Stochastische Modelle zur Ionendynamik in komplexen Systemen

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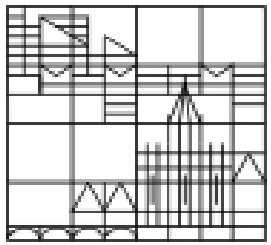

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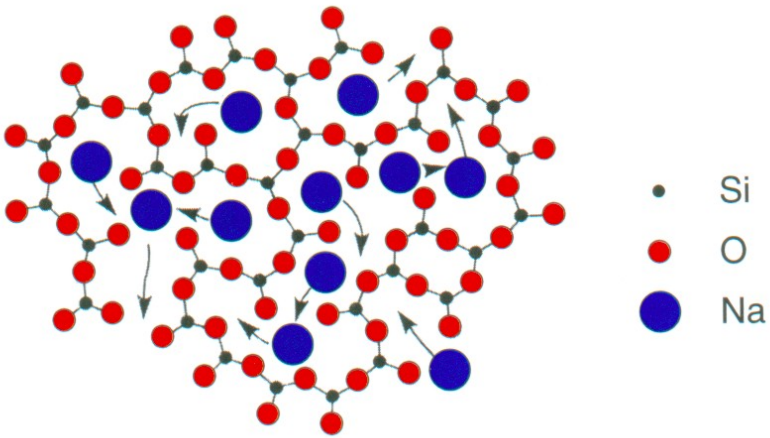
Glassy and polymeric ionic conductors

Glasses (e.g. $(Na_2O)_x(SiO_2)_{1-x}$)

Rigid matrix

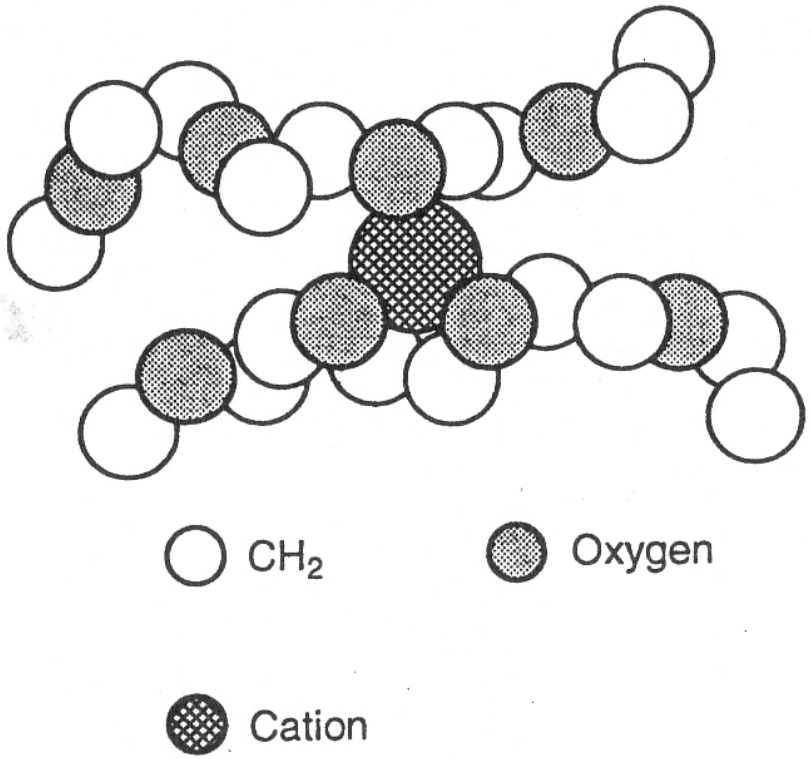
Ion hopping among preferred sites



Polymers (e.g. polyethylenoxid/salt-complex)

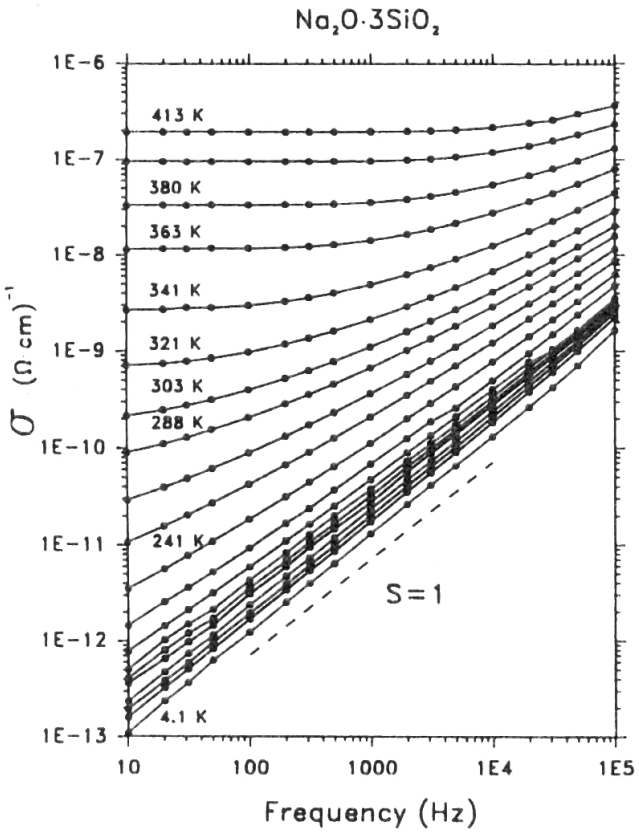
Fluctuating matrix

Ion diffusion $\Leftrightarrow$ motion of polymer segments



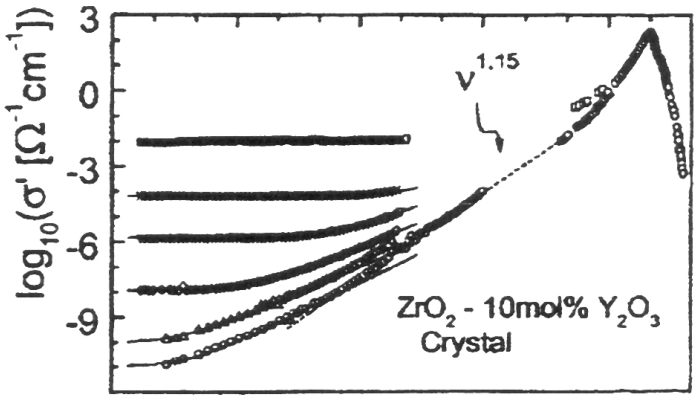
Experiments

Glasses A. Nowick et al. (1994)



Heavily doped crystals

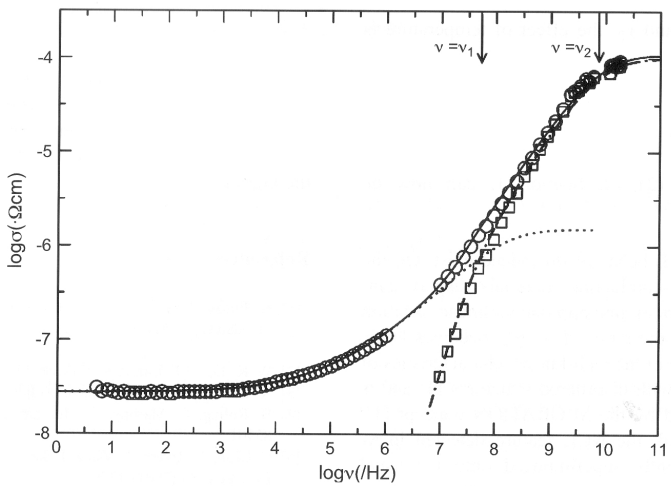
Pimenov et al. (1998)



Pure crystal (structural disorder)

γ - Rb Ag_4 I_5

K. Funke et al. SSI **175**, 819 (2004)



General mechanism for NCL?

