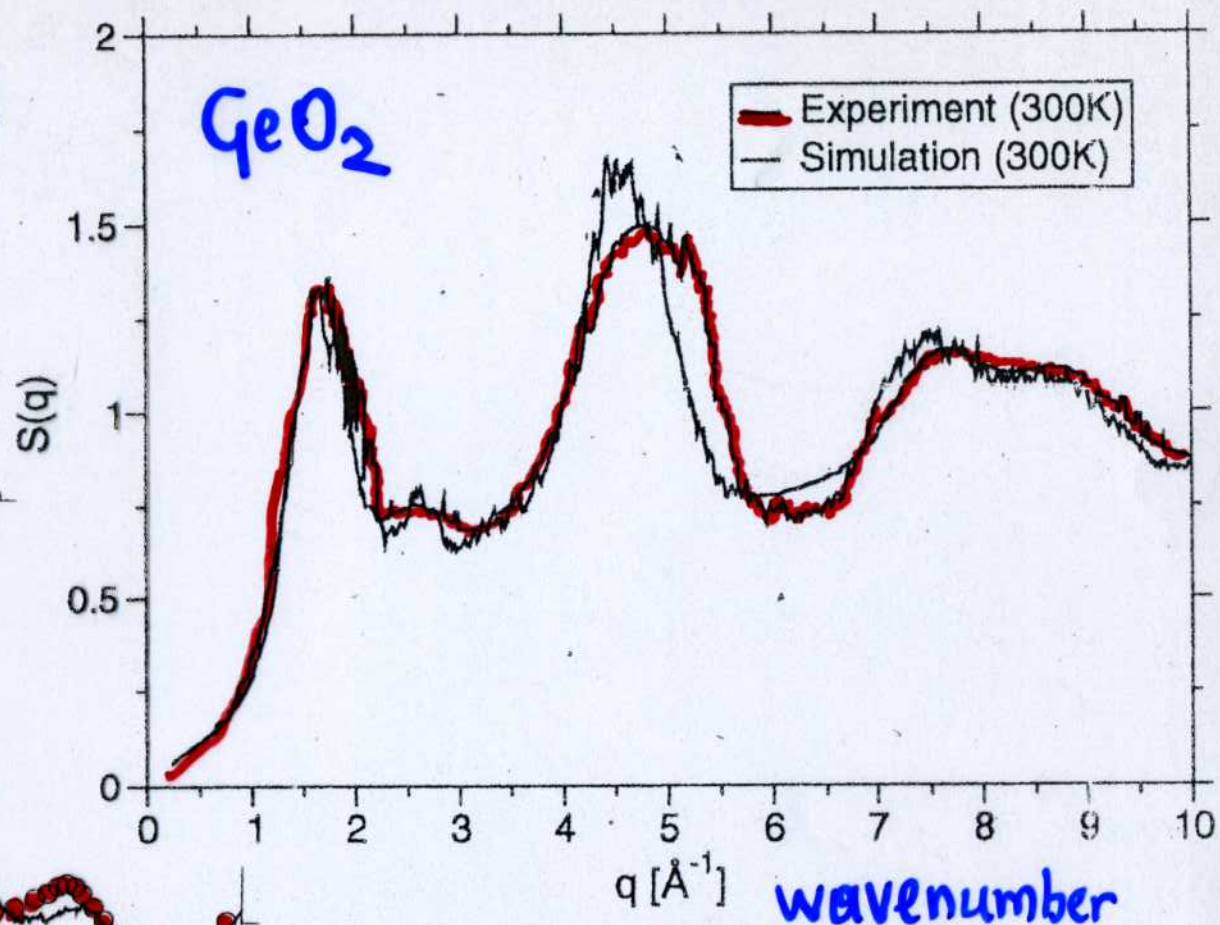
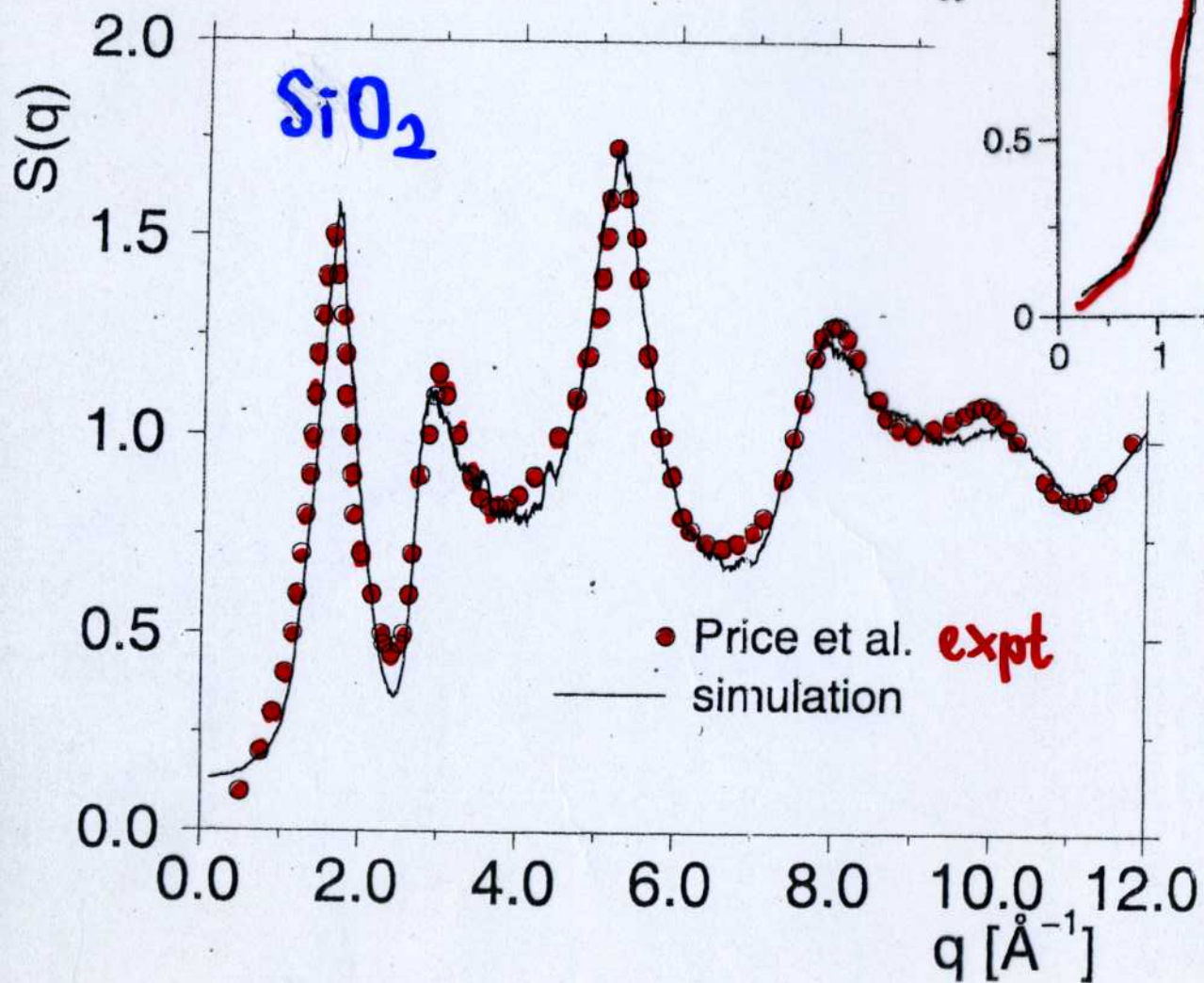
System
"quasi-unendlich"

BOX \Rightarrow Atome wechselwirken mit allen periodischen Bildern

\Rightarrow EWALD-Summation notwendig

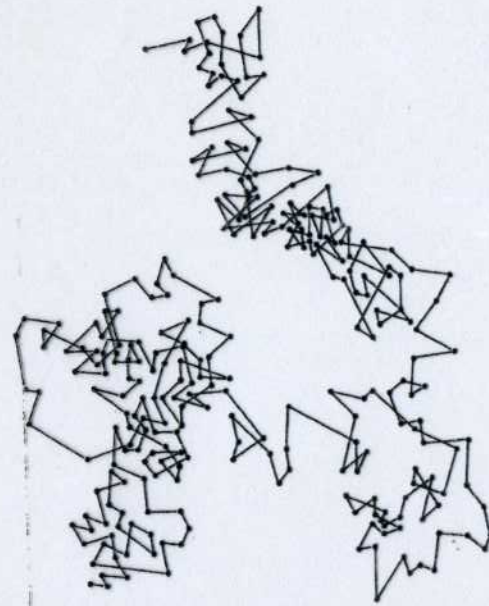
3. Diskreter Zeitschritt: $dt \rightarrow \Delta t = 1.6 \times 10^{-15} \text{ sec}$ \rightarrow 12 Mio Zeitschritte \cong 20 Nanosek. Realzeit

