

# Kinetic Monte Carlo

## Day 2

*Wolfgang Paul*

*Institut für Physik*

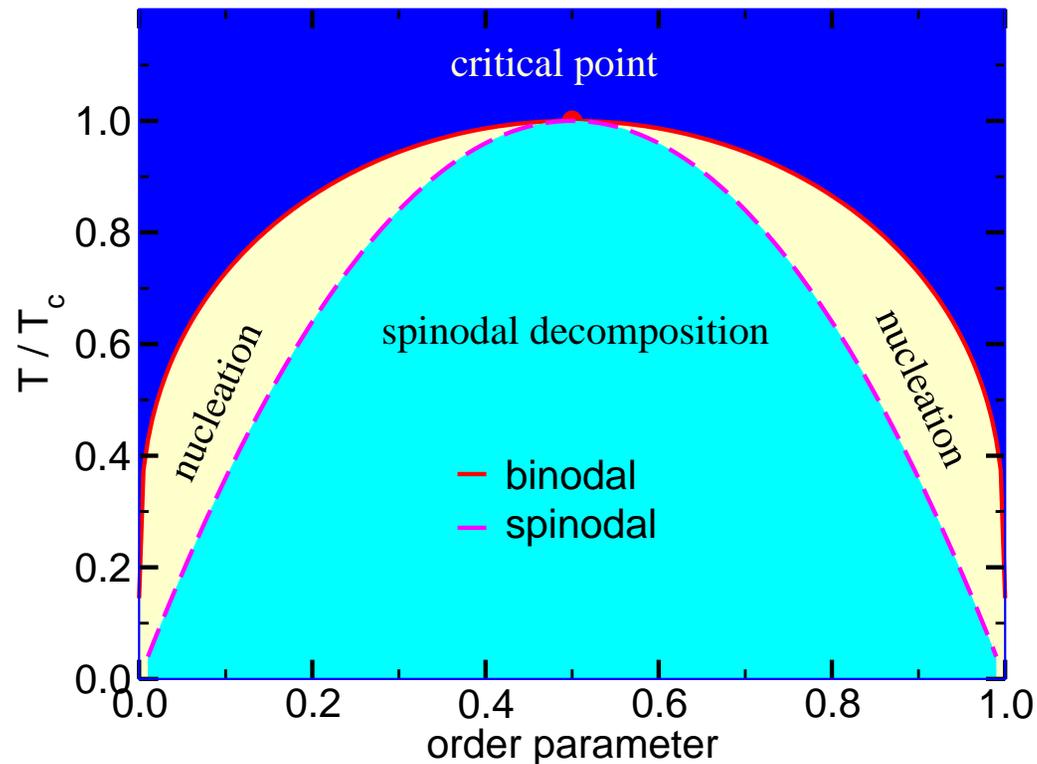
*Johannes-Gutenberg Universität*

*55099 Mainz*

# Outline of Day 2

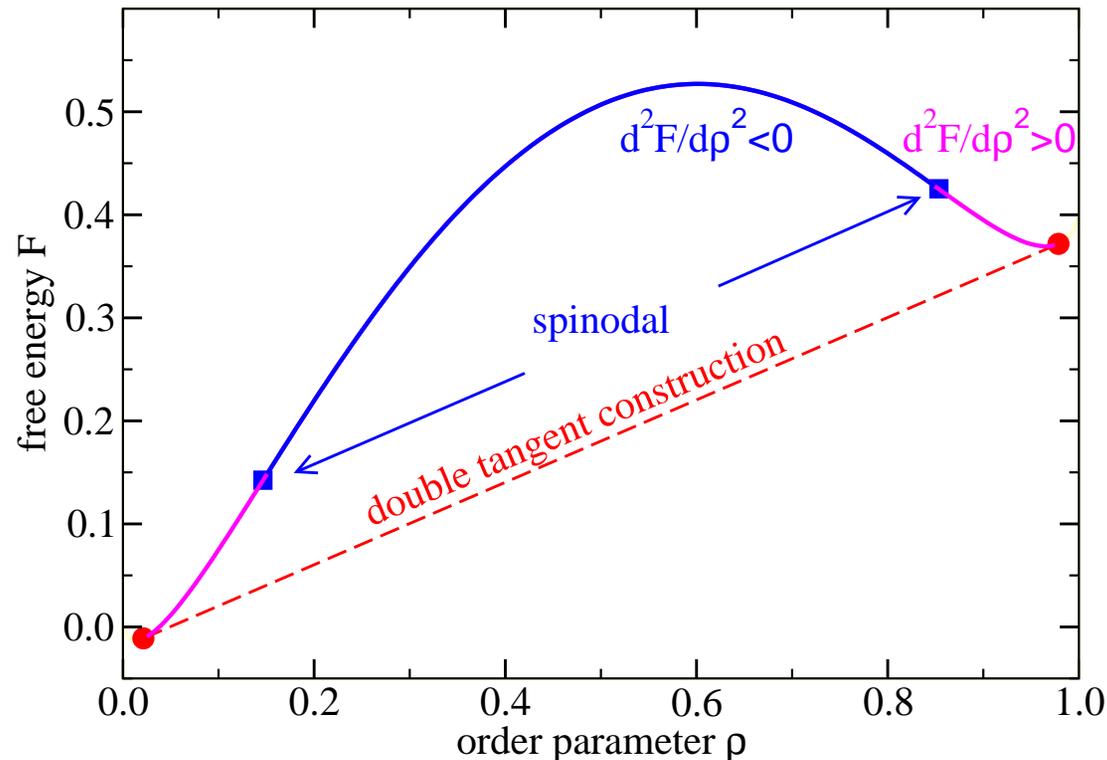
- Background on phase transformation kinetics
- The Ising model and its lattice gas interpretation
- Phase transition kinetics studied with the Ising model
- The physics of polymer chain dynamics
- Chemically realistic versus lattice polymer modeling
- Kinetic MC simulation of polymer melt dynamics

# Background on phase transformation kinetics



Many systems show a two-phase coexistence below a critical temperature  $T_c$ . Examples include the **paramagnetic-ferromagnetic transition**, the **liquid-gas transition** or the **demixing of a binary mixture**.

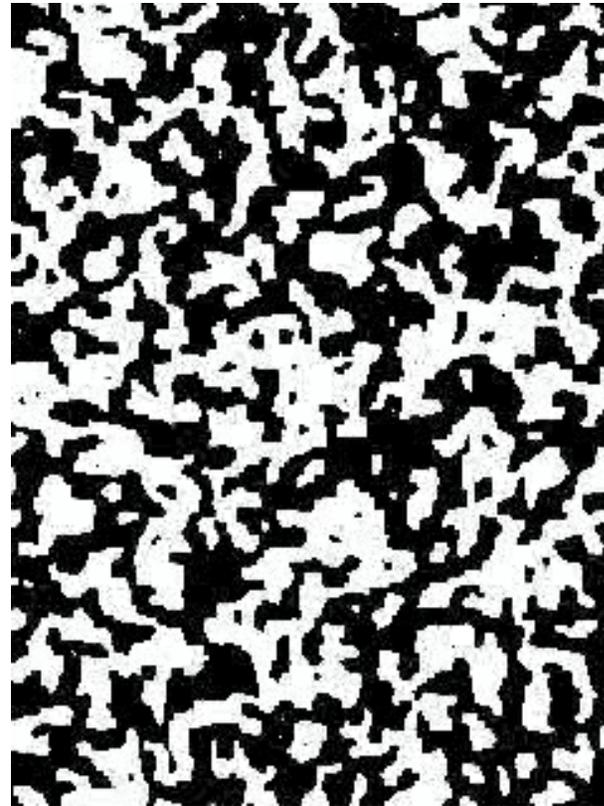
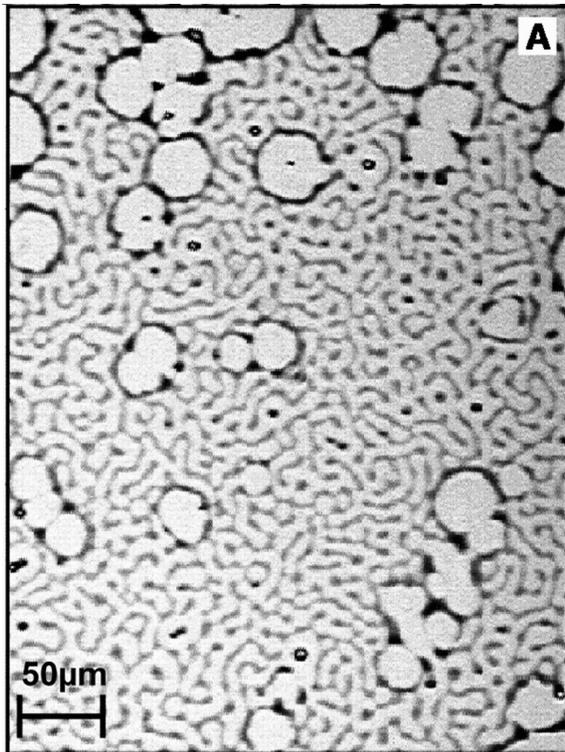
# Background on phase transformation kinetics