Linear response theory:

$$\begin{aligned} \chi''(\omega) &= (\omega/k_B T)\int_0^\infty \mathrm{d}t \langle \vec{P}(t)\vec{P}(0)\rangle \cos\omega t \\ \sigma(\omega) &= \epsilon_0 \omega \chi''(\omega) \end{aligned}$$

If $\langle \vec{P}(t)\vec{P}(0)\rangle = \langle(\vec{P}(0))^2\rangle e^{-t/\tau} \Rightarrow \chi''(\omega) = \chi(0)\frac{\omega\tau}{1+(\omega\tau)^2}$ Debye

$\chi''(\omega) \approx$ const. or $\sigma(\omega) \propto \omega$ requires
an extremely slow decay of $\langle \vec{P}(t)\vec{P}(0)\rangle$.
Crossovers at short and long times!

Microscopic mechanism?

- ADWP-model
- Beyond ADWP

Asymmetric double well potential (ADWP) model

Pollak, Pike (1972); Gilroy, Phillips (1983)

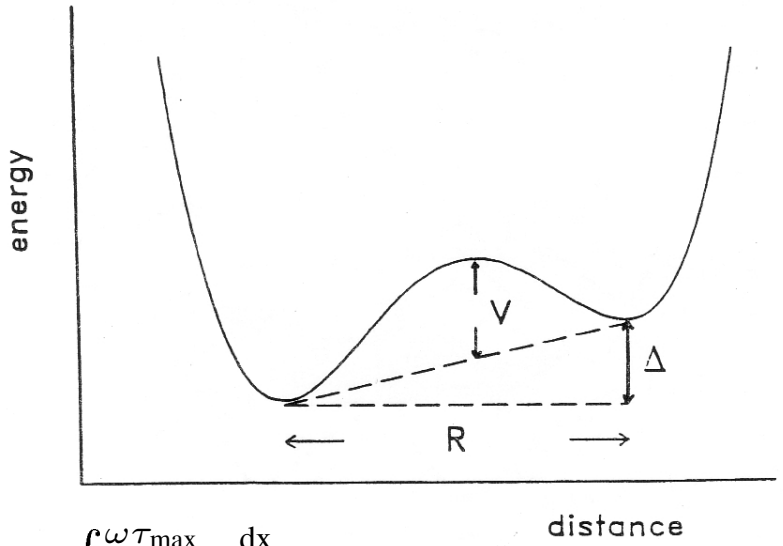
- $\Delta = 0$

$$k_B T \sigma(\omega) \propto \left\langle \frac{\omega^2 \tau(E)}{1+\omega^2\tau^2(E)} \right\rangle_{av}$$

where $\tau(E) \simeq \tau_0 \exp(E/k_B T)$

Let $P_E(E) \simeq$ const. for $E_{\min} < E < E_{\max}$

$P_E(E)\mathrm{d}E = P_\tau(\tau)\mathrm{d}\tau \Rightarrow P_\tau(\tau) \propto \tau^{-1}$



Then $\left\langle \frac{\omega^2\tau(E)}{1+\omega^2\tau^2(E)} \right\rangle_{av} = \int_{E_{min}}^{E_{max}} P_\tau(\tau) \frac{\omega^2\tau}{1+\omega^2\tau^2} \mathrm{d}\tau \propto \omega \int_{\omega\tau_{\min}}^{\omega\tau_{\max}} \frac{\mathrm{dx}}{1+\mathrm{x}^2}$

$$k_B T \sigma(\omega) \propto \omega \frac{k_B T}{E_{\max}} \quad \text{if } \omega\tau_{\min} \ll 1 \text{ and } \omega\tau_{\max} \gg 1$$

- $\Delta \neq 0$

Let $P_\Delta \simeq$ const. $\Rightarrow$ extra factor $\frac{k_B T}{\Delta_{\max}}$

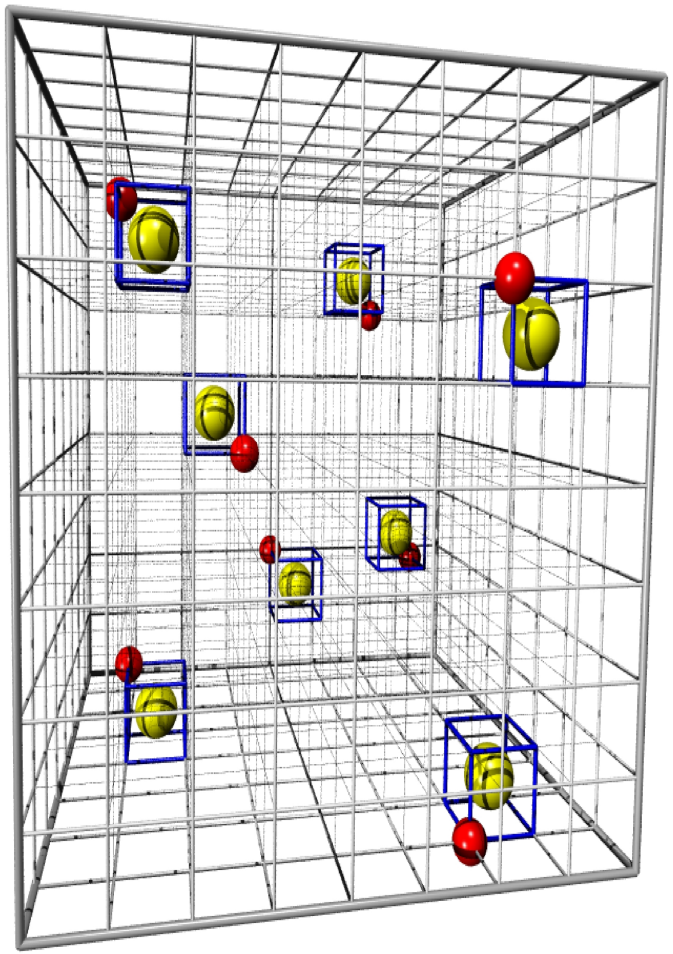
Problems: ADWP requires extremely wide distribution P_E;
effective T-dependent parameters (Jain et al. (1995));
c-dependence in doped crystals (Nowick et al. (1995), Jain et al. (2005));
electrostatic interactions are there!

Dipolar lattice gas model (review: W.D. and P. Maass, Chemical Physics **284**, 439 (2002))

Localized motions of charged defects centered at random positions.

- Immobile charges at random positions $\vec{R}$; concentration $c \ll 1$
- Mobile charges bound to NN-positions; thermally driven orientational moves (discretized local motion).