STATIC STRUCTURE FACTOR neutron scattering data



**NO ADJUSTABLE
PARAMETERS !**

Mittleres Verschiebungsquadrat der Teilchen



Brownsche Bewegung

Brown'sche
Bewegung:
Zufallsweg

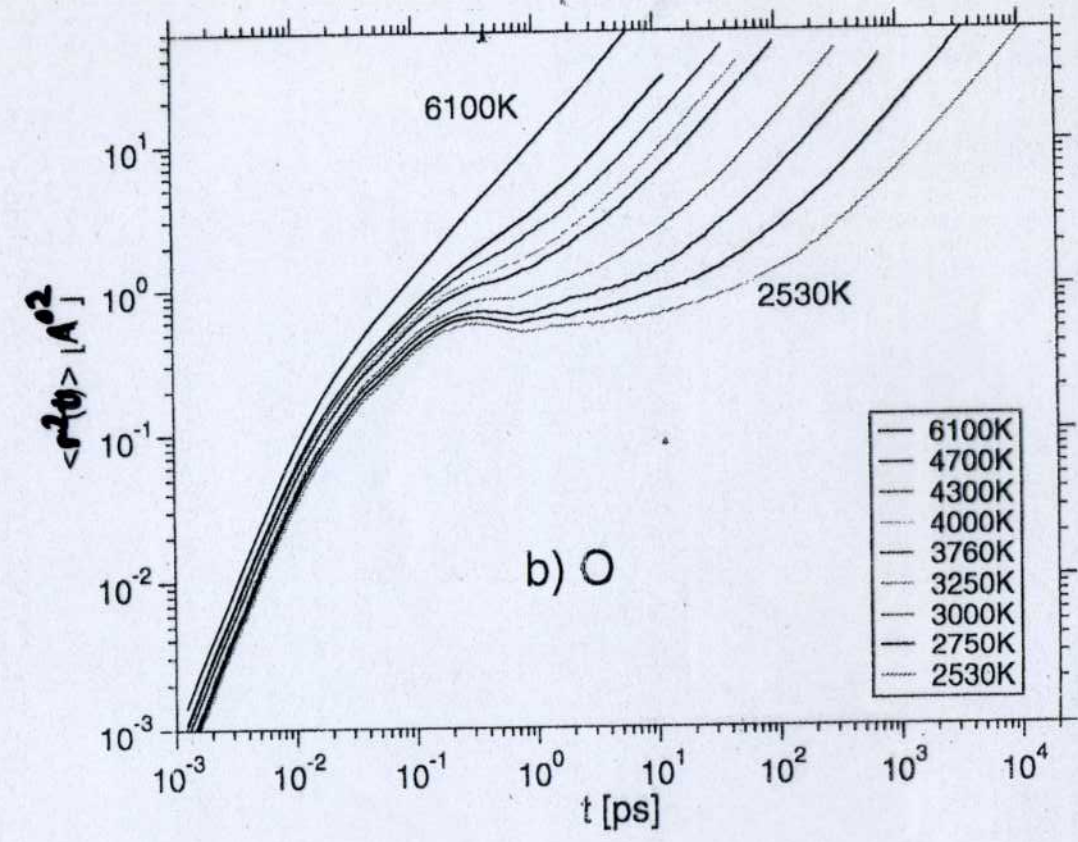
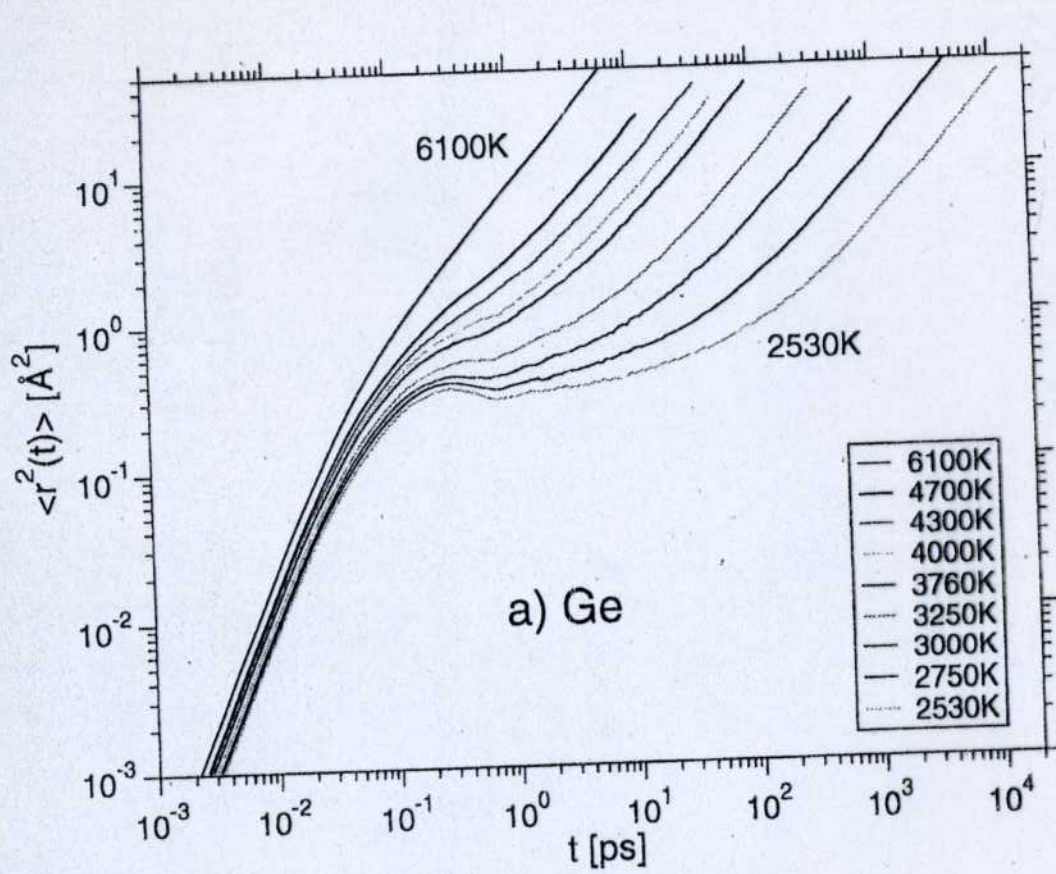
EINSTEIN:

$$\langle [\vec{r}(t) - \vec{r}(0)]^2 \rangle = 6 D t$$

ZEIT

Diffusionskonstante

MEAN SQUARE DISPLACEMENTS of the particles



$\langle r^2(t) \rangle \propto t^2$
ballistic regime

$\langle r^2(t) \rangle \approx \text{constant}$
CAGE EFFECT

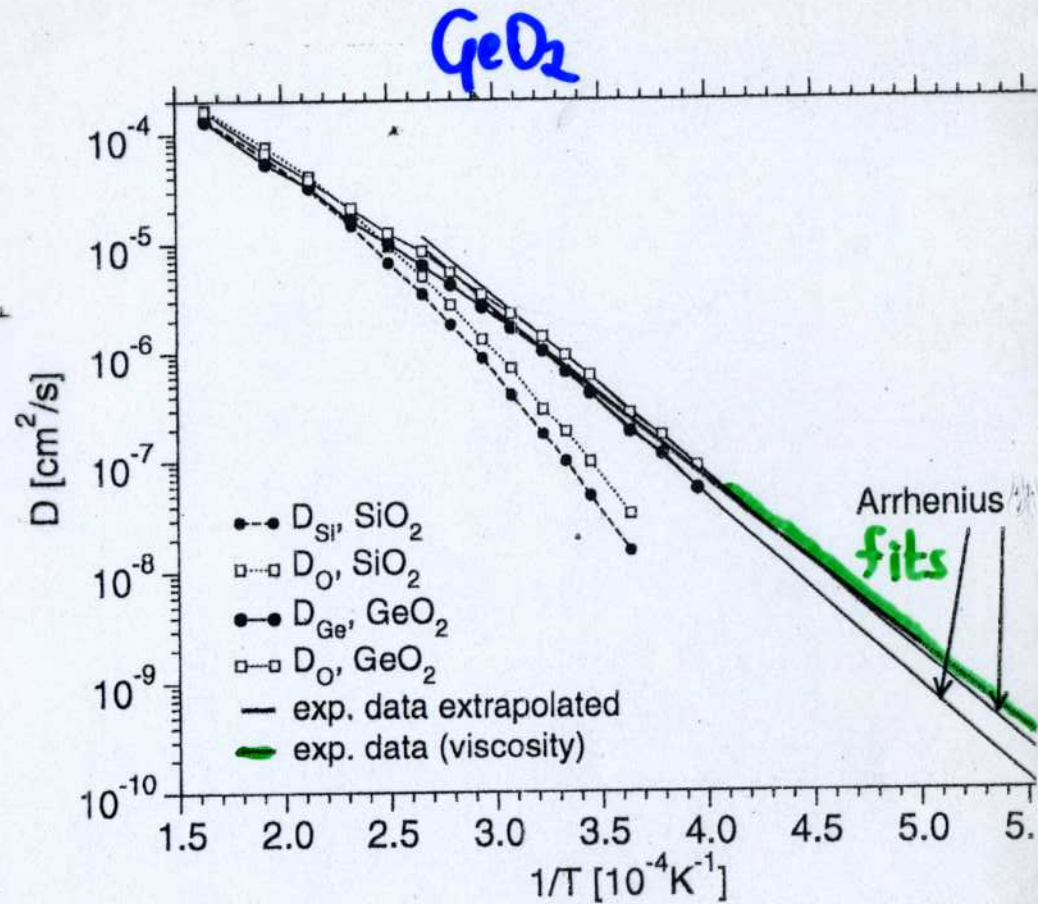
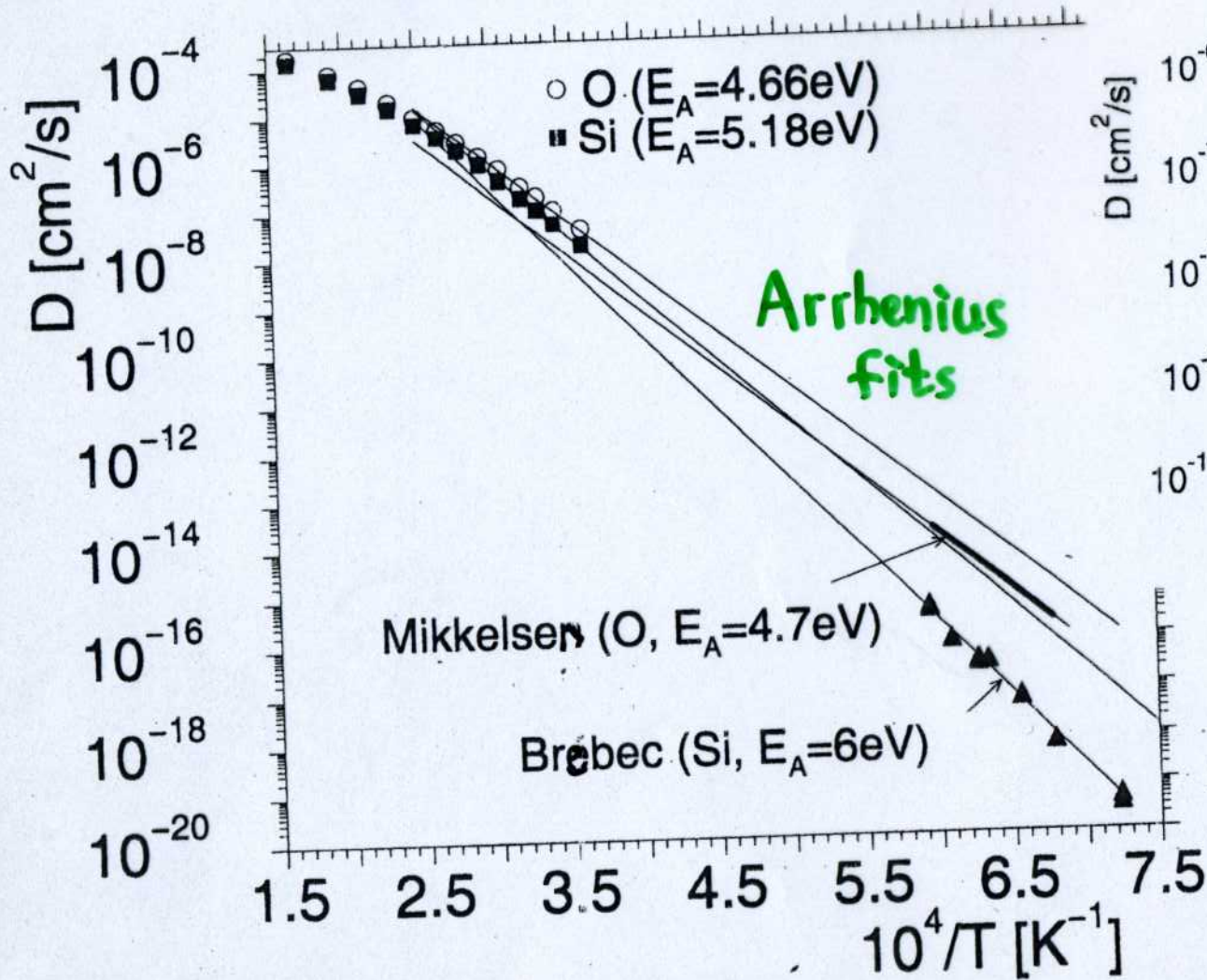
$\langle r^2(t) \rangle = 6 D_\alpha t$
diffusive regime (Einstein relation)

D_α = self diffusion coefficient
($\alpha = \text{Ge or O}$)