Within the **spinodal** the homogeneous (disordered) phase is **thermodynamically unstable**. Between the spinodal and binodal one needs **nucleation events** of the opposite phase (**thermal activation**) to induce the phase transformation.

# Background on phase transformation kinetics

The relaxational kinetics of phase transformations can be simulated using, for instance kinetic Ising models.



Left: S. Herminghaus et al. *Science* **282**, 916 (1998)

Right: J.Sethna, Ising simulation, published on the WEB

## Background on phase transformation kinetics

The patterns we saw on the last page **coarsen self-similarly** in time, i.e., when we take a pattern at time  $t_2 > t_1$  and rescale its linear dimension by a factor  $b(t_1, t_2)$  we regain the pattern from time  $t_1$ .

Experimentally we would see this in the **intermediate scattering function (dynamic structure factor)**

$$S(q, t) = S(q/L(t))$$

The time dependence of the typical scale  $L(t)$  depends on the presence of **conservation laws** in the system

- **non-conserved order parameter:**  $L(t) \propto t^{1/2}$  (Allen-Cahn law)
- **conserved order parameter:**  $L(t) \propto t^{1/3}$  (Lifshitz-Slyozov law)
- **importance of hydrodynamics:**  $L(t) \propto t^{2/3}$  or  $t$  depending on the regime

# Ising Model

The Hamiltonian of the Ising model is given as

$$\mathcal{H}(\vec{s}) = -J_q \sum_i \sum_{j \in n(i)} s_i s_j - \mu_B H \sum_i s_i ,$$

where the spins  $s_i = \pm 1$  represent the magnetic moments fixed in space on some lattice structure,  $n(i)$  denotes the set of spins interacting with spin  $i$ ,  $J_q$  is the strength of interaction between spins,  $q$  is the number of interacting neighbors ( $qJ_q = \text{const} = k_B T_c$  where the last equality is valid in mean field), and  $H$  is an external magnetic field .

The lattice gas interpretation of the Ising model is obtained by the transformation  $s_i = 2c_i - 1$ ,  $c_i = 0, 1$

$$\mathcal{H} = -4J_q \sum_i \sum_{j \in n(i)} c_i c_j + 2(qJ_q - \mu_B H) \sum_i c_i - N(qJ_q - \mu_B H)$$

# Ising Model

The canonical probability for a microstate is

$$\mu(\vec{s}) = \frac{1}{Z} e^{-\beta \mathcal{H}(\vec{s})} ,$$

with  $\beta = 1/k_B T$  and the partition function

$$Z = \sum_{\vec{s}} e^{-\beta \mathcal{H}(\vec{s})} .$$

The kinetics is given by a master equation in discrete time

$$\begin{aligned} p(\vec{s}, n + 1) &= p(\vec{s}, n) + \sum_{\vec{s}'} w(\vec{s} | \vec{s}') p(\vec{s}', n) \\ &\quad - \sum_{\vec{s}'} w(\vec{s}' | \vec{s}) p(\vec{s}, n) . \end{aligned}$$

# Ising Model

Two popular choices are the **Glauber** and the **Metropolis** transition probabilities:

$$w(\vec{s}'|\vec{s}) = w_0(\vec{s}'|\vec{s}) \frac{1}{2} \left[ 1 + \tanh \left( -\frac{1}{2} \beta \Delta \mathcal{H} \right) \right] \quad (\text{Glauber}) ,$$

$$w(\vec{s}'|\vec{s}) = w_0(\vec{s}'|\vec{s}) \min (1, \exp [-\beta \Delta \mathcal{H}]) \quad (\text{Metropolis}) ,$$

where  $\Delta \mathcal{H} = \mathcal{H}(\vec{s}') - \mathcal{H}(\vec{s})$ , and  $w_0(\vec{s}'|\vec{s})$  is the probability to suggest  $\vec{s}'$  as the next state, starting from  $\vec{s}$ . We have to require the symmetry

$$w_0(\vec{s}'|\vec{s}) = w_0(\vec{s}|\vec{s}') .$$

In a computer simulation of we would choose an arbitrary starting configuration  $\vec{s}_0$  and then use some algorithm to generate the next configurations  $\vec{s}_1$ ,  $\vec{s}_2$  and so on. One such algorithm is the **single spin-flip kinetic Ising model**, in which we select one spin at random

# Ising Model

(i.e.,  $w_0(\vec{s}'|\vec{s}) = 1/N$ ) and try to reverse it.

$$w_G(\vec{s}'|\vec{s}) = \frac{1}{2N} \left[ 1 + \tanh \left( -\frac{1}{2}\beta\Delta\mathcal{H} \right) \right] \quad (\text{Glauber}),$$

$$w_M(\vec{s}'|\vec{s}) = \frac{1}{N} \min(1, \exp[-\beta\Delta\mathcal{H}]) \quad (\text{Metropolis}),$$

We can therefore write the master equation in the form

$$\begin{aligned} & p(s_1, \dots, s_i, \dots, s_n, n+1) \\ &= p(s_1, \dots, s_i, \dots, s_n, n) + \sum_i w(-s_i \rightarrow s_i) p(s_1, \dots, -s_i, \dots, s_n, n) \\ &\quad - \sum_i w(s_i \rightarrow -s_i) p(s_1, \dots, s_i, \dots, s_n, n). \end{aligned}$$

# Ising Model

## Monte Carlo algorithm

- generate a starting configuration  $\vec{s}_0$ ,
- select a spin,  $s_i$ , at random,
- calculate the energy change upon spin reversal  $\Delta\mathcal{H}$ ,
- calculate the probability  $w$  for this spin-flip to happen, using the chosen form of transition probability,
- generate a uniformly distributed random number,  $0 < r < 1$ ,
- if  $w > r$ , flip the spin, otherwise retain the old configuration.

# Ising Model

So far we have discussed a Monte Carlo method for **non-conserved order parameter** (magnetization).