Model of electrostatically coupled ADWP's



Two dimensionless parameters:
concentration of centers c
reduced temperature $\theta \simeq k_B T / V_{\mathrm{dip}}(r_s)$

KMC-simulations

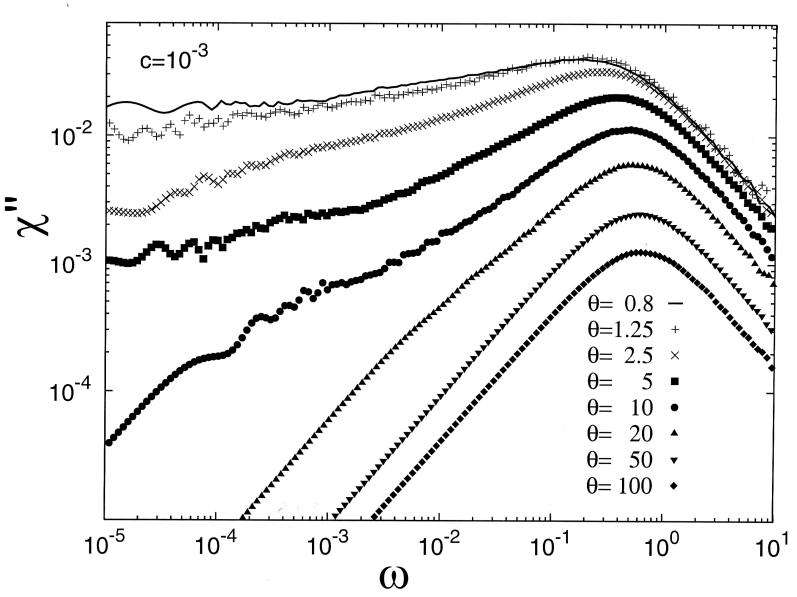
$$\hat{\chi}(\omega) = \beta\langle(\vec{P}(0))^2\rangle(1 + i\omega \int_0^\infty C(t)e^{i\omega t}\mathrm{dt})$$

$$C(t) = \frac{\langle\vec{P}(t)\vec{P}(0)\rangle}{\langle(\vec{P}(0))^2\rangle}$$

$$\hat{\sigma}(\omega) = -i\omega\epsilon_0\hat{\chi}(\omega)$$

Closer analysis of KMC reveals two processes:

- short times:
  relaxation towards local equilibrium state of one dipole in the random static field produced by other dipoles.
  $\Rightarrow$ nearly Debye
- long times:
  fluctuations in the environment large enough to change local equilibrium state $\Rightarrow$ non-Debye!



Separation of time scales - details

A) ADWP-type analysis

Simulation $\Rightarrow$ static distribution function $W(..\epsilon_\alpha..)$ of site energies

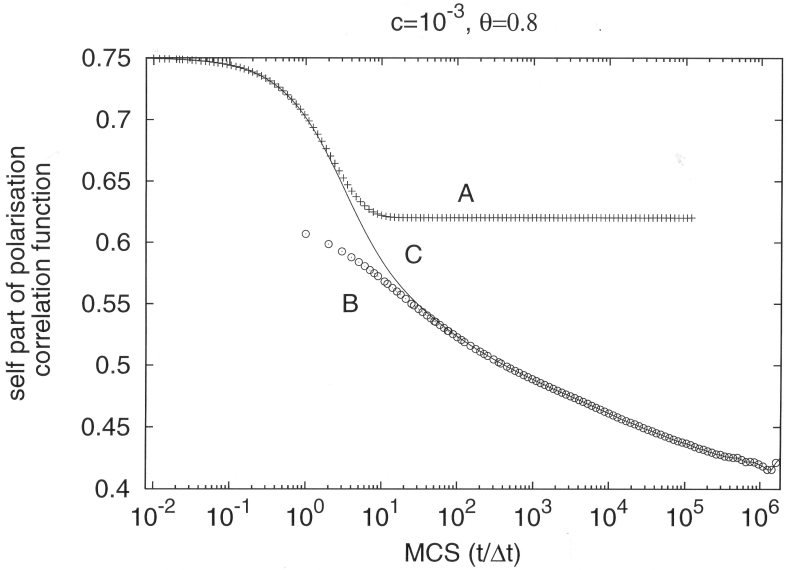
$\Rightarrow$ single-dipole master equation $\Rightarrow$ Debye-like spectrum (τ_D)

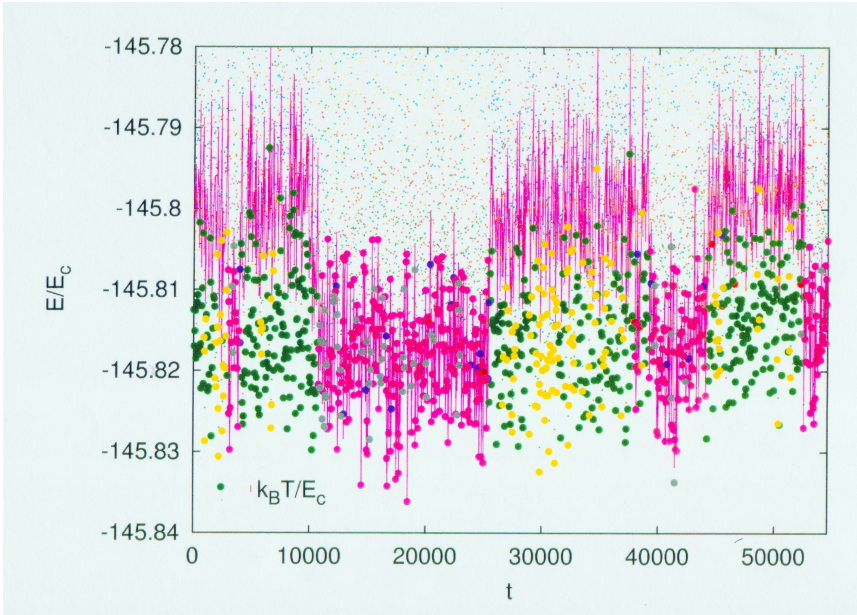
B) Local equilibrium idea

Assume $\epsilon_\alpha(t)$ slow in comparison with τ_D

$\Rightarrow$ compute $\vec{p}_i^{\,l.eq}(t) \propto \sum_\alpha \vec{p}_{i,\alpha} e^{-\beta\epsilon_\alpha(t)}$

$$\frac{1}{N}\langle \vec{P}(t)\vec{P}(0)\rangle_{self}^{l.eq} = \left[\frac{1}{N}\sum_i \vec{p}_i^{\,l.eq}(t)\vec{p}_i^{\,l.eq}(0)\right]_{av}$$