SELFDIFFUSION COEFFICIENTS

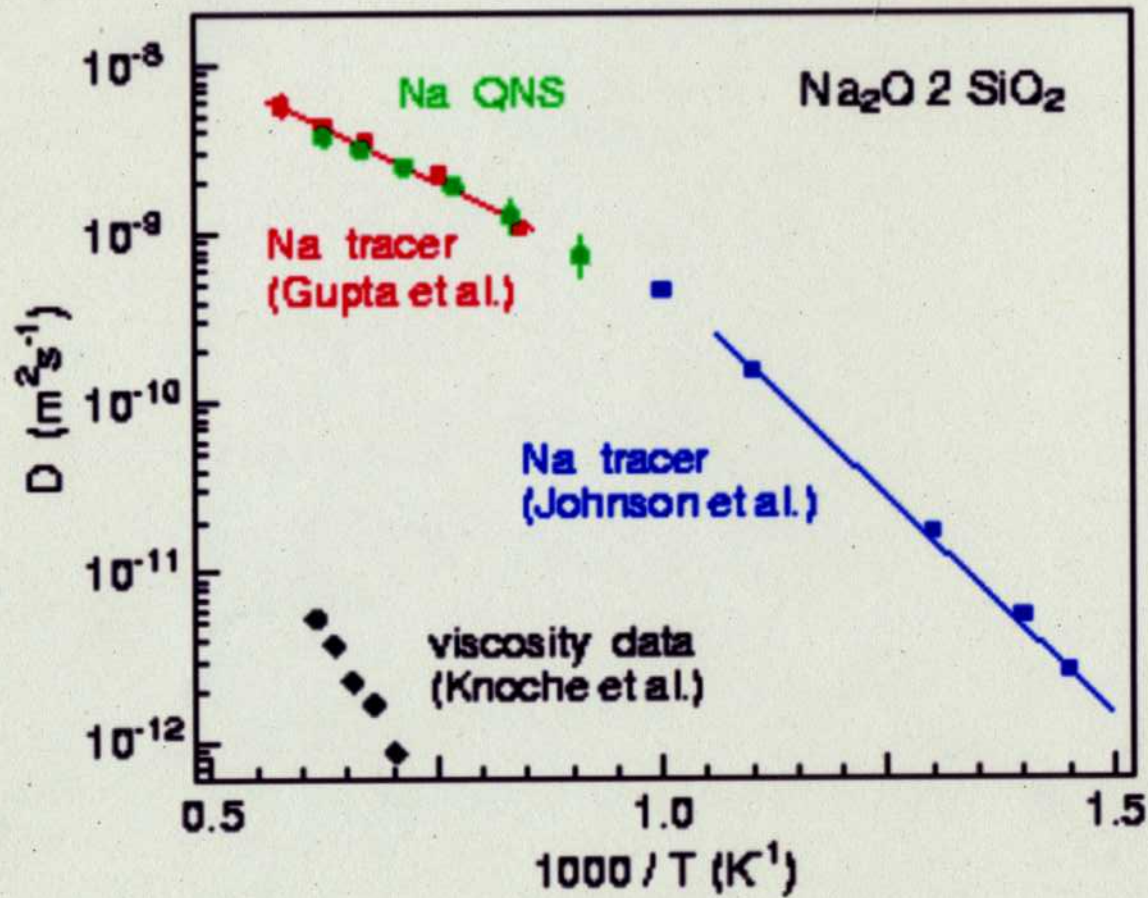
$$D \propto \exp(-E_A/k_B T)$$

SiO₂ (Horbach & Kob 1999)



curvature at high T:
 qualitatively similar
 to FRAGILE
 glassformers

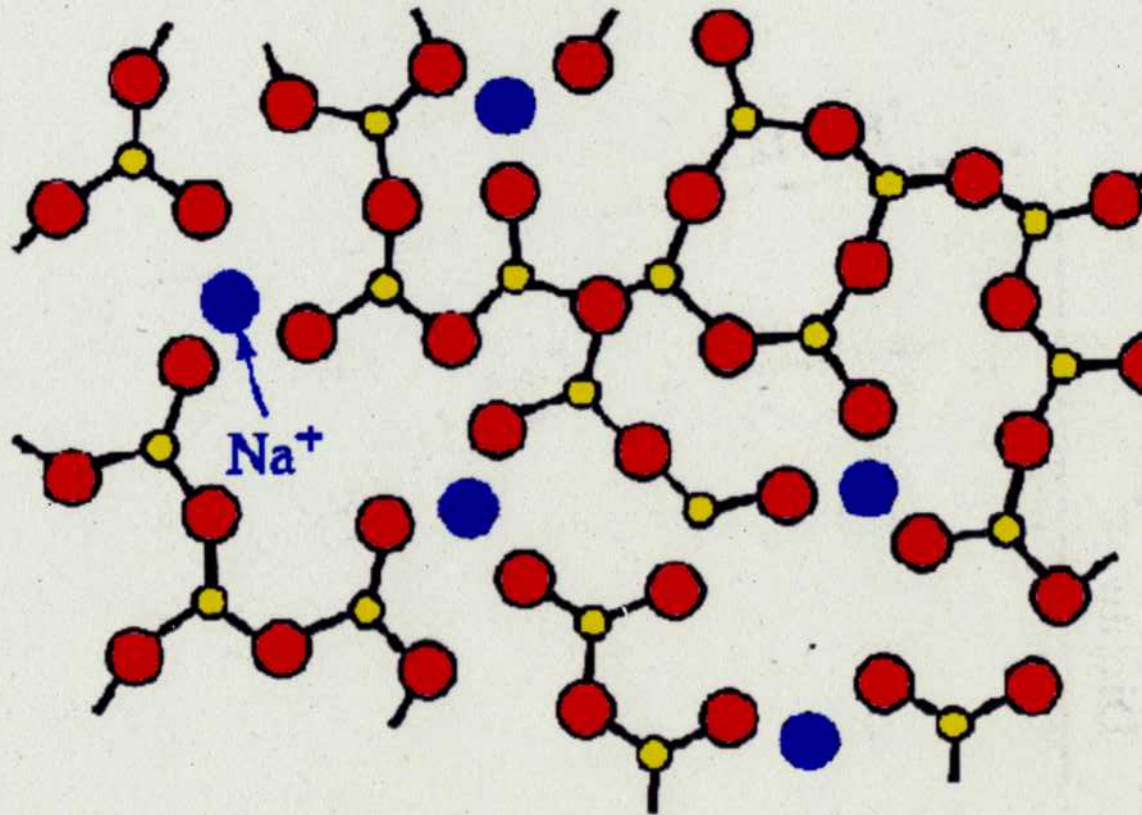
Diffusion in Sodium Silicates



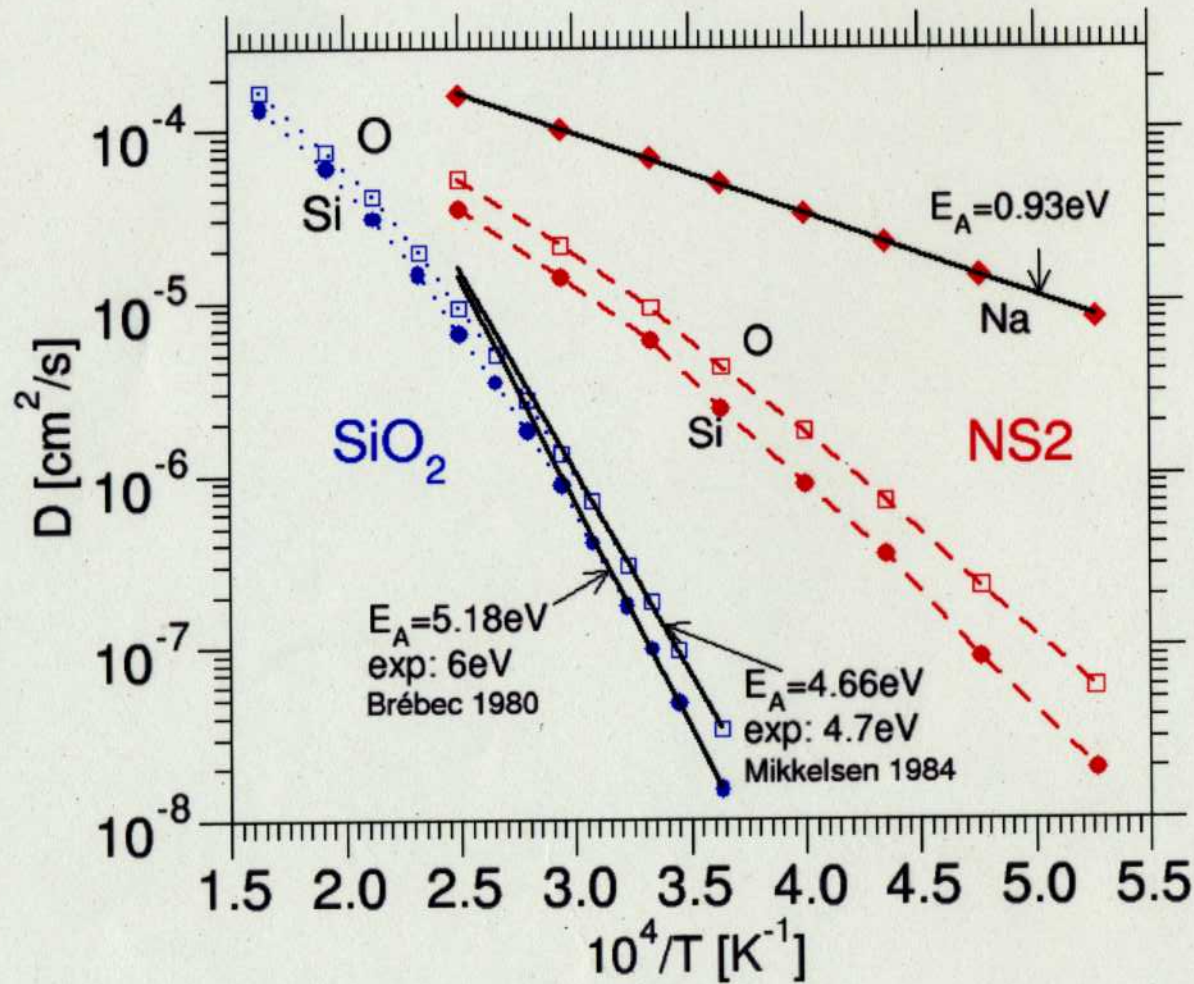
ion conductor:
fast sodium motion
in "SiO₂ matrix"
even around **1700K**

Structure of Sodium Silicates

- structure of pure SiO_2 : disordered network of SiO_4 tetrahedra
- + Na_2O : disrupted network structure:

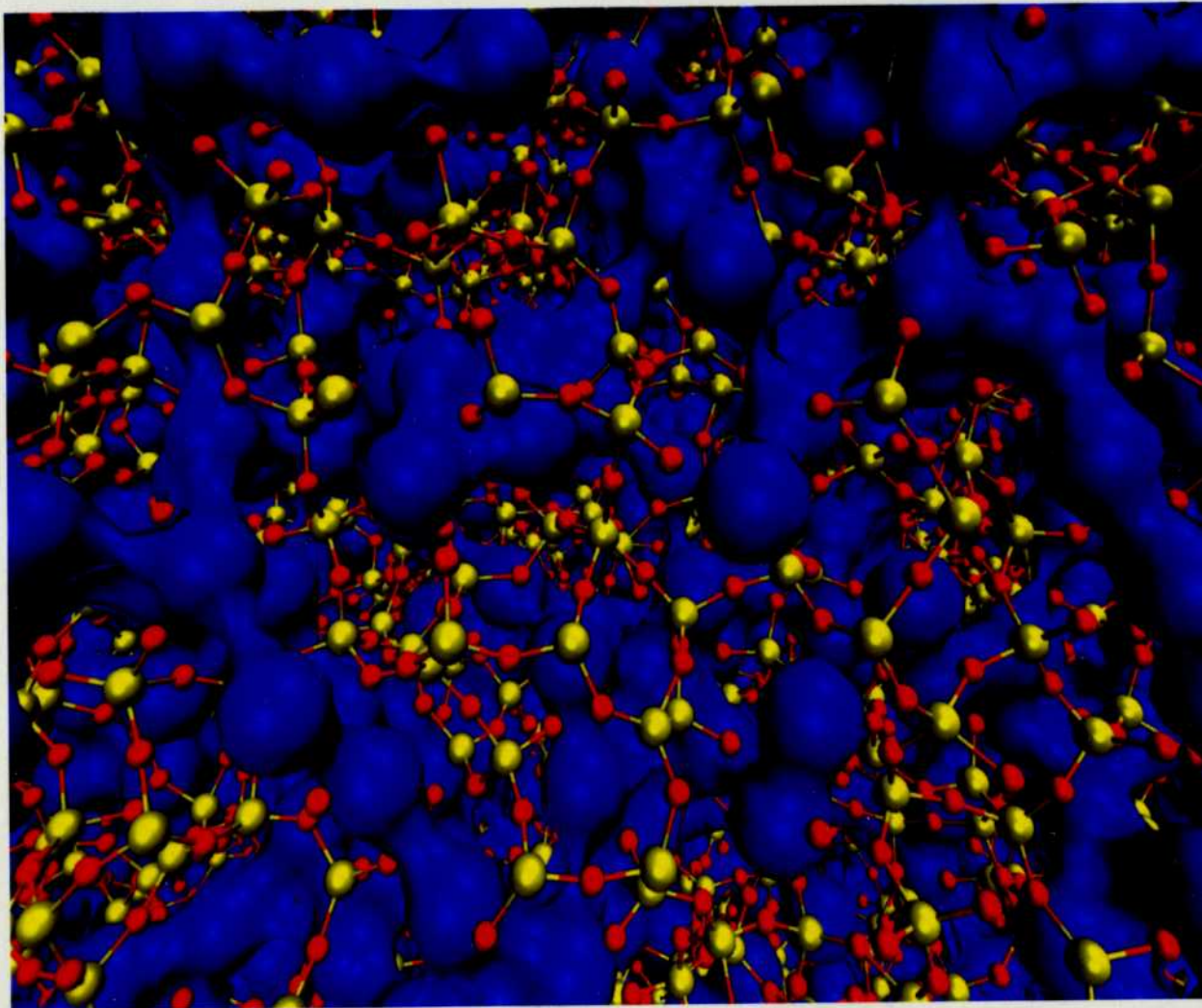


Self Diffusion Constants for NS2



- Na diffusion 2 orders of magnitude faster around 2000 K
- relation of Na motion to intermediate range order?