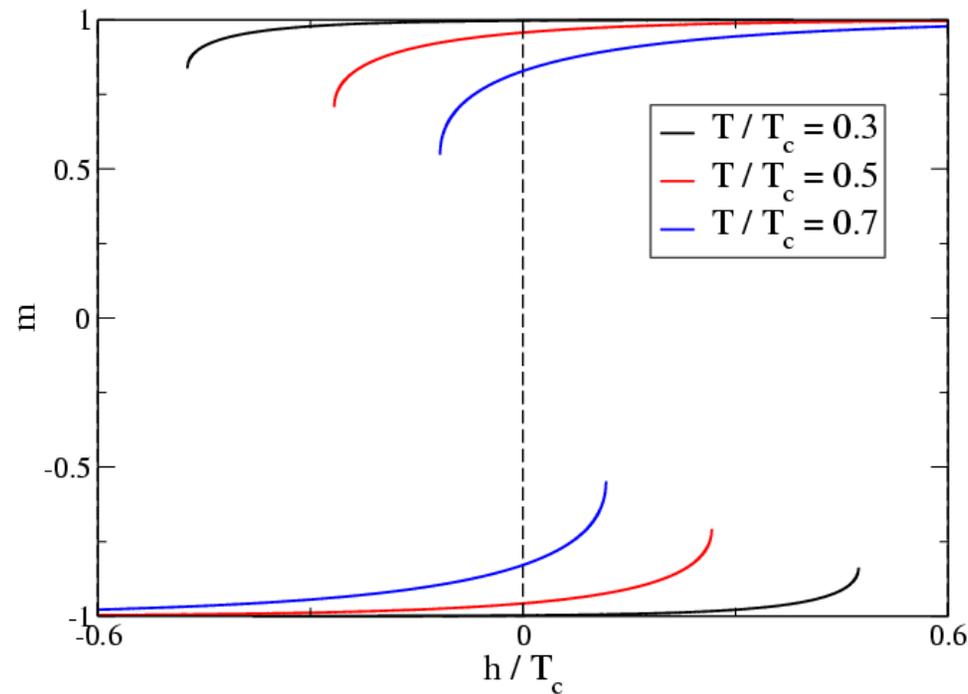
For a **conserved order parameter** (concentration) one uses **Kawasaki dynamics**:

- choose a pair of (neighboring) spins, i.e.,  $w_0(\vec{s}'|\vec{s}) = 1/2dN$  if we chose a spin at random and then a neighbor on a simple cubic lattice at random
- exchange the spins subject to the Metropolis acceptance criterion

This algorithm would suggest itself for the lattice gas interpretation. For surface diffusion one often works with non-conserved particle number mimicking desorption/adsorption events.

# Ising Model

Let us now discuss the case of a magnetization reversal induced by a switching of the external field below  $T_c$ . In mean field we have



$$m = \tanh \left[ \frac{\mu_B H}{k_B T} + \frac{T_c}{T} m \right]$$

# Ising Model

For the mean-field kinetic Ising model the kinetic equation can be greatly simplified. For the single spin-flip mean-field kinetic Ising model, the energy change can be written (for large  $N$ )

$$\begin{aligned}\Delta\mathcal{H}(s_i \rightarrow -s_i) &= 2J_N s_i \sum_{j \in n(i)} s_j + 2\mu_B H s_i \\ &= 2J_N s_i N m + 2\mu_B H s_i .\end{aligned}$$

Noting that  $\delta m = -2s_i/N$ , we get

$$\Delta\mathcal{H}(m, \delta m) = -J_N N^2 m \delta m - \mu_B H N \delta m ,$$

The transition probabilities in the master equation are therefore given by

# Ising Model

$$w(s_i | -s_i) \rightarrow w(m - \delta m, \delta m)$$

$$w(-s_i | s_i) \rightarrow w(m, -\delta m)$$

if  $m$  is supposed to be the magnetization of the state  $(s_1, \dots, s_i, \dots, s_N)$  and  $\delta m$  the magnetization difference between this state and the one with  $s_i$  reversed. Summing the master equation over all configurations  $\vec{s}$  with a fixed  $m$ , we get

$$\begin{aligned} & p(m, n + 1) - p(m, n) \\ &= \sum_{\vec{s}_m} \sum_{i=1}^N w(m - \delta m, \delta m) p(s_1, \dots, -s_i, \dots, s_N, n) \\ &\quad - \sum_{i=1}^N w(m, -\delta m) p(m, n) , \end{aligned}$$

# Ising Model

in which we have used  $p(m, n) = \sum_{\vec{s}_m} p(\vec{s}, n)$ . Performing the combinatorics for magnetization changes  $\delta m = 2/N$  and  $\delta m = -2/N$  leading to or leaving from the magnetization  $m$ , one arrives at

$$\begin{aligned} & p(m, n + 1) - p(m, n) \\ &= \frac{N}{2} \left( 1 + m + \frac{2}{N} \right) w(m + 2/N, -2/N) p(m + 2/N, n) \\ & \quad + \frac{N}{2} \left( 1 - m + \frac{2}{N} \right) w(m - 2/N, 2/N) p(m - 2/N, n) \\ & \quad - \frac{N}{2} (1 + m) w(m, -2/N) p(m, n) \\ & \quad - \frac{N}{2} (1 - m) w(m, 2/N) p(m, n) . \end{aligned}$$

# Ising Model

Let us introduce a time scale  $\delta t$  for a single spin-flip and consider the limit  $\delta t \rightarrow 0$ ,  $N\delta t = \tau = \text{const.}$  Dividing the master equation by  $\delta t$  we derive in this limit

$$\begin{aligned} \frac{\partial}{\partial t} p(m, t) &= \frac{N}{2} \left( 1 + m + \frac{2}{N} \right) \tilde{w}(m + 2/N, -2/N) p(m + 2/N, n) \\ &+ \frac{N}{2} \left( 1 - m + \frac{2}{N} \right) \tilde{w}(m - 2/N, 2/N) p(m - 2/N, n) \\ &- \frac{N}{2} (1 + m) \tilde{w}(m, -2/N) p(m, n) \\ &- \frac{N}{2} (1 - m) \tilde{w}(m, 2/N) p(m, n) . \end{aligned}$$

# Ising Model

The **transition rates** are now given as (with  $T_c = J_N N / k_B$ ):

$$\begin{aligned}\tilde{w}_G(m, \delta m) &= \frac{1}{2\tau} \left[ 1 + \tanh \left( \frac{T_c}{2T} N m \delta m + \frac{\mu_B H}{2k_B T} N \delta m + \frac{T_c}{NT} \right) \right], \\ \tilde{w}_M(m, \delta m) &= \frac{1}{\tau} \min \left( 1, \exp \left[ \frac{T_c}{T} N m \delta m + \frac{\mu_B H}{k_B T} N \delta m + \frac{2T_c}{NT} \right] \right).\end{aligned}$$

The master equation we obtained is one for a so-called **birth-and-death process**. It can be elegantly rewritten following van Kampen using the following definitions:

# Ising Model

- rate of jumps to the right:  $r(m) = (1 - m)\tilde{w}(m, 2/N)$ ,
- rate of jumps to the left:  $l(m) = (1 + m)\tilde{w}(m, -2/N)$ ,
- translation by  $2/N$ :  $\mathcal{T} = \exp\left(2/N \frac{\partial}{\partial m}\right)$ ,
- translation by  $-2/N$ :  $\mathcal{T}^{-1} = \exp\left(-2/N \frac{\partial}{\partial m}\right)$ .

# Ising Model

The master equation becomes

$$\frac{\partial}{\partial t} p(m, t) = \frac{N}{2} (\mathcal{T} - 1) [l(m)p(m, t)] + \frac{N}{2} (\mathcal{T}^{-1} - 1) [r(m)p(m, t)] .$$

Considering that the translation operator is defined through the Taylor series of the exponential function, we can see that this equation is a version of the so-called **Kramers–Moyal expansion of the master equation**. The expansion parameter is the magnetization change  $\delta m = \pm 2/N$  upon a single spin-flip. The expansion contains an infinite series of terms.