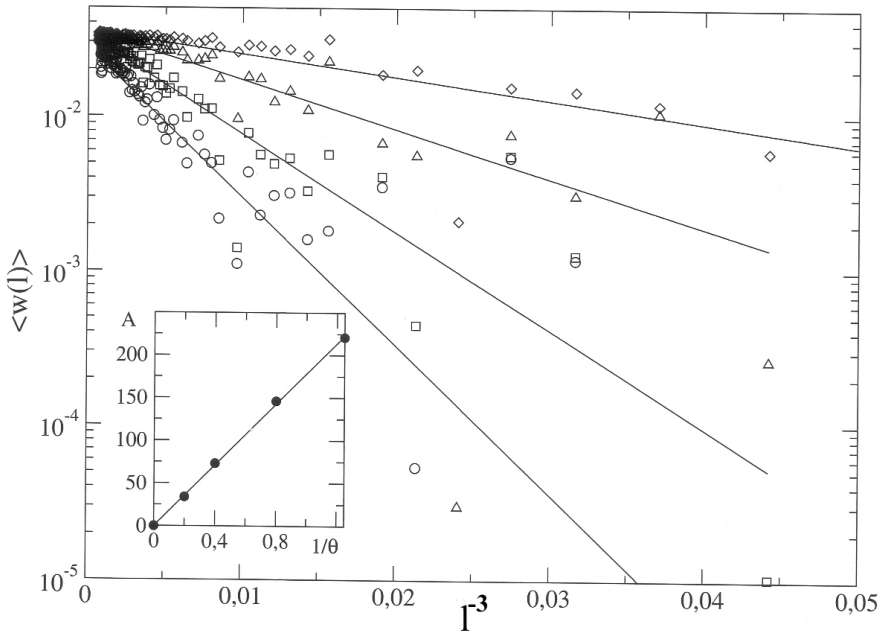


Note: $\epsilon_\alpha(t)$ fluctuates rapidly, but lowest energy orientation is slowly varying

Analytic approaches

- Scaling approach

$V_{\rm dip}(l) \propto V_0 l^{-3} \Rightarrow$ classification of randomly placed dipoles according to distance l to closest neighbor



Prob. distrib. for NN distance l:
$\phi(l) = 4\pi c l^2 \exp[-(4\pi c/3) l^3]$

Av. relaxation rate:
$w(l) = w_0 \exp(-A/l^3)$
$A = V_0/k_B T$

$t \to \infty$:
Only pairs of dipoles with $l > l^*(t)$ can relax until time t, where $t\, w(l^*(t)) = 1$ or $l^*(t) \sim (A/\ln w_0 t)^{1/3}$. Fraction of dipoles which cannot relax until time t:

$$f(t) = \int_0^{l^*} \phi(l) dl, \quad \text{and } C(t) \sim f(t) \sim [\ln(w_0 t)]^{-1}$$

$$\Rightarrow \chi''(\omega) \sim (\ln \omega)^{-2}$$

- **Field-theoretic approach** (M. Schulz, P. Maass, W. D., Z. Phys. Chem. **218**, 1375 (2004) and in preparation)

$$\frac{\partial \vec{p}_i(t)}{\partial t} = -\gamma \frac{\partial F\{p\}}{\partial \vec{p}_i} + \vec{\eta}_i(t)$$

Calculate free energy $F\{p\}$ by Hubbard-Stratonovich transformation:

$$\exp(\tfrac{\beta}{2}\Gamma p^2) = \int_{-\infty}^{+\infty} \mathrm{d}\varphi \exp\left[-\tfrac{1}{2\beta}\hat{\Gamma}\varphi^2 + p\varphi\right]; \qquad \beta = 1/k_B T; \quad \hat{\Gamma}\Gamma = 1$$

$$\Gamma \longrightarrow \Gamma^{ij}_{\alpha\beta} = \tfrac{1}{G}\sum_{\vec{k}} \Gamma_{\alpha\beta}(\vec{k}) \exp[i\vec{k}(\vec{R}_i - \vec{R}_j)]$$

$$\Gamma_{\alpha\beta}(\vec{k}) = C\delta_{\alpha\beta} - \tfrac{k_\alpha k_\beta}{k^2}; \qquad C > 1$$

$$Z = \text{const.} \int \left(\prod_{\alpha,i} d\varphi_{\alpha,i}\right) \exp[-\beta(H_0 + H_1)]$$

$$\beta H_0 = \tfrac{T}{2G^2} \sum_{\substack{i,j \\ \alpha,\beta}} \varphi_{\alpha i} \hat{\Gamma}^{ij}_{\alpha\beta} \varphi_{\beta j} - \tfrac{2\pi p_0^2}{3V} \sum_{\alpha,i} \varphi^2_{\alpha,i} + \tfrac{4\pi^2 p_0^4}{45 V^2 N} \left(\sum_{\alpha,i} \varphi^2_{\alpha,i}\right)^2$$

βH_1: anisotropy in 4th order; $O(\varphi^6)$

Mean-field approximation:

$$H_0 = \text{min.} \Rightarrow \quad \begin{array}{lcll} \varphi & = & 0 & \text{for} \quad T > T_c \\ \varphi & \neq & 0 & \quad\;\; T < T_c \end{array}$$

with $T_c = 4\pi p_0^2/3\theta_0$

θ_μ's eigenvalues of $\hat{\Gamma}$; $\quad \theta_0 = \min \theta_\mu$

Disordered system: expect no sharp T_c!

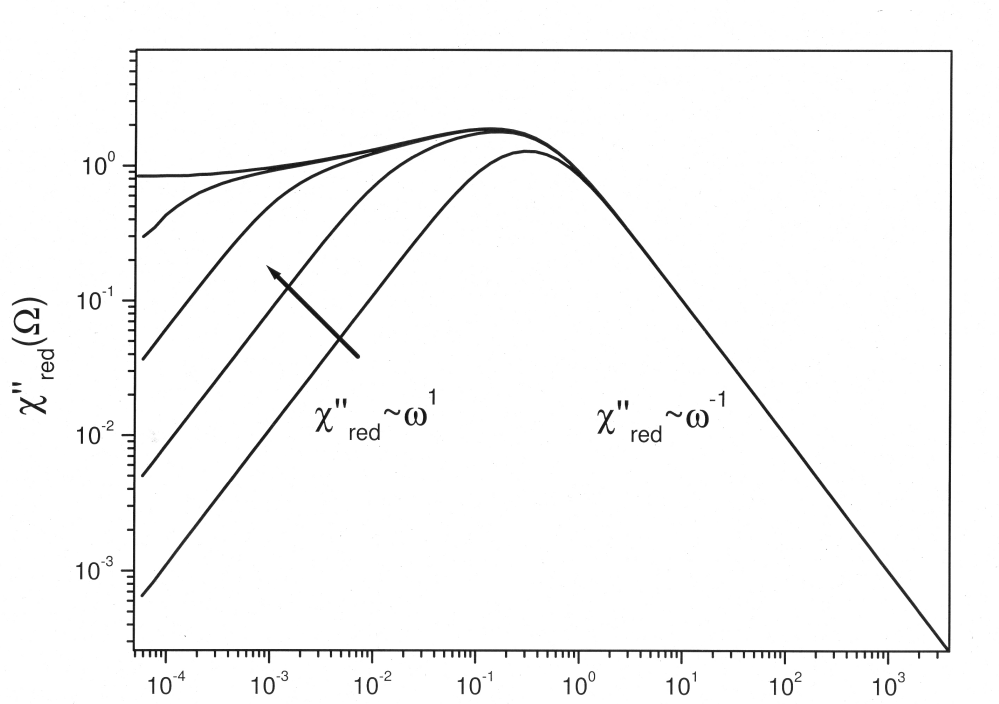
Harmonic approximation for $T > T_c$:

$$\chi''_{inc}(\omega) = \omega \sum_\mu \text{Re} \frac{\chi_\mu}{-i\omega + \gamma\mu}$$

where

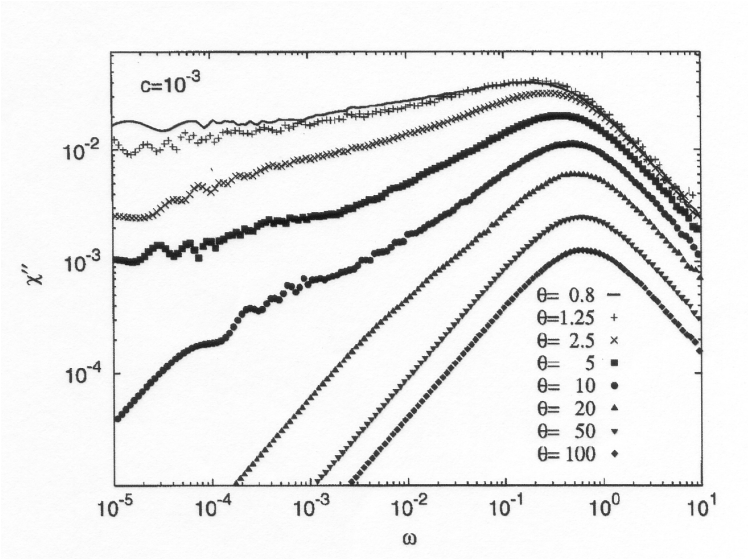
$$\begin{array}{lcl} \chi_\mu & = & \frac{p_0^2}{3} \frac{\theta_\mu}{\theta_\mu T - \theta_0 T_c} : \\ \gamma_\mu & = & \gamma/\chi_\mu \end{array}$$

From pre-averaged eigenvalue equation:

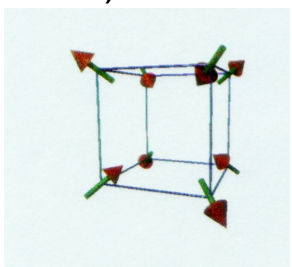


Dependence on details of interaction

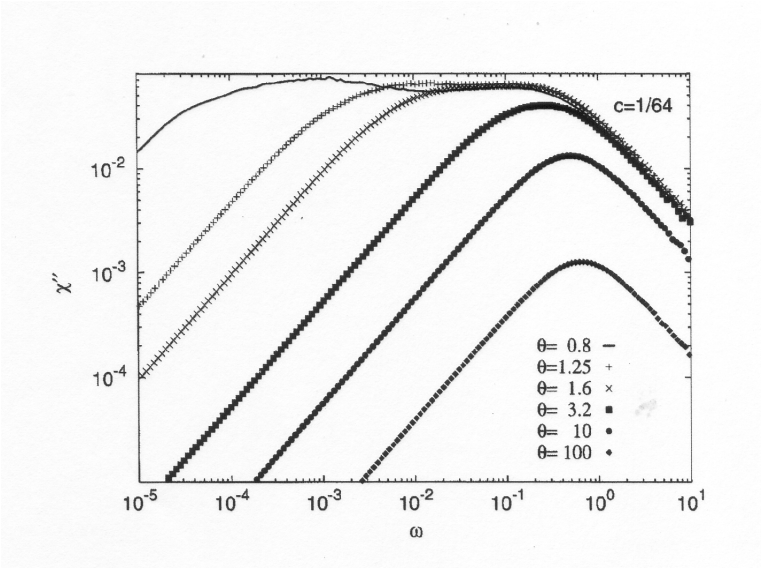
- Dilute system $c = 10^{-3}$ ("pure" dipole - dipole interaction)



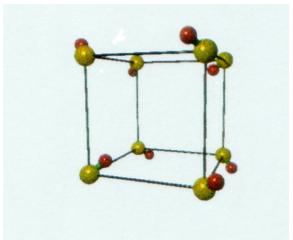
ground state of ordered array of centers ($l = 10$): (Luttinger, Tisza)



- Increased concentration $c = 1/64$ (higher multipoles)



ground state of ordered array of centers ($l = 4$):

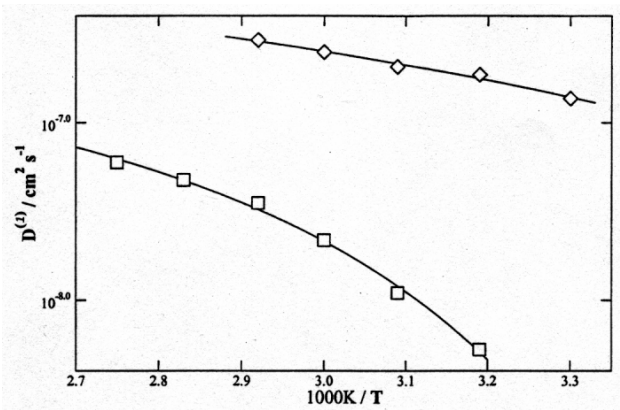


PEO-based electrolytes: typical experiments

Cation/anion diffusion

C.A. Vincent, 1995

$(LiPF_6)_x$ PMEO; $x = 1/50$
PFG-NMR



Similar: $(NaI)(PEO)_{30}$

N. A. Stolwijk et al., 2004

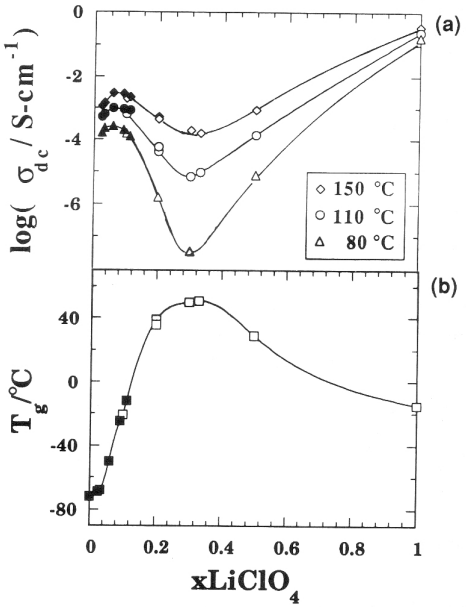
^{22}Na; ^{125}I radiotracer

Non-Arrhenius

Glass transition

S. Lascand et al., 1994

PEO-KMPSA

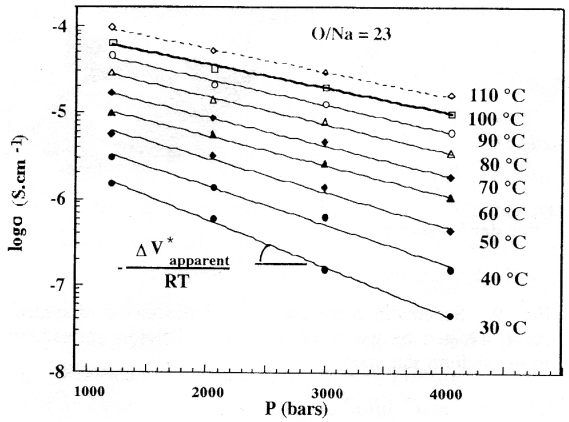


Adding ions:
T_g increases,
cation mobility drops

Pressure effects

J. L. Souquet et al., 1998

Na^+-polyether



Exponential decrease with p

Mechanical Stretching

Golodnitzky, Peled (2003)