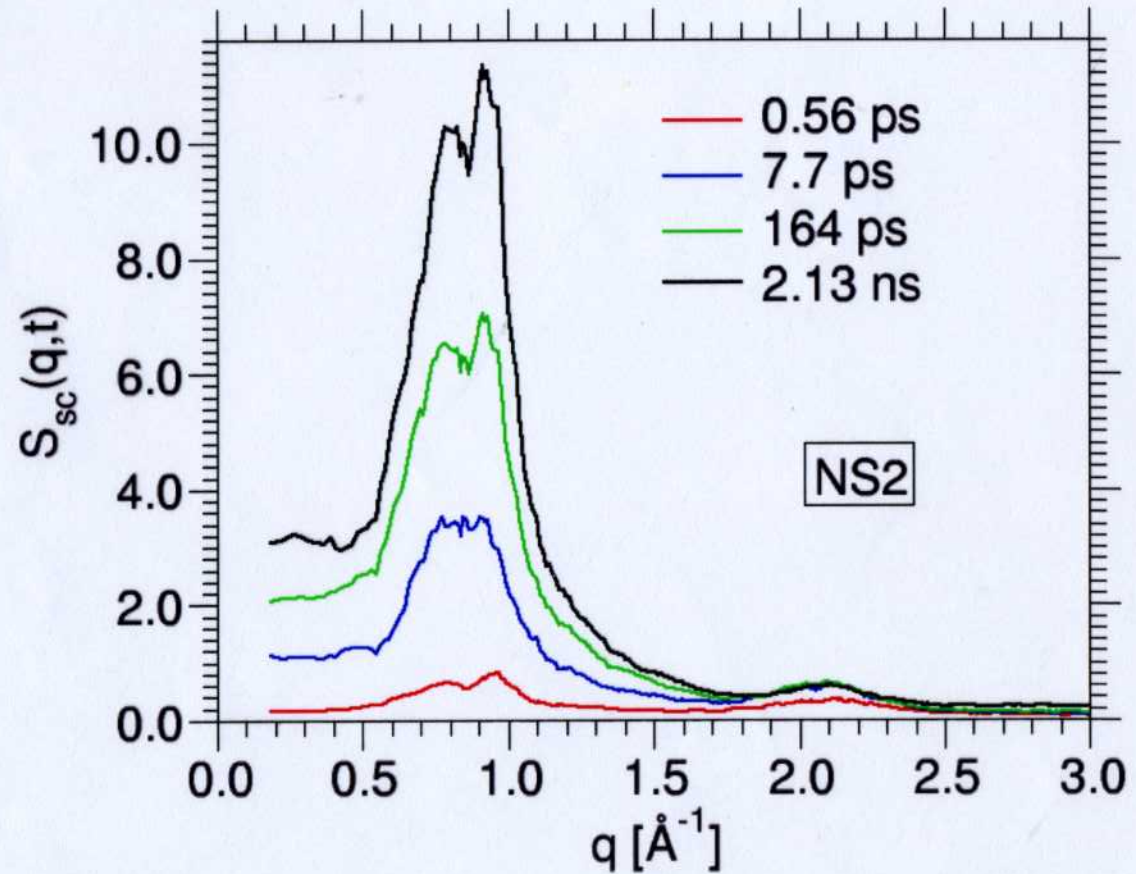
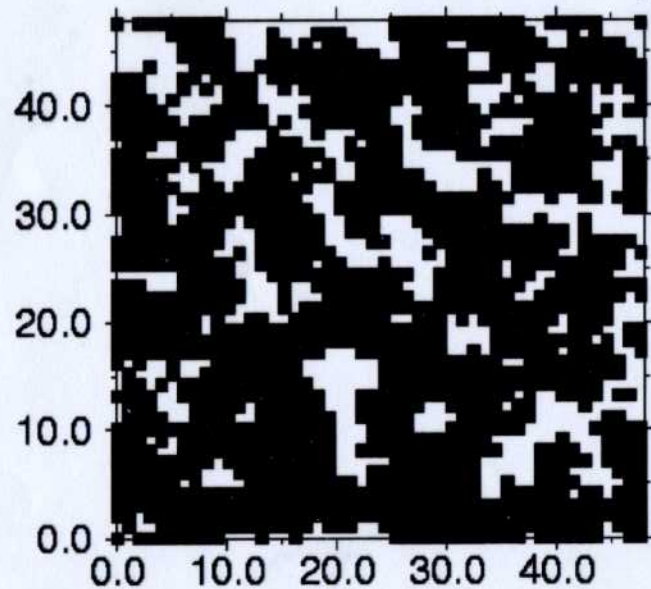
Schnappschuss: NS3 bei 2100 K



- **Diffusionskanäle** für **Na** in der statischen Struktur
- Nachweis durch **AFM** ?

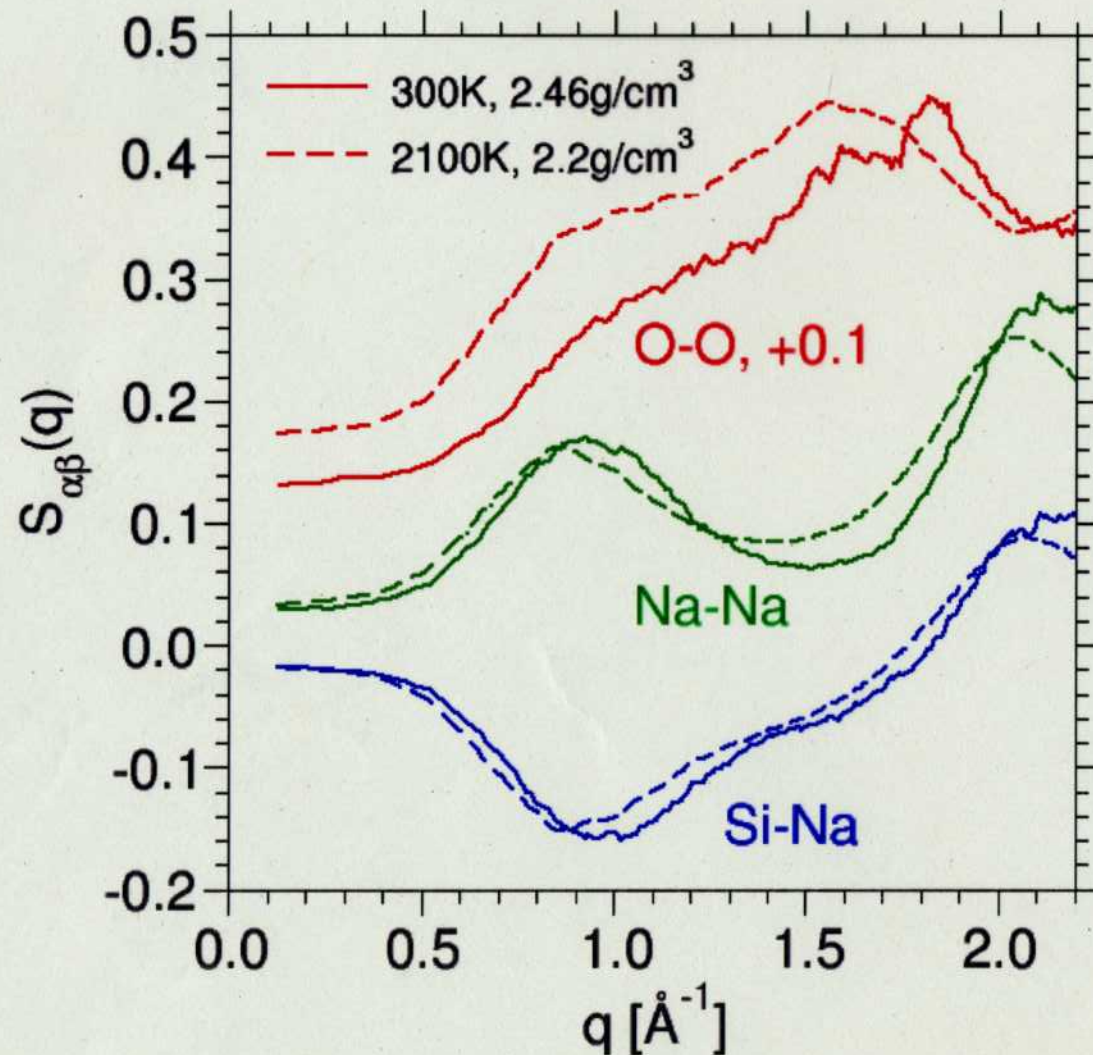
Structure Factor of Channel Network

$t=164$ ps:



structure of **Na** trajectories reflected by **prepeak** in static structure factor at **0.9 \AA^{-1}**