# Ising Model

For large  $N$  we will now use the **Fokker–Planck approximation** to this equation, truncating the expansion after the second order:

$$\tau \frac{\partial}{\partial t} p(m, t) = \frac{\partial}{\partial m} [U'(m)p(m, t)] + \frac{1}{2} \frac{\partial^2}{\partial m^2} [D(m)p(m, t)] .$$

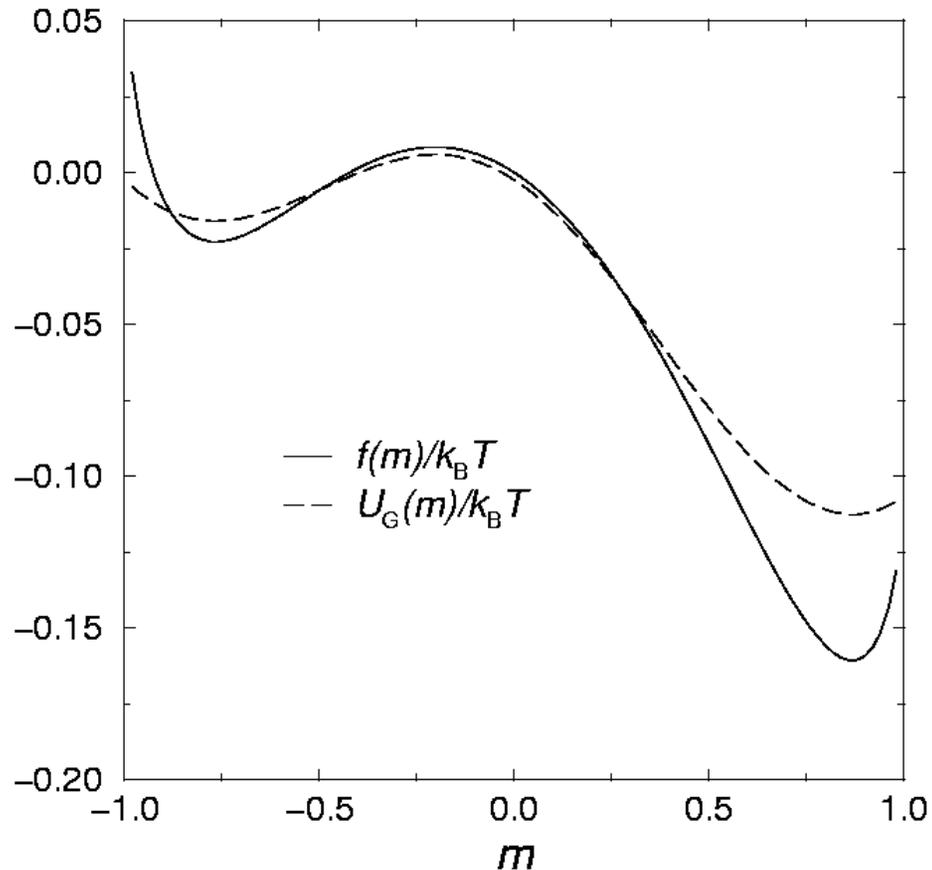
This equation describes a **diffusion process in an external potential** with the derivative

$$U'(m) = \tau [l(m) - r(m)]$$

and a **position dependent diffusion coefficient**

$$D(m) = \frac{2\tau}{N} [l(m) + r(m)] .$$

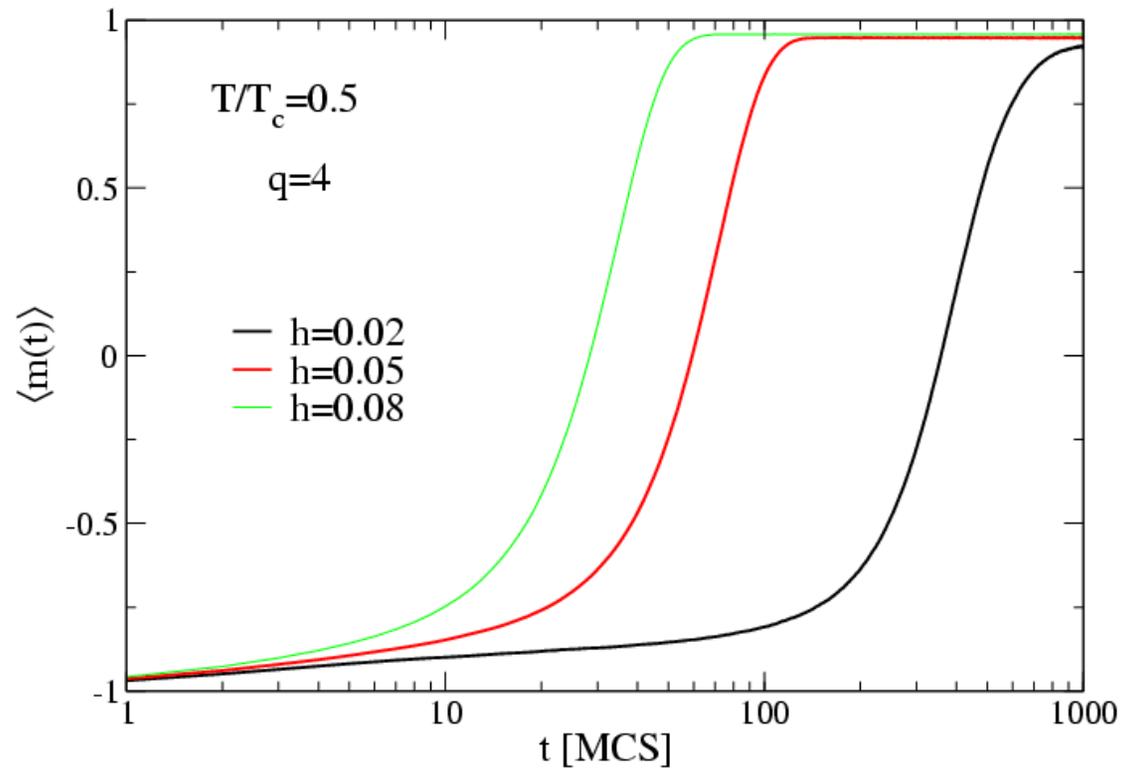
# Ising Model



Comparison of the **external potential** for the magnetization relaxation in mean field approximation as applicable to the choice of Glauber rates and the **mean field free energy per particle** ( $T = 0.7T_c, h = 0.5h_{sp}$ ).

# Ising Model

The form of the external potential is mirrored in the time dependence of the magnetization relaxation upon a field switch for  $T < T_c$ .



# Polymer Dynamics

- linear polymers, the chemist's view

- $X - (CH_2)_n - X$ , polyethylene
- $X - (C_4H_6)_n - X$ , polybutadiene
- . . . .

- linear polymers, the physicist's view

- the configuration of a lattice random walk
- a sequence of hard spheres connected by finite tethers
- . . . .

These views are compatible because of the **large degree of universality** in polymer physics.

# Polymer Dynamics

- static properties

- end-to-end distance  $R_e^2 = \sigma^2 N$
- radius of gyration  $R_g^2 \propto N$
- . . . .