σ increases along stretch direction

Simulation of lattice chains and ions

Pendzig et al. 1998; O. Dürr et al. 2004

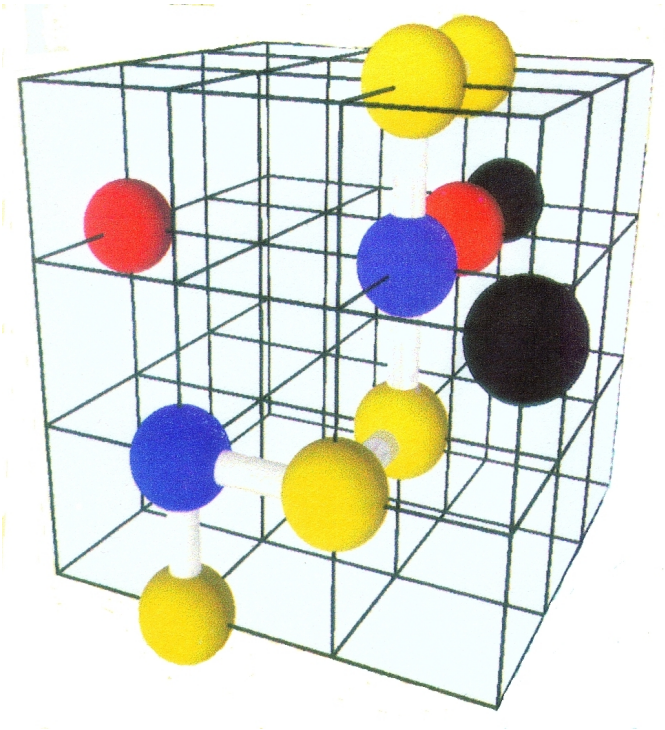
Chain beads:

CH_3-(O-CH_2-CH_2)$_4$

Interactions:

- hard core
- repulsion among chain beads: $\epsilon > 0$
- $M^+ - 0$ attraction: $-\epsilon_0 < 0$
- ion-ion: Coulomb
- Put $\epsilon = \epsilon_0 = q^2/4\pi\varepsilon_0 a \Rightarrow$ 1 parameter $k_B T/\epsilon$

Dynamics: Generalized Verdier-Stockmayer moves, kink jumps, end jumps, rotational jumps (crankshaft); compatible with Rouse dynamics

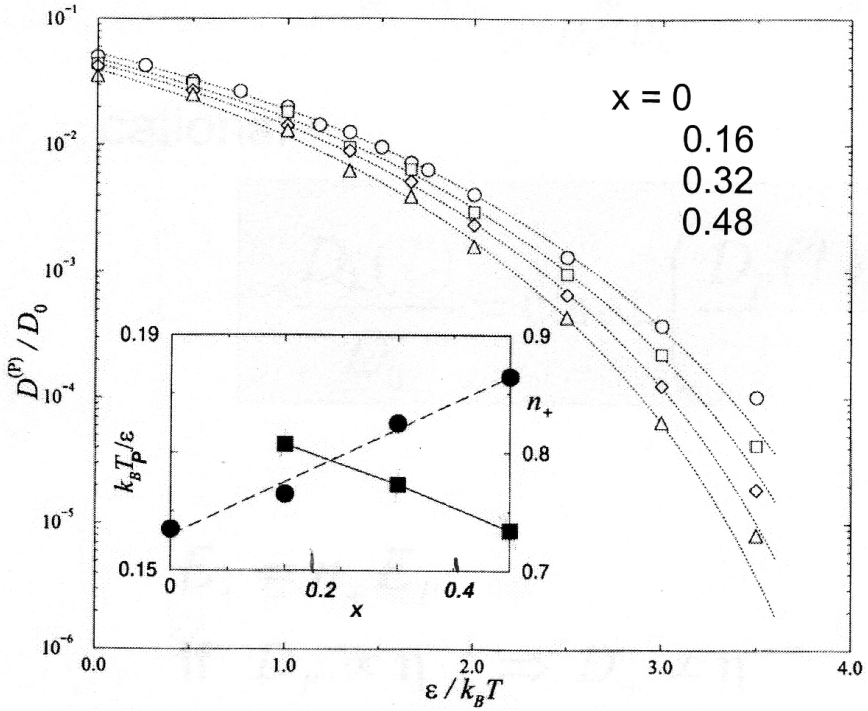


Simulation results

Polymers:

$D_P = \lim_{t\to\infty} \frac{1}{6tN_P} \sum_{i=1}^{N_P} \langle (\vec{R}_i(t) - \vec{R}_i(0))^2 \rangle$

$\vec{R}_i$ = center of mass of i-th chain

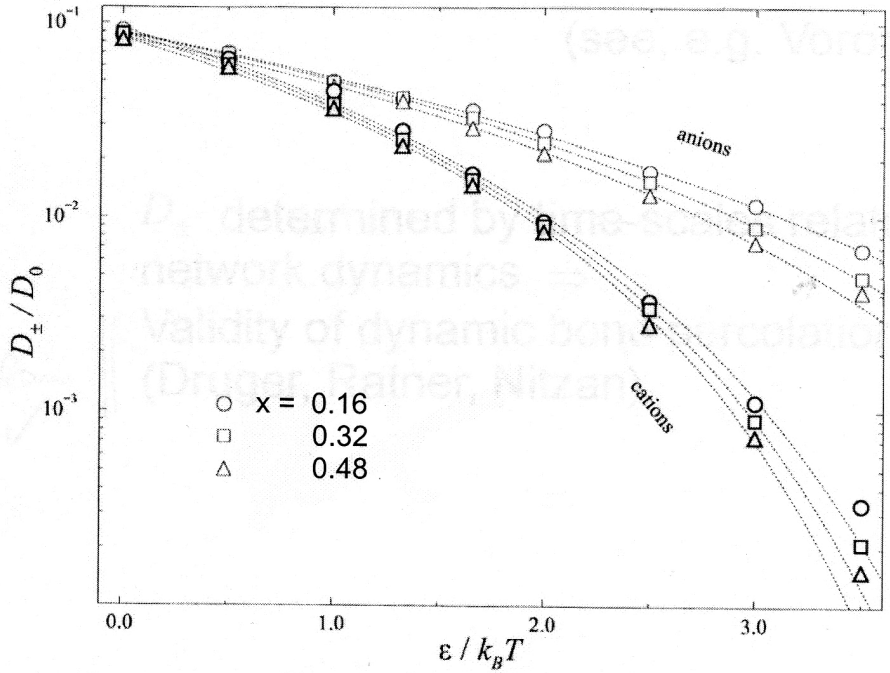


Vogel-Tammann-Fulcher (VTF):

$$D_P(T,x) = D_\infty \exp\left[-\frac{E_P(x)}{k_B(T-T_P(x))}\right]$$

Ions:

x = nb. of cations/nb. of oxygens



Again VTF behavior:
cations: $T_+ = T_P$; $E_+ = n_+ E_P$
anions: $T_- < T_P$

Ion diffusion versus chain diffusion

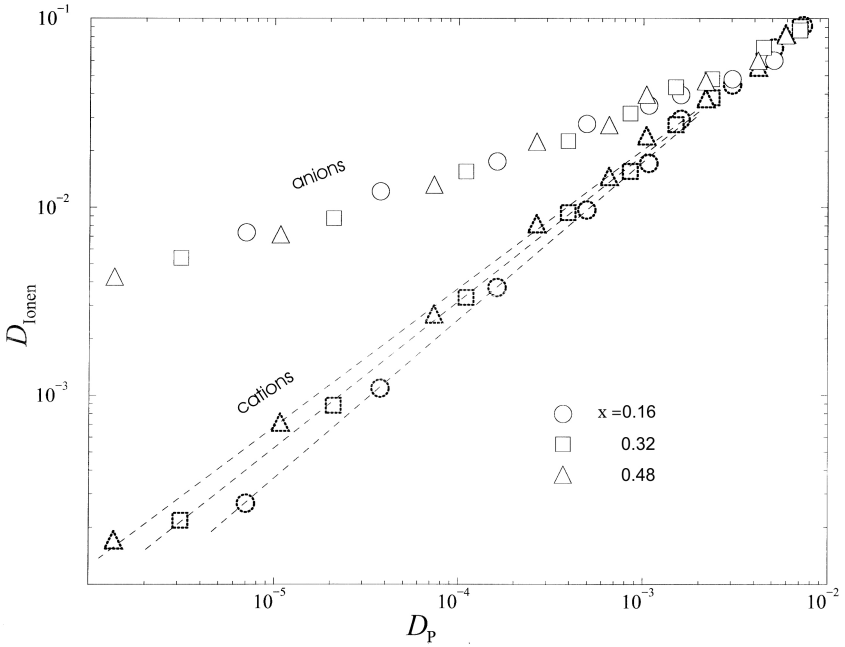
$VTF-$ behaviors : $E_+ = n_+ E_P$
with $n_+ < 1$
("decoupling")

$$\frac{D_+(T)}{D_0} = \left(\frac{D_P(T)}{D_\infty}\right)^{n_+}$$

Viscosity of polymer network:
$\eta \propto D_P^{-1}$

Then $D_+ \propto \eta^{-n_+}$

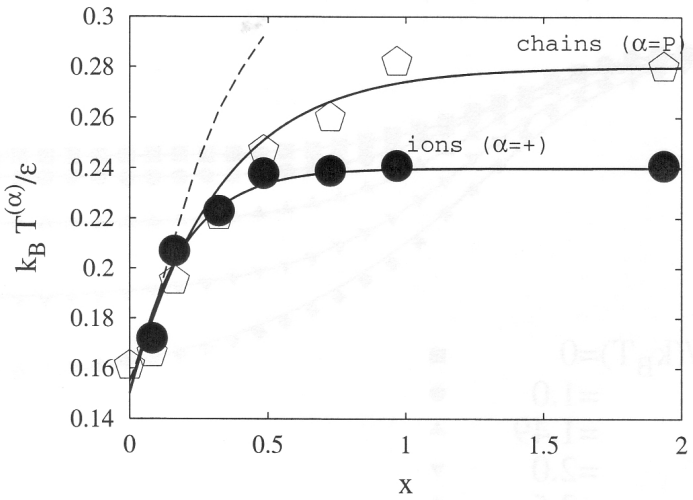
"fractional
Stokes-Einstein"



VTF-temperature and configurational entropy

Reduced model: only one species of mobile ions

$T_P(x)$ from VTF-fits of diffusion constants vs. T:



Interpretation in terms of configurational entropies?

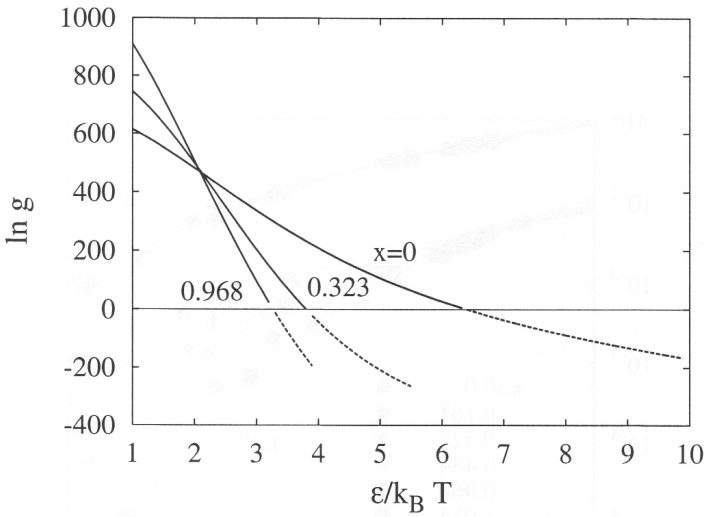
$x \nearrow \Rightarrow S_c \searrow$ due to crosslinking of chains through cations.

Di Marzio concept:

$S_c(T, x) = 0 \Rightarrow T = T_c(x)$

"ideal glass transition temperature"

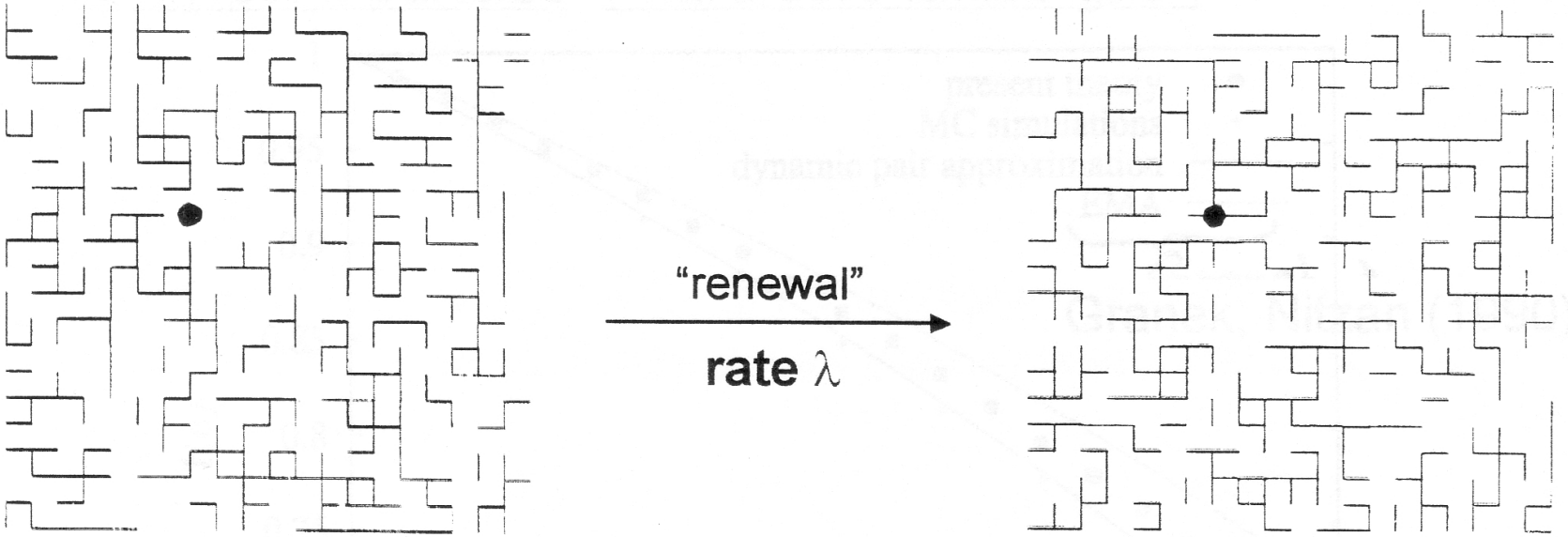
$S_c = k_B T \ln g$ from "quasi-chemical approximation" (QCA):