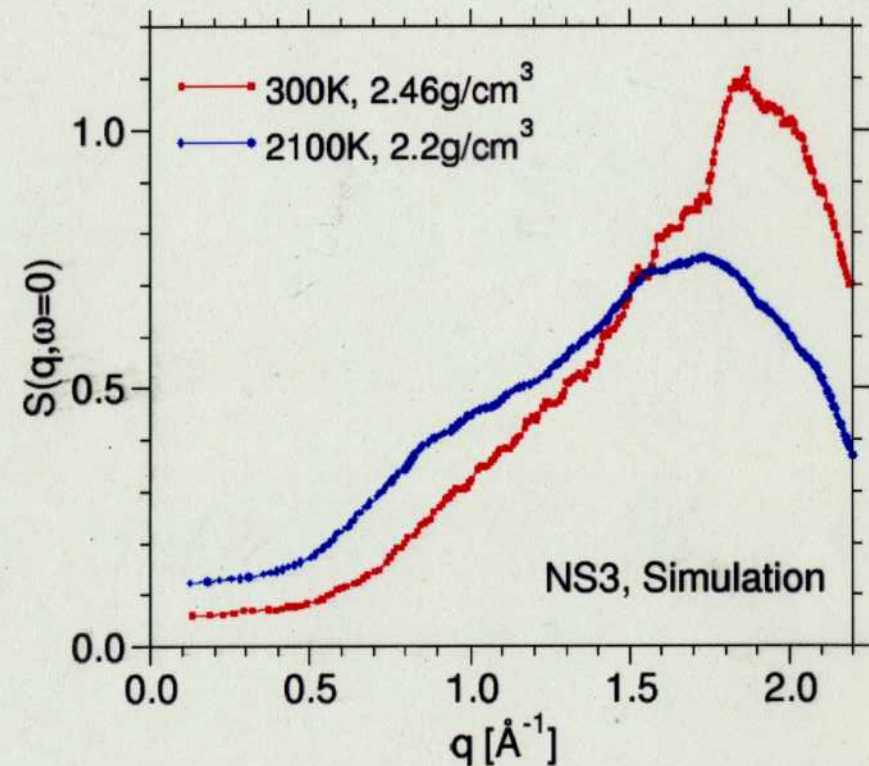
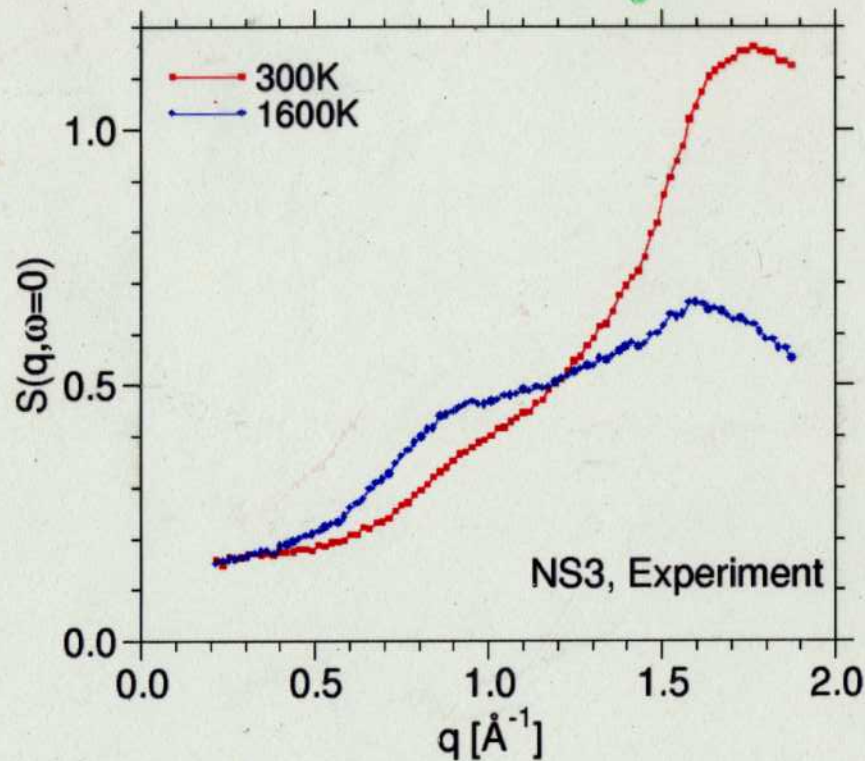
NS3: Partial Structure Factors



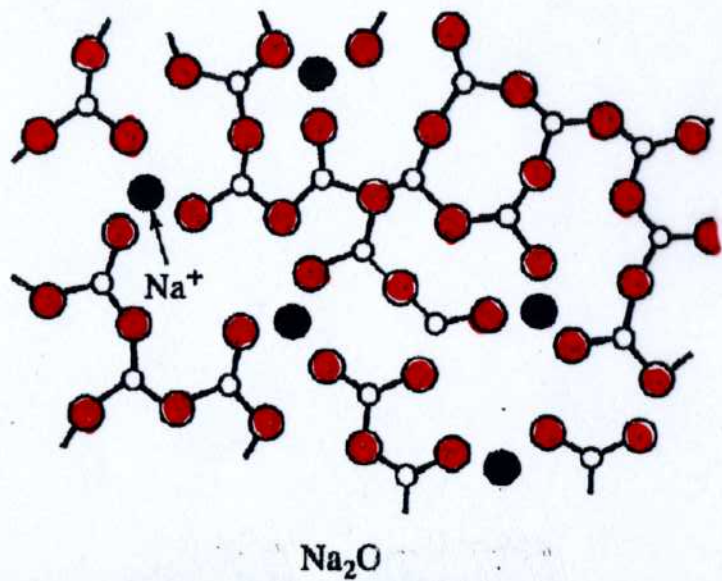
→ due to **smaller density** peak in total $S(q)$ at **0.9 \AA^{-1}** for the **molten system** more pronounced

NS3: Neutronenstreuung vs. MD

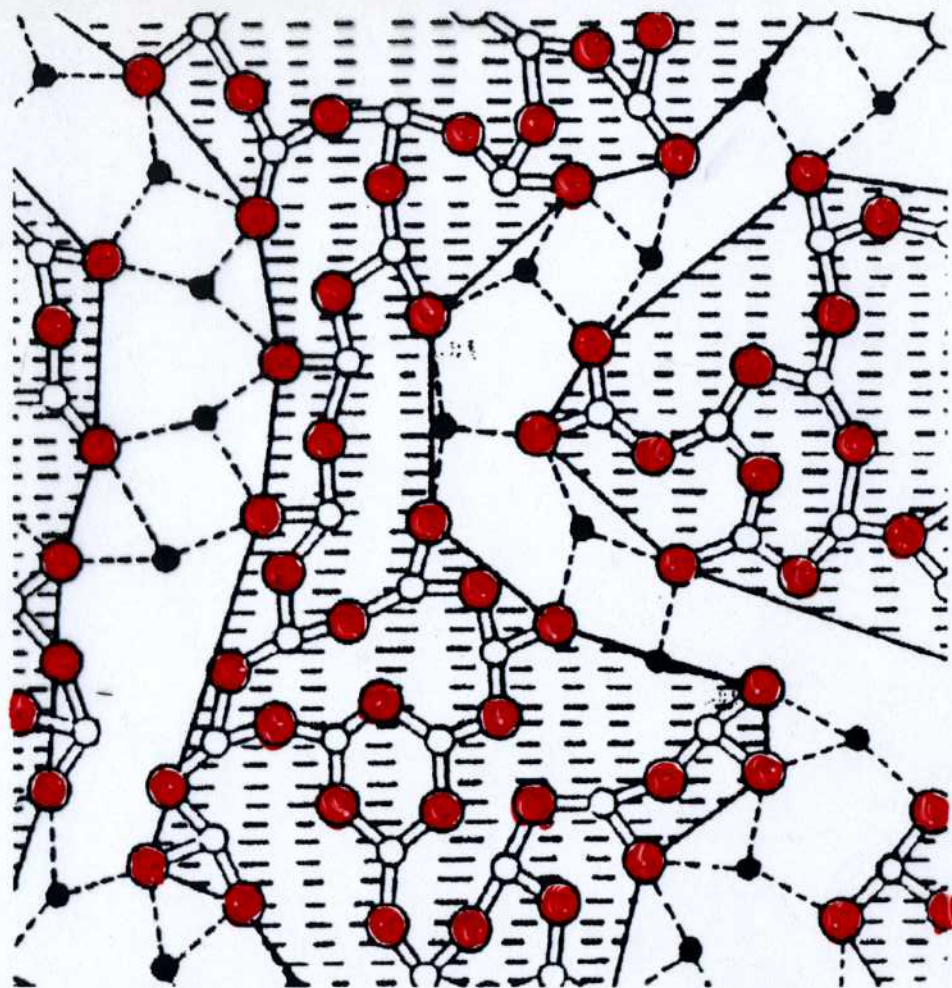
A. Meyer



Schulter bei 0.9\AA^{-1} weniger ausgeprägt im Glas:
intermediäre Ordnung, die mit abnehmender Temperatur
verschwindet?



network broken up



formation of Na-rich channels

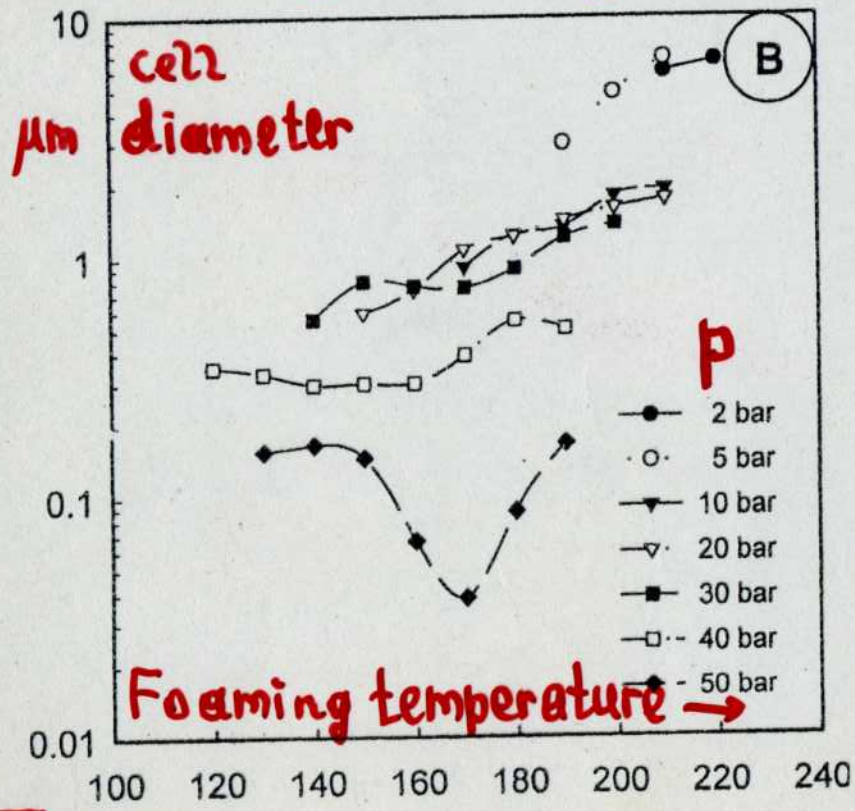
additional control variable: PRESSURE p

Recent Developments in Materials Synthesis and Processing Using Supercritical CO₂**

By Andrew I. Cooper*

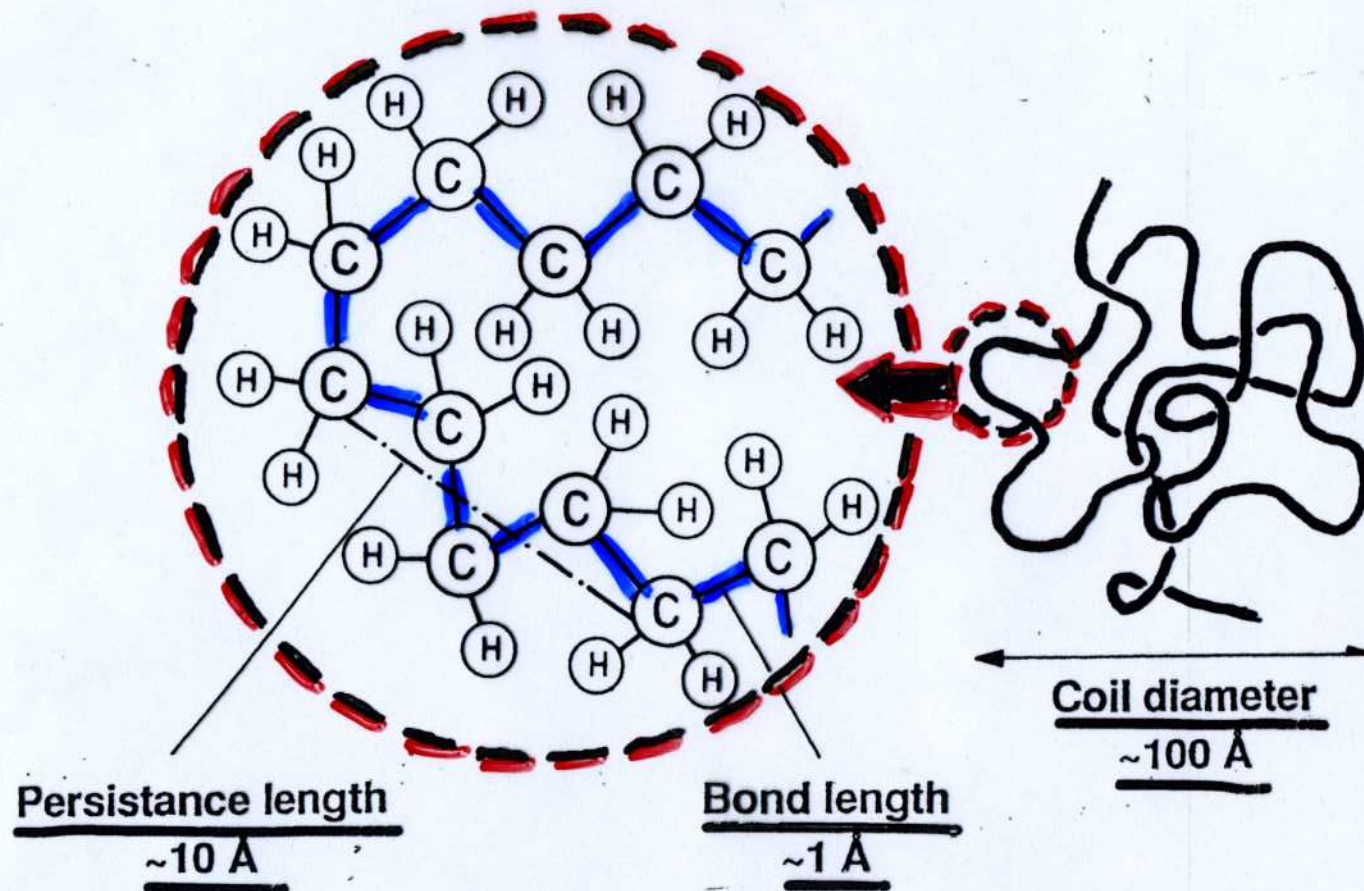
B. Krause et al., *Macromolecules* 2001: polysulfone, polyethersulfone, ...