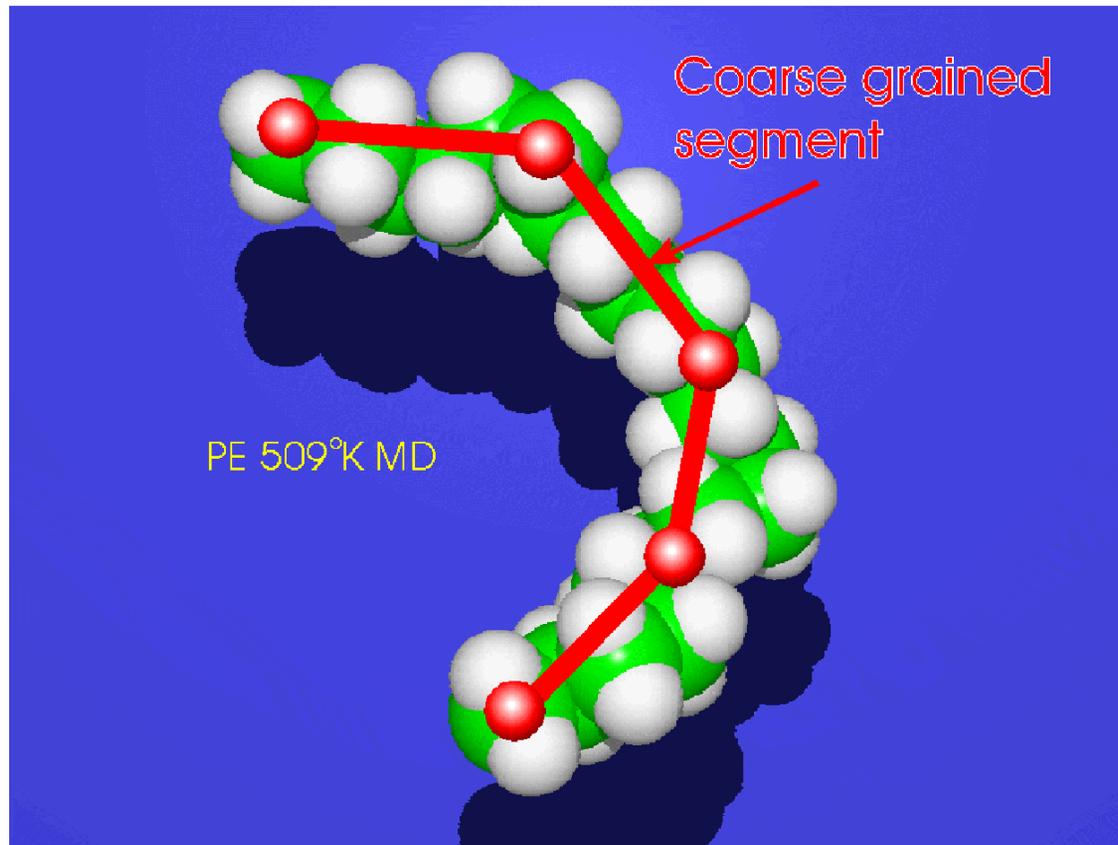
- dynamic properties

- chain center of mass diffusion  $D = \frac{k_B T}{\zeta N}$ , where  $\zeta$  is the segmental friction
- longest relaxation time  $\tau_R \propto N^2$
- . . . .

The proportionality constants are material (model) dependent.

Can one devise a mapping between a chemically realistic polymer model and for instance a lattice model, such that the prefactors of the universal laws are reproduced?

# Polymer Dynamics



A segment of a polyethylene chain overlaid with the repeat units of a coarse-grained representation of this chemically realistic chain.

What is the statistics (effective potential) for  $P(L)$  and  $P(\Theta)$ ? What is the mobility of the coarse-grained segments?

# Polymer Dynamics

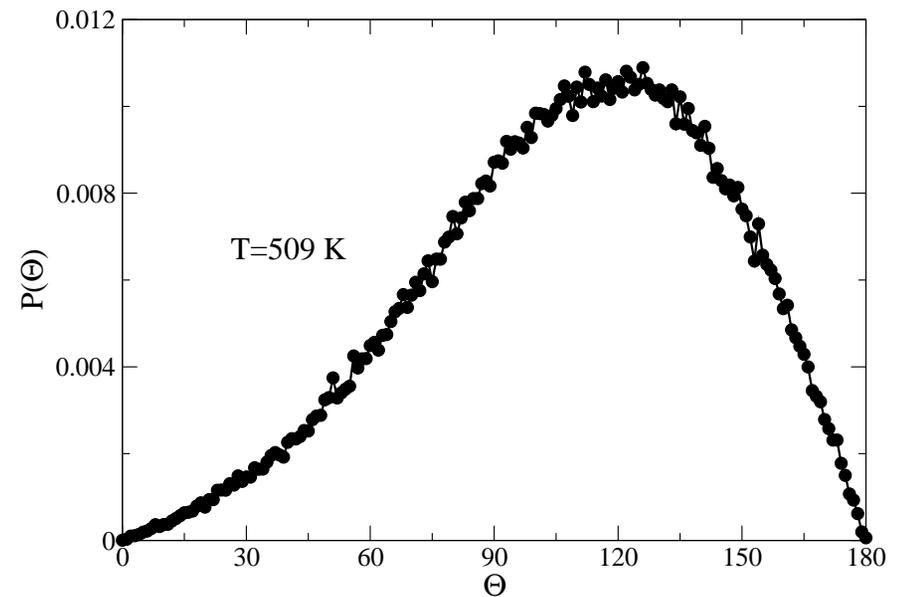
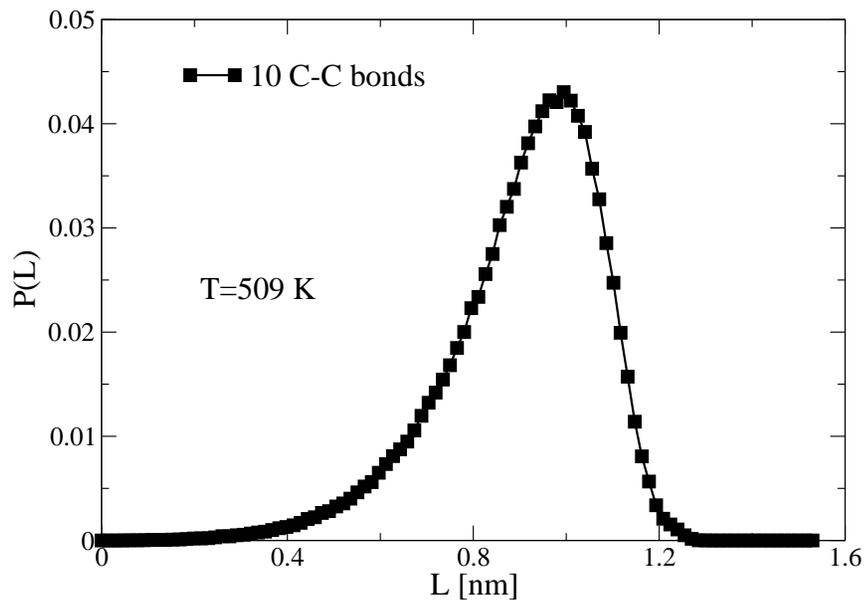
A chemically realistic united atom model of polyethylene is given by

- bond lengths:  $l_{CC} = \text{const.} = 1.53 \text{ \AA}$
- bond angles:  $U(\theta) = \frac{1}{2}k_{\theta}(\cos(\theta) - \cos(\theta_0))^2$
- torsion angles:  $U(\Phi) = \sum_{n=0}^6 a_n \cos(n\Phi)$
- non-bonded interaction:  $U_{LJ}(r_{ij}) = \epsilon_{\alpha\beta} \left[ \left( \frac{\sigma_{\alpha\beta}}{r_{ij}} \right)^{12} - 2 \left( \frac{\sigma_{\alpha\beta}}{r_{ij}} \right)^6 \right]$

energy scales:  $k_{\theta} \approx 10^5 \text{ K}$ ,  $a_n \approx 10^3 \text{ K}$ ,  $\epsilon_{\alpha\beta} \approx 10^2 \text{ K}$