$T_c = 31^\circ C$



MACROMOLECULES: 100 - 10 000 MONOMERS

⇒ HIERARCHY OF LENGTH SCALES

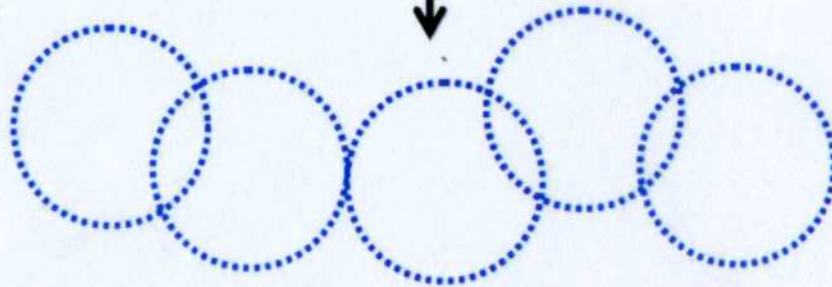
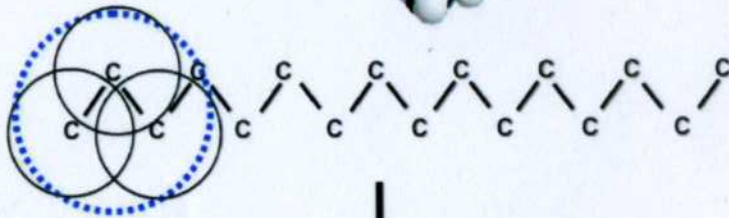
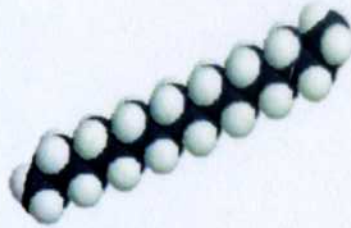


collective phenomena in multi-chain systems:

characteristic lengths $\sim 10^3 \text{Å}$ e.g. POLYMER MIXTURES

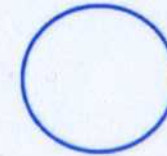
Coarse graining

hexadecane



$C_{16}H_{34}$ - chain of 5 monomers

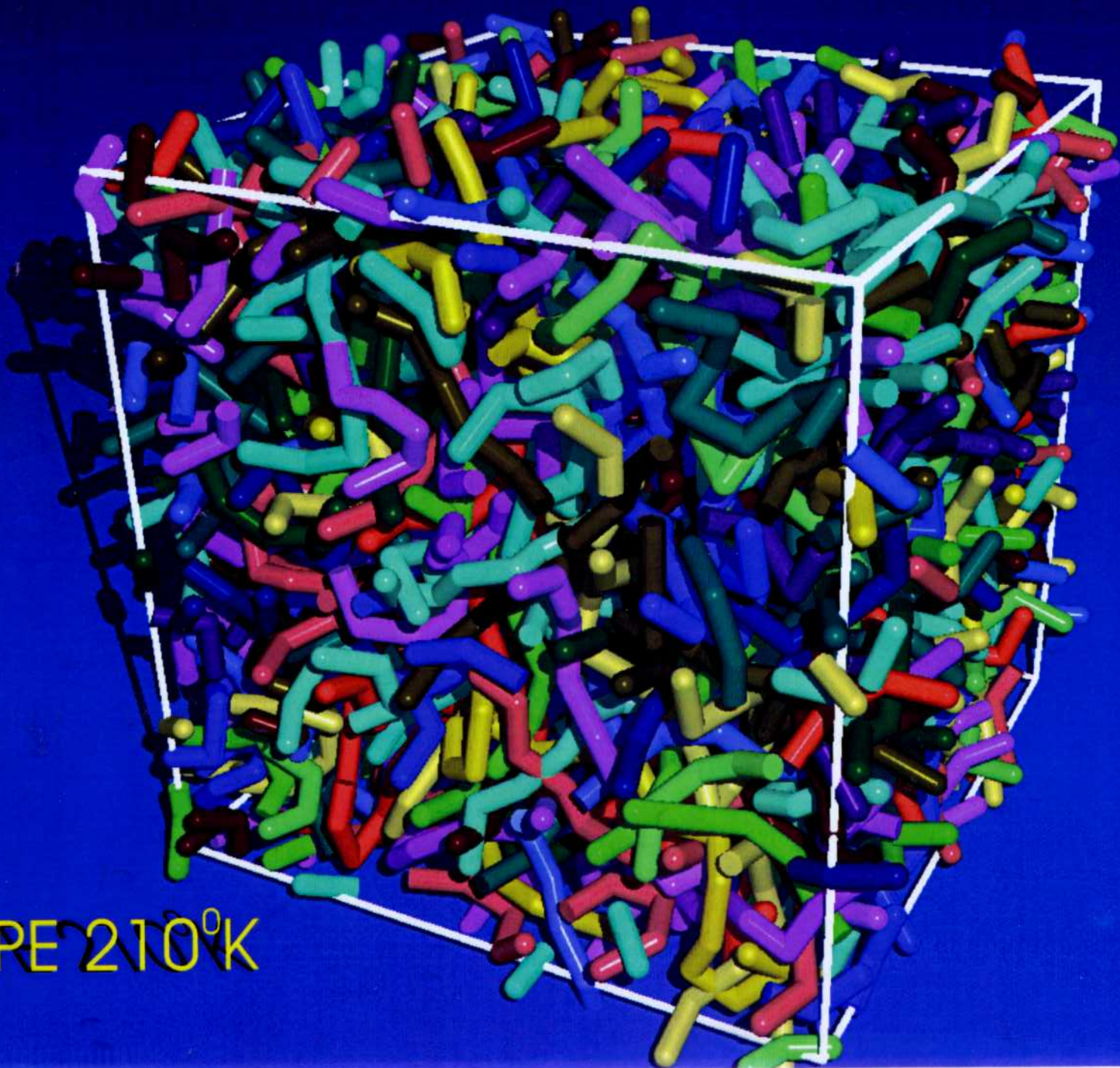
carbon dioxide



CO_2 - a single LJ-bead

Bead-spring model : LJ+FENE potential

PE 210°K



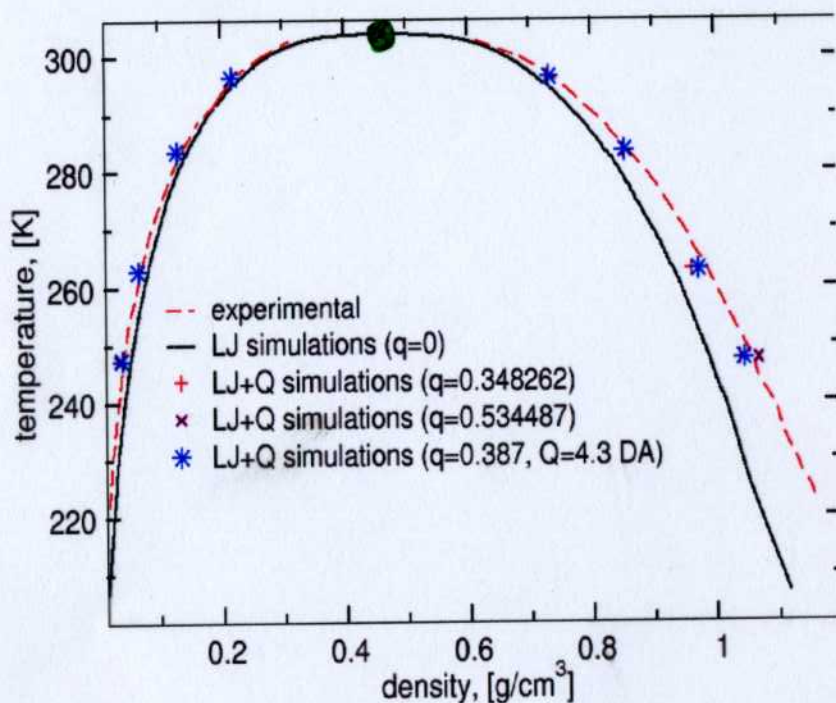
B. Mognetti et al. (2008)



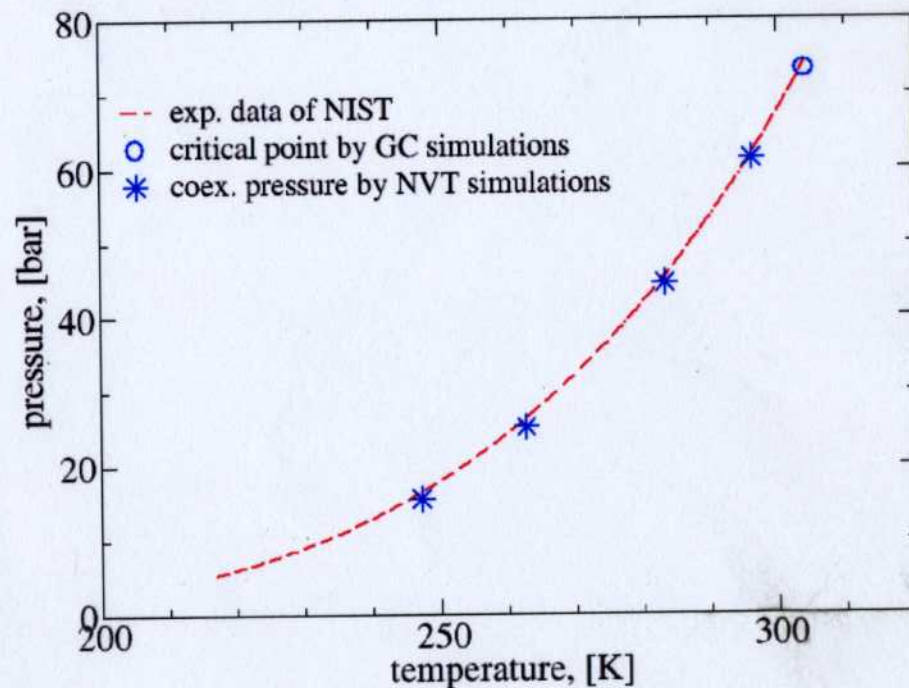
MC simulations of CO₂ using Isotropic Quadrupolar Potential