# Polymer Dynamics

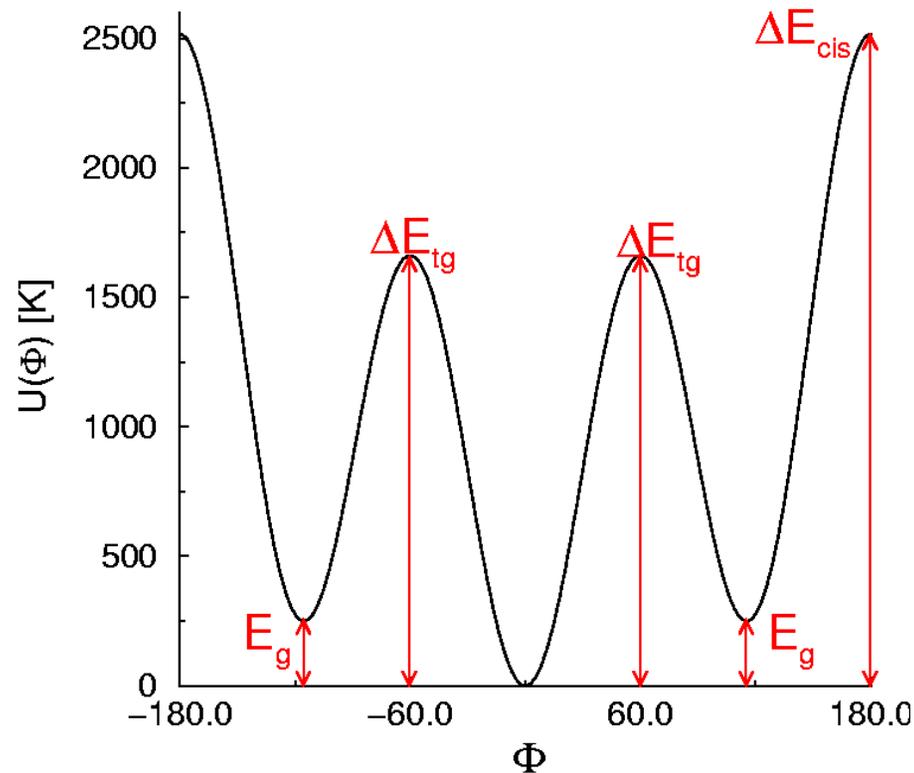
The distributions  $P(L)$  and  $P(\Theta)$  for atoms along the polyethylene chain which are 10 bonds apart.



These distributions contain **structural information** about the polymer chain but no information on its **local mobility**.

# Polymer Dynamics

The local mobility on the length and time scales on which we want to model the polymer is determined by transitions among different states of the local torsion potential.



# Polymer Dynamics

To map this mobility onto the lattice model, the jump probability per Monte Carlo step in the simulation is equated with the average jump rate of the torsional degrees of freedom

$$\frac{1}{\tau_{MC}(T)} \left\langle \min \left( 1, \exp \left\{ \frac{-\Delta \mathcal{H}}{k_B T} \right\} \right) \right\rangle = \frac{1}{\tau_0} \frac{\sum_i \exp \left\{ \frac{-E_i}{k_B T} \right\} \sum_j \exp \left\{ \frac{-\Delta E_{ij}}{k_B T} \right\}}{\sum_i \exp \left\{ \frac{-E_i}{k_B T} \right\}},$$

where  $\tau_0$  is a typical time constant for the torsional degrees of freedom setting their attempt frequency,  $\tau_{MC}$  is the Monte Carlo time unit,  $E_i$  is the energy of minimum  $i$  in the torsional potential and  $\Delta E_{ij}$  is the barrier to minimum 'j'.

# Polymer Dynamics

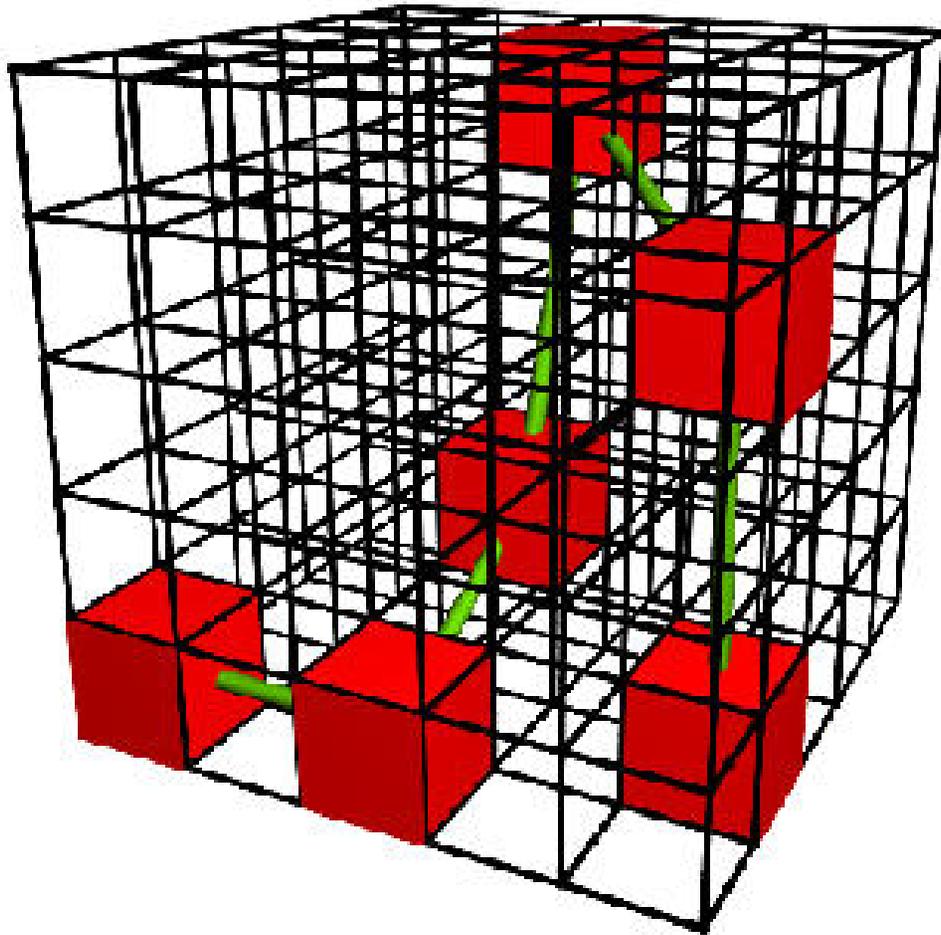
We can now make use of the fact that the Monte Carlo time step  $\tau_{MC}$  is as yet undefined in its relation to physical time. We can fix our Monte Carlo time unit, which is then a function of temperature, to be always equal to the mean time between two such transitions for the fastest degree of freedom

$$\tau_{MC}(T) = A_{BFL}(\infty)\tau_0 \exp \left\{ \frac{\Delta E_{min}}{k_B T} \right\}.$$

We end up with the mapping condition

$$\left\langle \min \left( 1, \exp \left\{ \frac{-\Delta \mathcal{H}}{k_B T} \right\} \right) \right\rangle = A_{BFL}(\infty) \exp \left\{ -\frac{\langle \Delta E \rangle - \Delta E_{min}}{k_B T} \right\}.$$

# Polymer Dynamics



5 different bond lengths  $L$ ,  
87 different bond angles  $\Theta$   
random hopping MC kinetics

The bond-fluctuation model of polymer chains

# Polymer Dynamics

We will use bond lengths and bond angles as the dynamic degrees of freedom

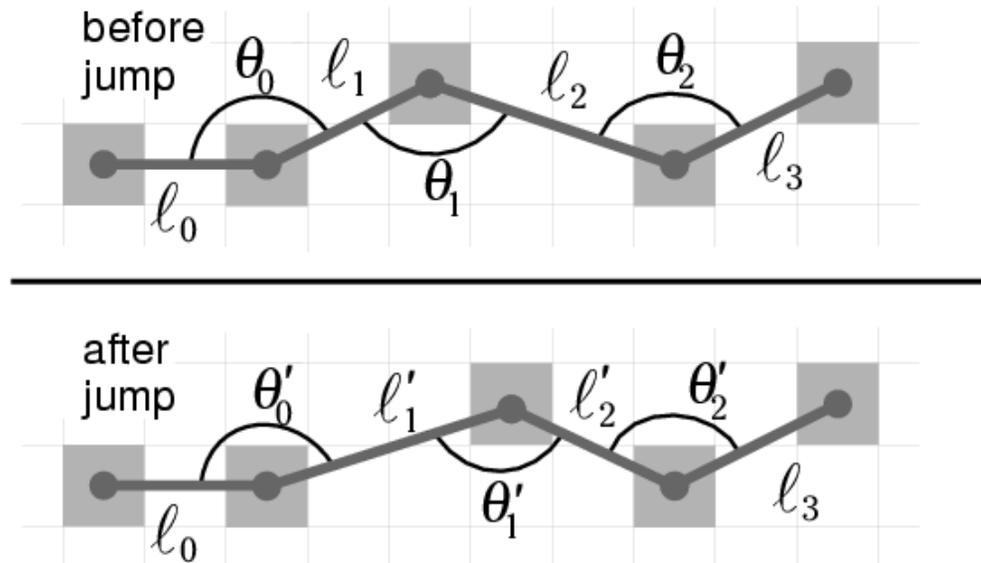
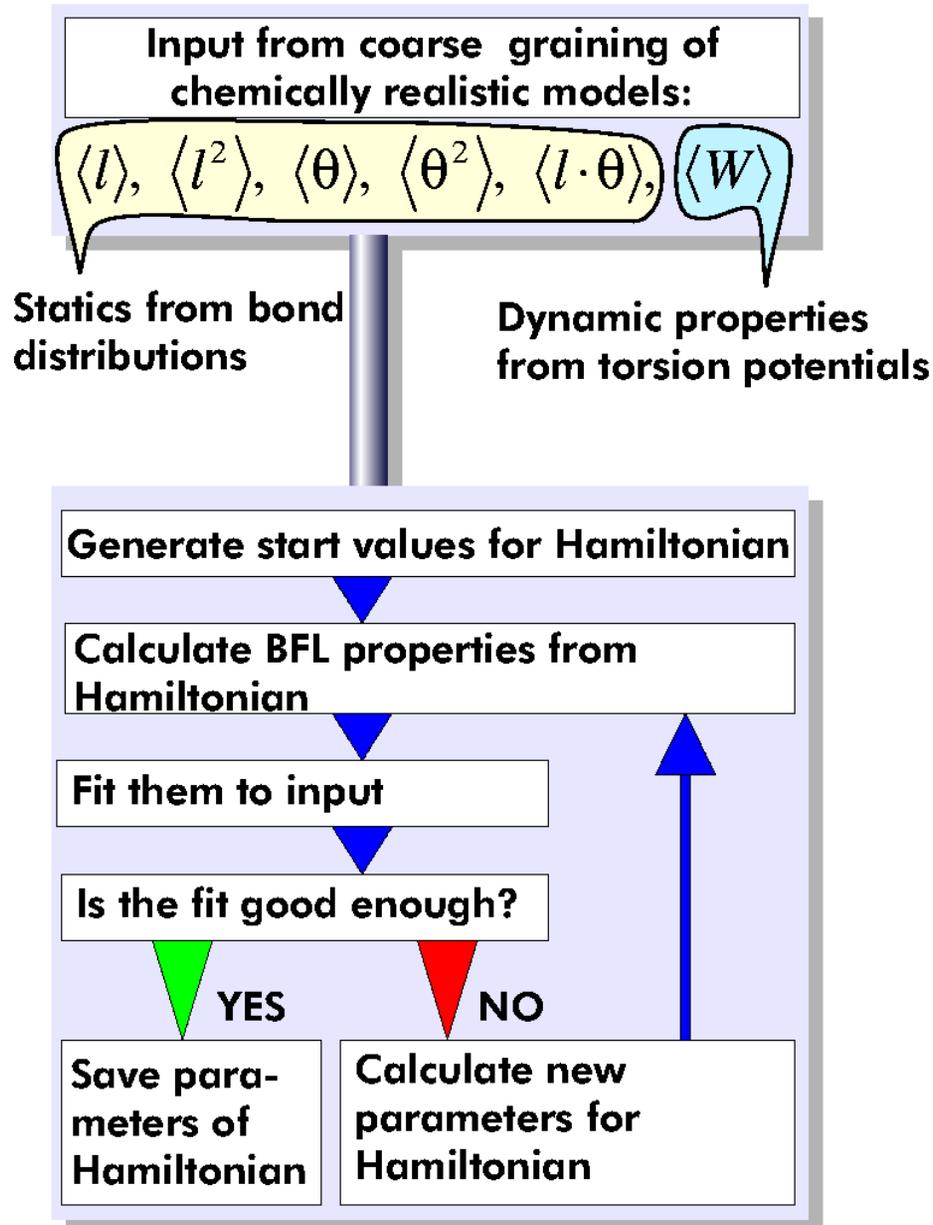
$$\begin{aligned}\mathcal{H}(l, \theta) &= \Phi_0 u_0 (l - l_0)^2 + \Phi_1 u_1 (l - l_1)^2 \\ &+ \Phi_0 v_0 (\cos \theta - c_0)^2 + \Phi_1 v_1 (\cos \theta - c_1)^2\end{aligned}$$

Here  $\Phi_0 = 1$  and  $\Phi_1(T) = \frac{1}{T} - \langle \frac{1}{T} \rangle$  are orthonormal basis functions on the set of temperatures, where input information for the mapping is given, i.e., we have determined the coarse-grained structure and mobility at temperatures  $T_1, T_2, \dots, T_n$  then

$$\Phi_1(T_i) = \frac{1}{T_i} - \frac{1}{n} \sum_{j=1}^n \frac{1}{T_j}$$

The last point assures that the parameters can be optimized independently.

# Polymer Dynamics



This 4-bond segment of a BFL chain can be treated by exact enumeration of its  $108^4$  states.

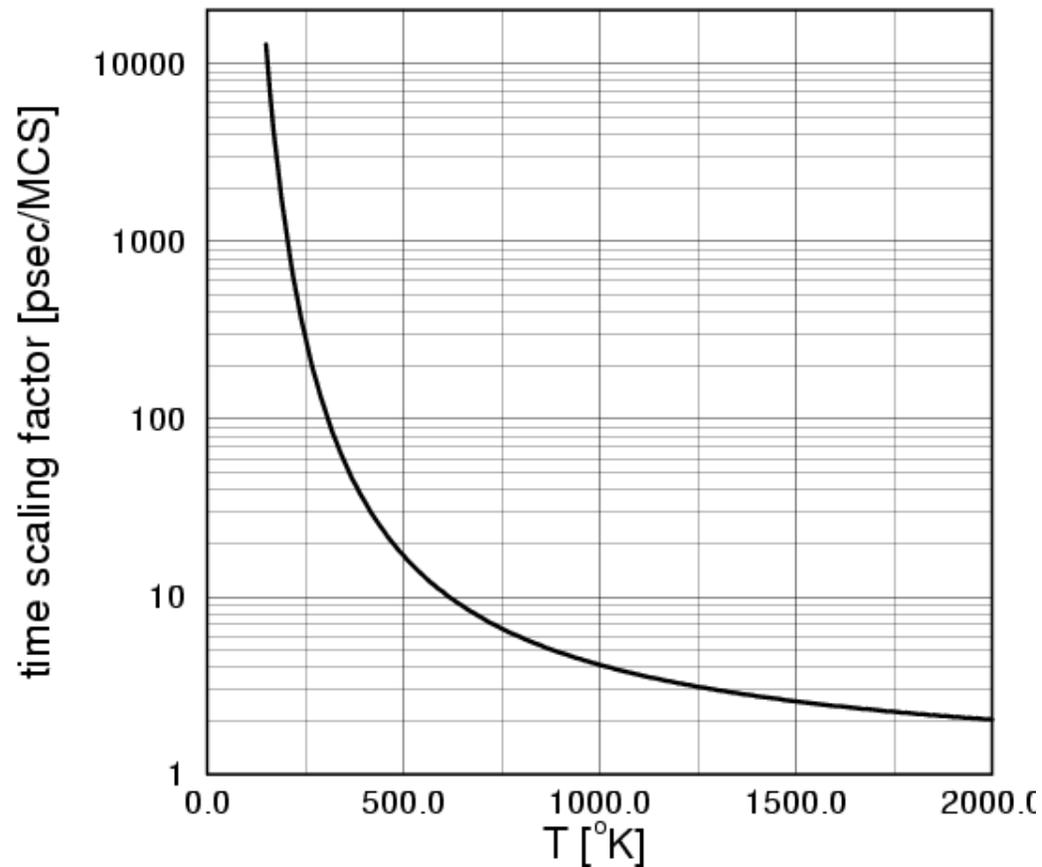
# Polymer Dynamics

After determination of the optimal parameters  $u_0, \dots, c_1$  in the Hamiltonian, Monte Carlo simulations of a dense melt in the bond fluctuation model are performed as a function of temperature. Measures of the kinetics are