$$U_{IQ}(r) = -\frac{7}{5}\epsilon q \left(\frac{\sigma}{r}\right)^{10}$$

coexistence curve



vapor-pressure curve



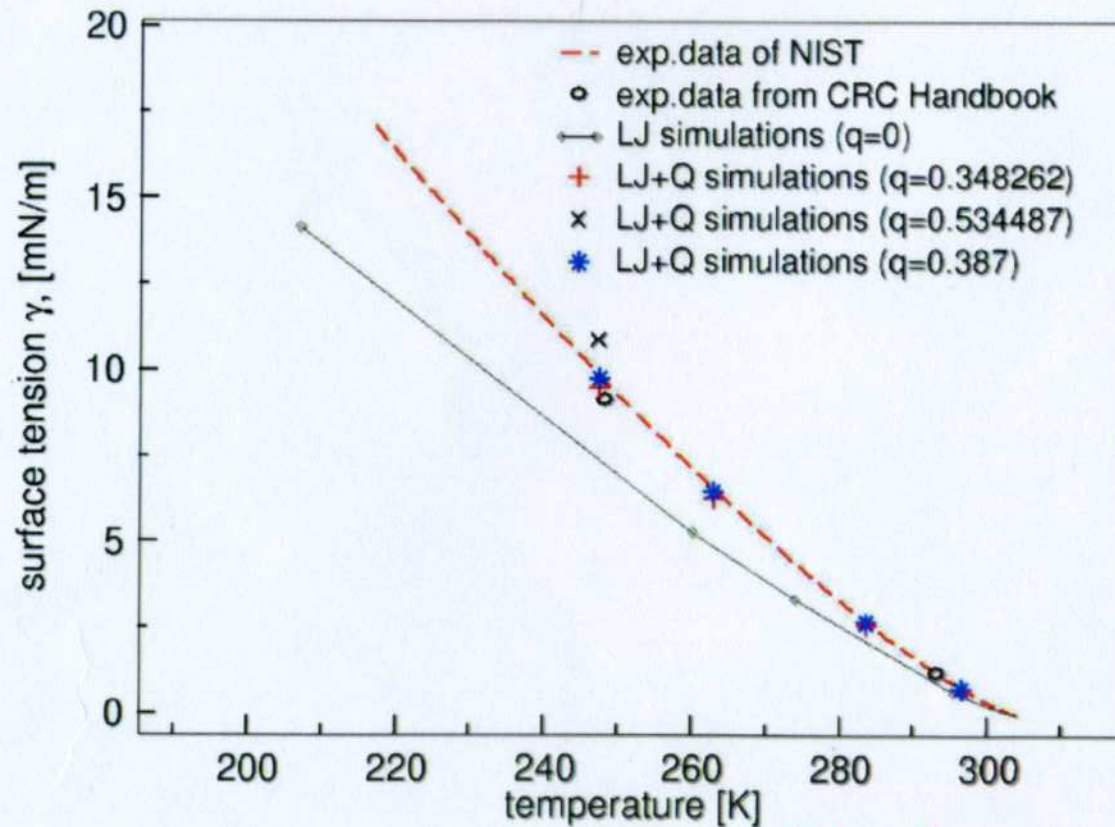
$$q = \frac{Q^4}{\epsilon \sigma^{10} k_B T}$$

Q = physical quadrupole moment

No fit parameter!

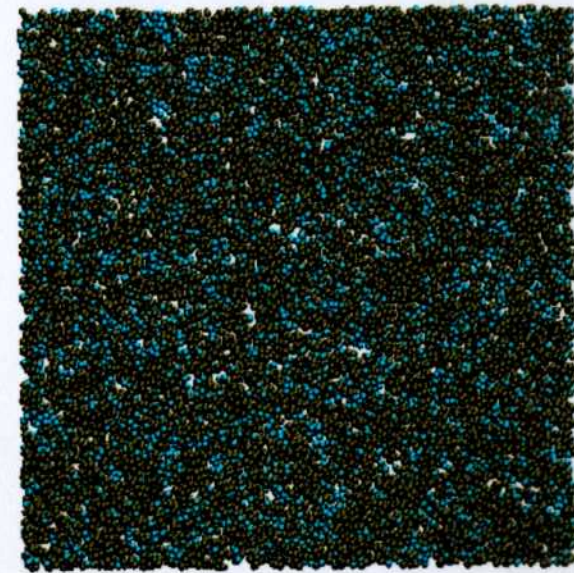
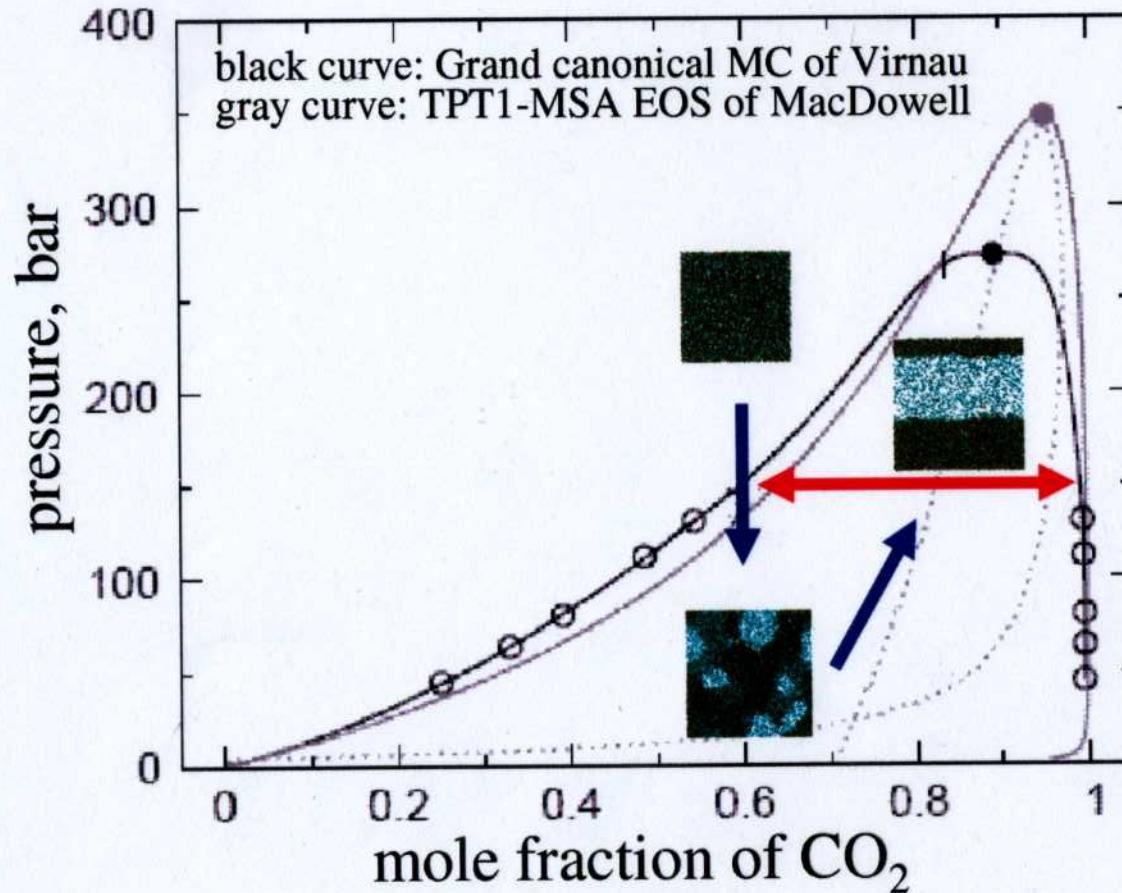
$$U_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$

Prediction of the surface tension of CO₂



No fit parameter!

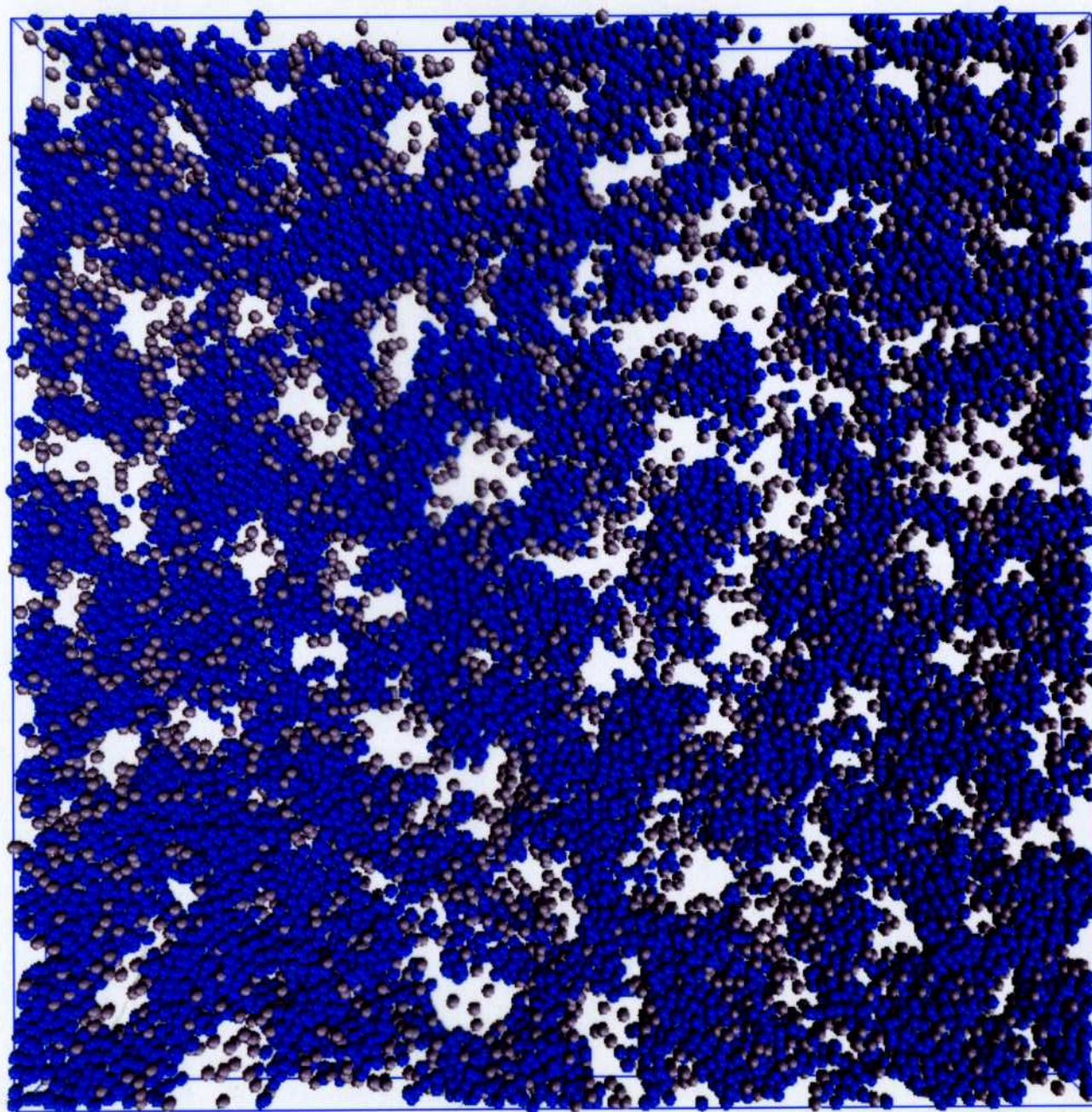
Phase diagram of CO₂+hexadecane at 185°C ($T^*=1.16$)



$\approx 100\sigma$
(435136 particles)

Simulations on a long length scale!