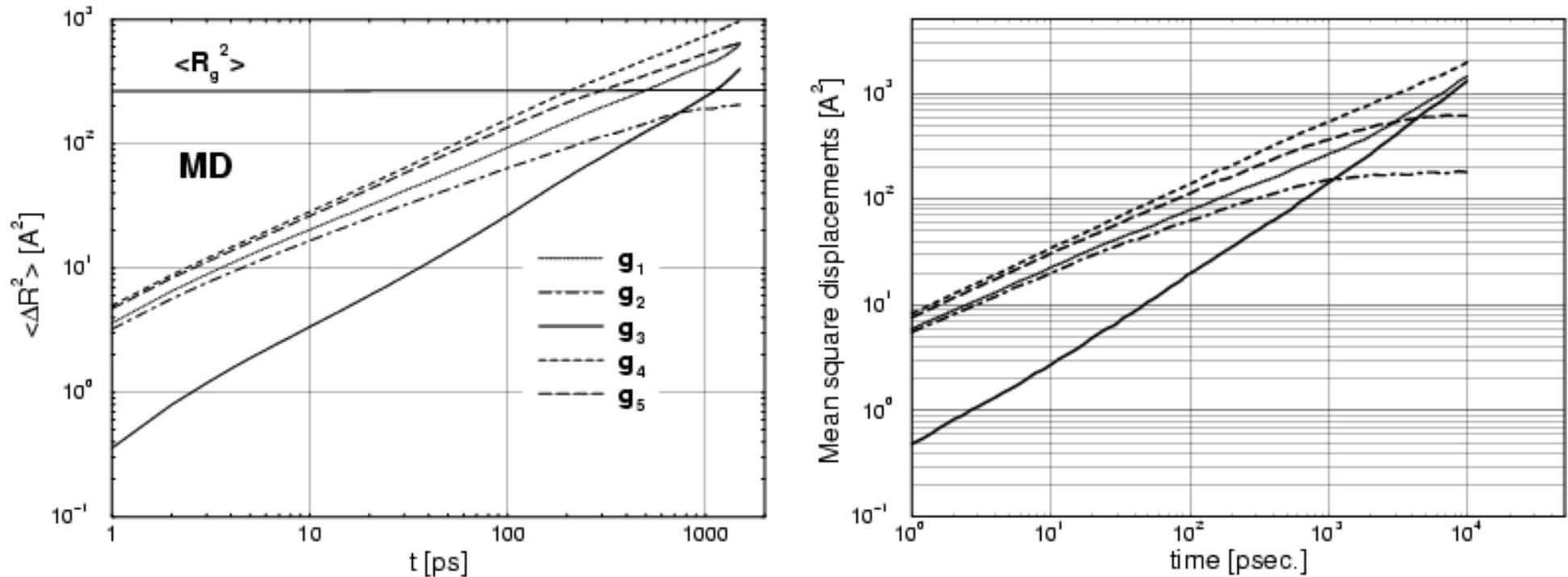
- $g_1(t)$ : mean square displacement of center monomers of a chain
- $g_2(t)$ : same in the center of mass reference frame of the chain
- $g_3(t)$ : mean square center of mass displacement of a chain
- $g_4(t)$ : mean square displacement of end monomers of a chain
- $g_5(t)$ : same in the center of mass reference frame of the chain

# Polymer Dynamics

To map the Monte Carlo time onto real time we equate the center of mass diffusion coefficient of a chain at  $T = 450$  K with the experimental value:  $S[ps/MCS] = D_{sim}[cm^2/MCS]/D_{exp}[cm^2/ps]$



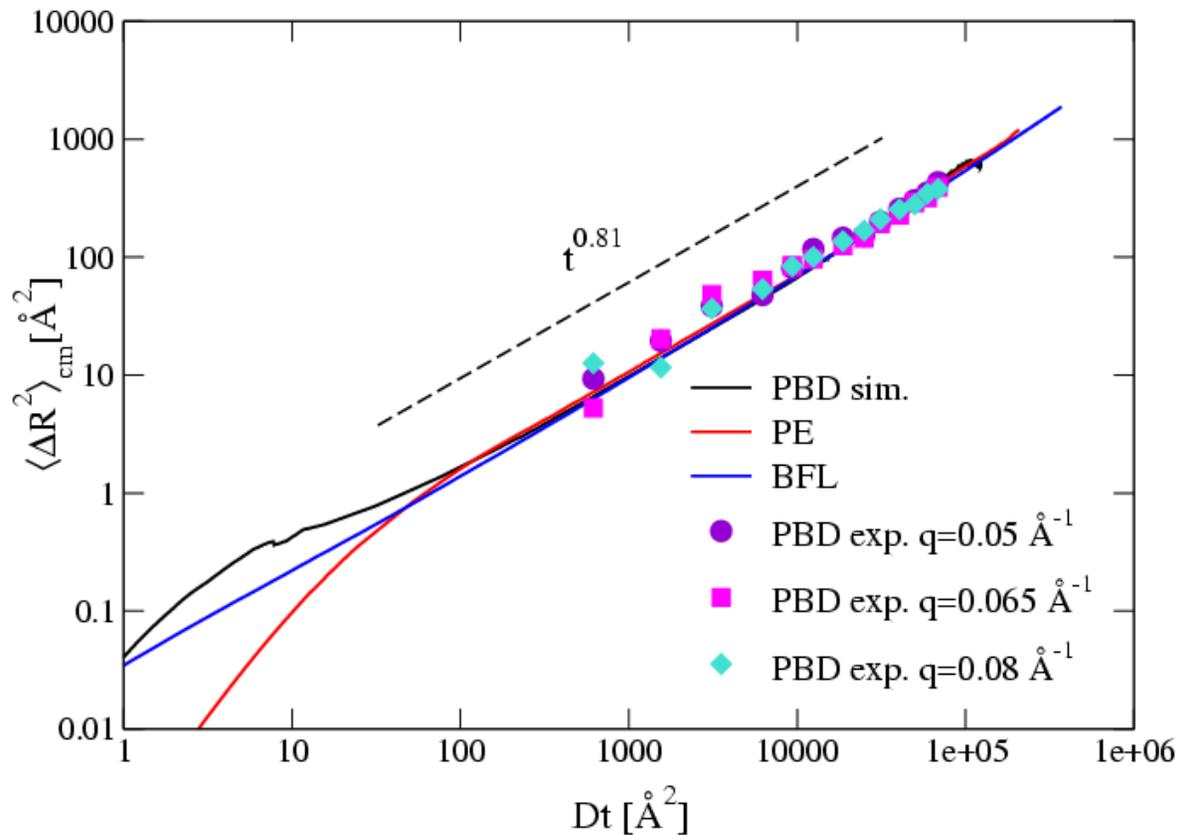
# Polymer Dynamics



Comparison of mean square displacements at 509 K from the MD simulation of the chemically realistic model (left, **3 months of CPU time**) and the MC simulation of the BFL model (right, **1 day of CPU time**). The agreement is within 40% which is about twice the typical discrepancy of a good chemically realistic model from experiment.

# Polymer Dynamics

To conclude I want to emphasize again that the ability of kinetic MC simulations to quantitatively model real relaxation and transport processes lies in their universality (general diffusion processes, polymer dynamics).



# Literature

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