ESPResSo parallelized simulation
package



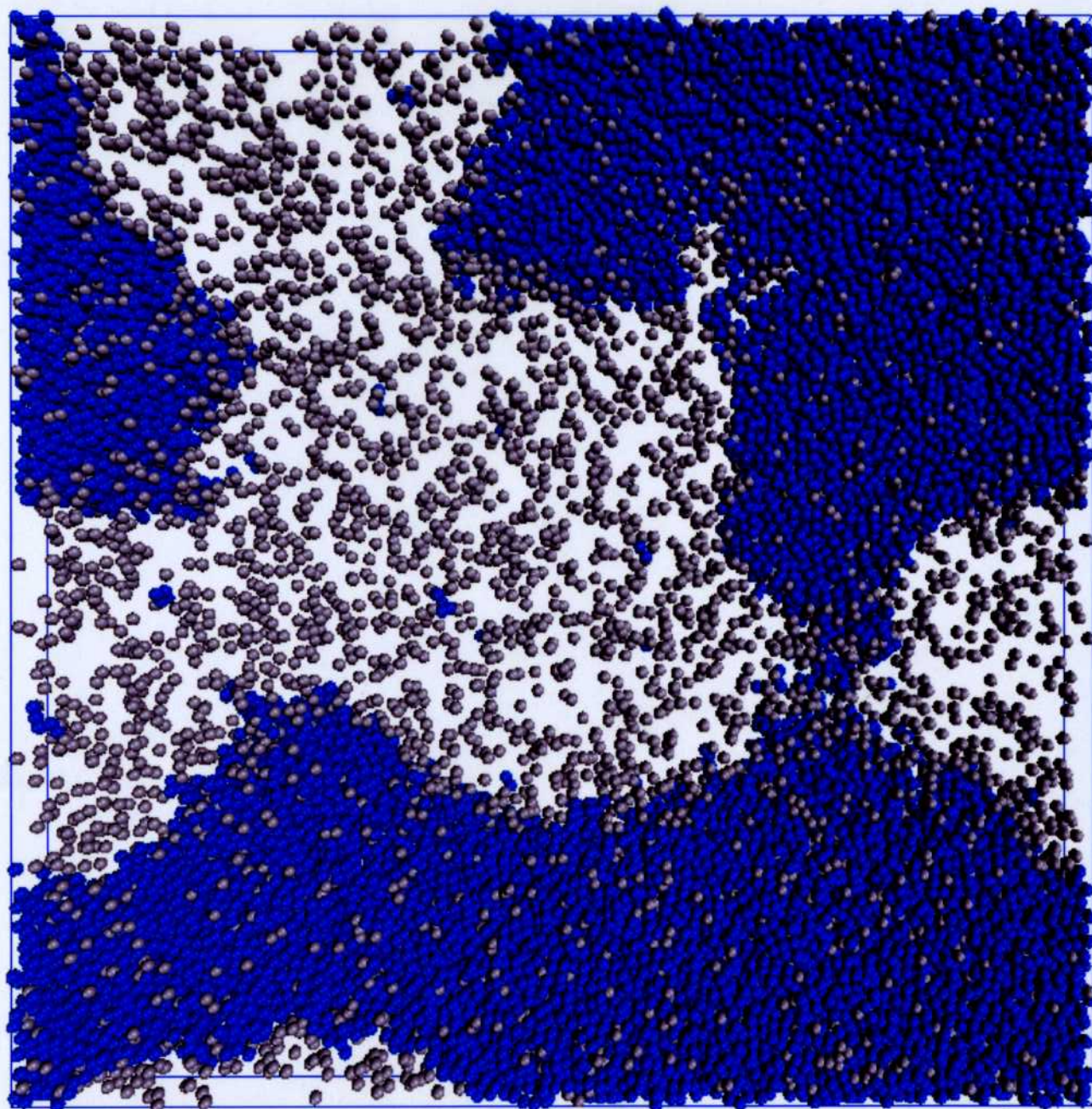
$$t = 100$$

$$\text{MD time unit} = 6 \left(\frac{m}{\epsilon} \right)^{1/2} \\ \approx 1.6 \text{ ps}$$

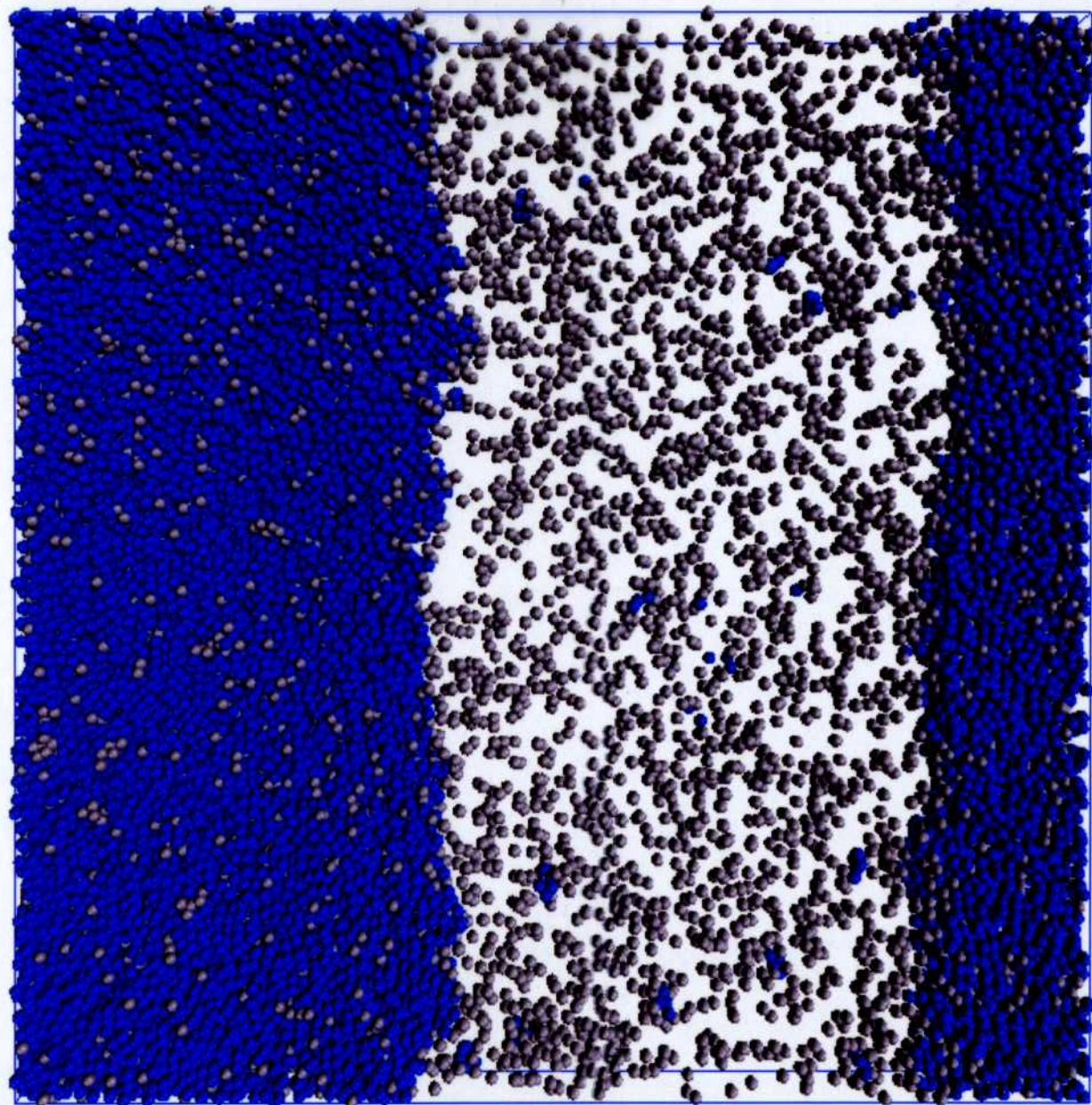
MD = Newton's
equations

$$\Delta t = 0.002$$

MD time units



$t=1000$



$\tau = 5000$

equilibrium

theory

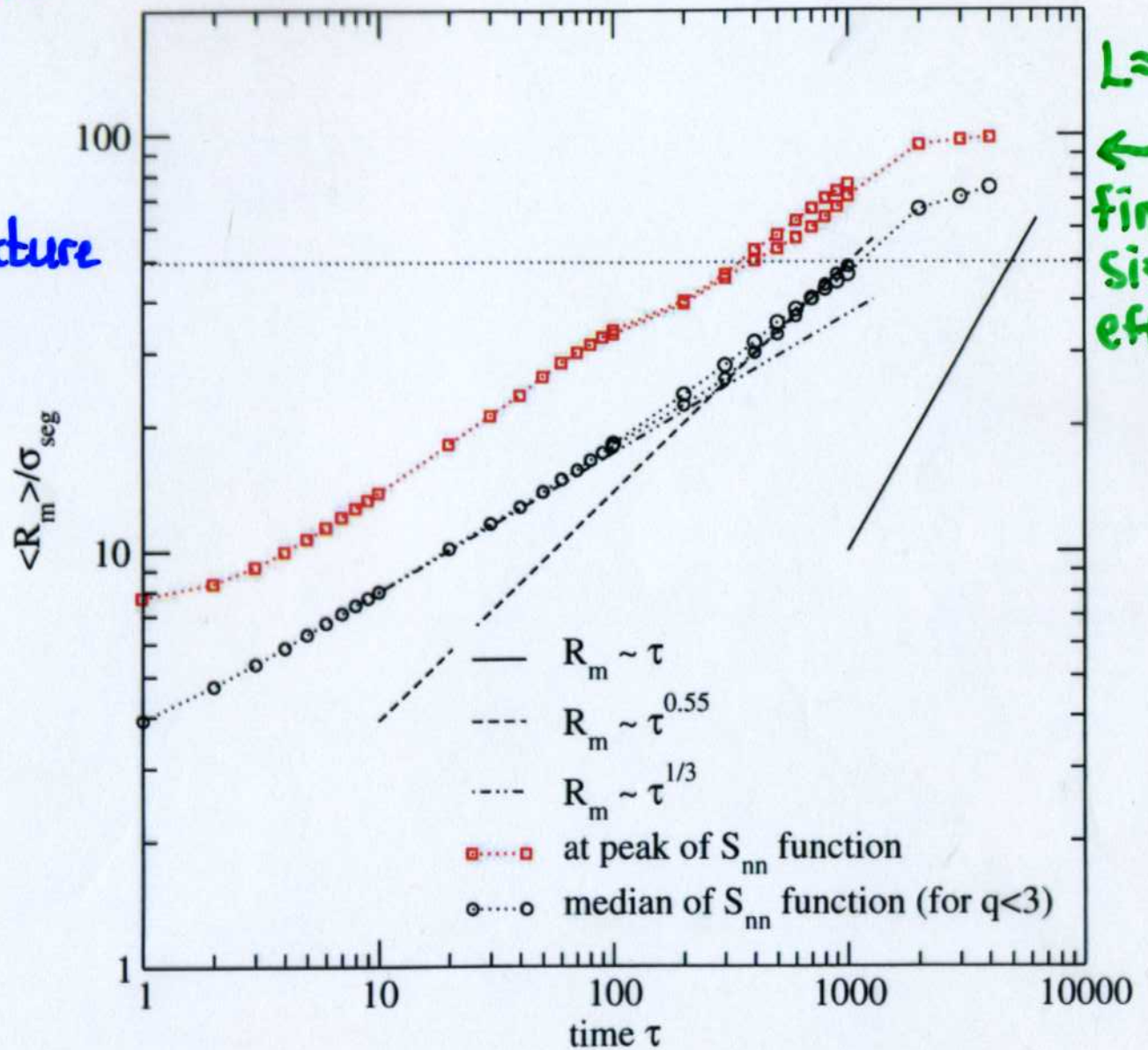
(off-critical) $R(\tau) \propto \tau^{1/3}$

(critical quench) $R(\tau) \propto \tau^1$
needs PERCOLATING structure

later times: crossover effects?

$$R_m(\tau) = 2\pi \frac{\sum_{q=0}^{q_c} S(q, \tau)}{\sum_{q=0}^{q_c} q S(q, \tau)}$$

Characteristic domain size calculated using the density-density structure function



SCHLUSSFOLGERUNGEN

- mit Molekulardynamik-Simulation lässt sich über KINETIK und DYNAMIK von KONDENSIRTER MATERIE viel lernen
- Grenzen der Methodik bewusst bleiben:
 - "stiefmütterliche" Berücksichtigung der Quantenmechanik
 - Güte der "effektiven Potentiale" schränkt Vergleich mit Experimenten wesentlich ein
 - nur nanoskopisch kleine Längenskalen und entsprechend kurze Zeiten zugänglich