Diffusion through a fluctuating network: Dynamic percolation (DP) approach

Aim: Further coarse-graining, eliminate irrelevant polymer degrees of freedom

Druger et al. (1985); Hilfer and Orbach (1985); Harrison, Zwanzig (1985)



Frozen disorder ($\lambda = 0$):

$$D_0(\omega) = -\frac{\omega^2}{6} \int_0^\infty \mathrm{d}t\, e^{i\omega t} \langle r^2(t) \rangle_0$$

Dynamic disorder ($\lambda \neq 0$):

$$D(\omega, \lambda) = D_0(\omega - i\lambda)$$

Generalization to cases of temporal correlations (Druger et al, 1988):

$\psi(t)$ = waiting time distribution for renewals

$$D = \frac{1}{6} \frac{\int_0^\infty \mathrm{d}t\, \psi(t) \langle r^2(t) \rangle_0}{\int_0^\infty \mathrm{d}t\, \psi(t) t}$$

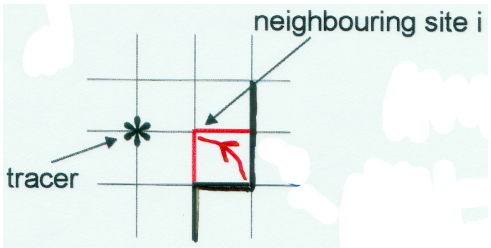
If $\psi(t) \propto e^{-\lambda t}$ (Poisson-process): analytic continuation rule!

Mapping of polymer system onto DP-theory?

Two complementary steps (implementation for athermal lattice chains, Dürr et al. 2002):

i) tracer moves through frozen network $\Rightarrow \langle r^2(t) \rangle_0$

ii) density fluctuations at a site next to a frozen tracer $\Leftrightarrow$ statistics of pathway openings
$\psi(t) \propto \ddot{\Phi}(t)$,
where $\Phi(t)$ = unconditioned prob. of no renewal (opening) within $[0, t]$.
$\Phi(t) = \frac{\langle n(t) n(0) \rangle - c^2}{c(1-c)}$



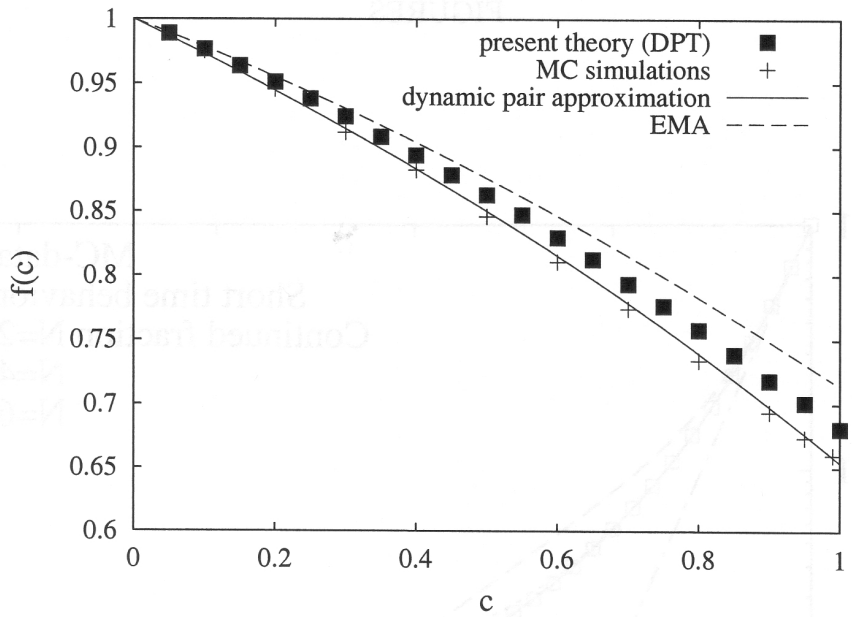
DP-scheme:
Results for athermal lattice chains plus point particles

Diffusion constant of point particles:

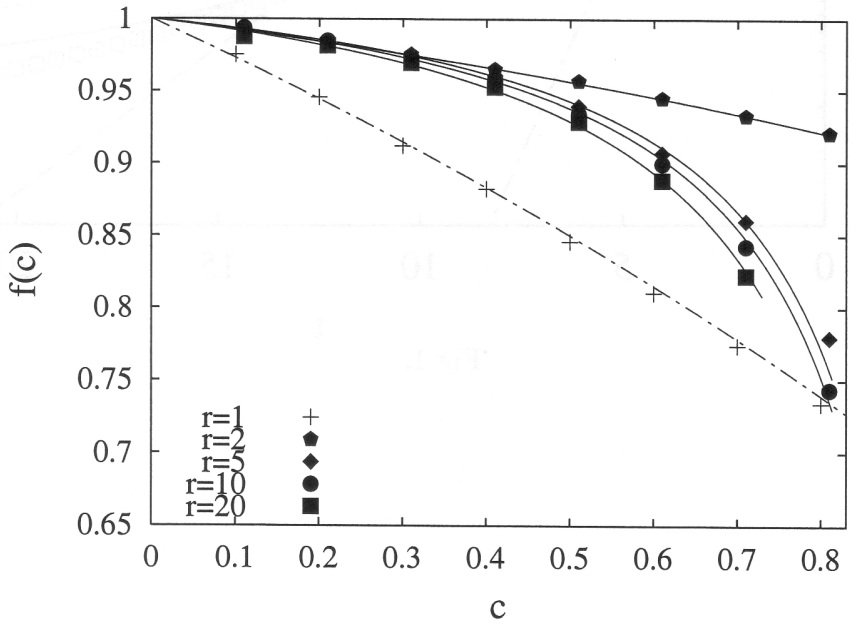
$$D(c) = D_0(1-c)f(c)$$

$f(c)$ = correlation factor

Only point particles:
(hard core lattice gas)



Chains of length $r = 10$



Extension to higher concentration c through “fluctuation site-bond algorithm”: signatures of anomalous tracer diffusion; DP concept only qualitatively valid.

(B. M. Schulz, A. Karatchentsev, M. Schulz, W.D., submitted)

Summary

Glasses

- Mechanism for “constant” dielectric loss response based on dipolar interactions between localized defect centers at random positions.
- Different scenarios, depending on density.
- Note that $V_{\mathrm{dip-dip}} \sim r^{-3}$
  $V_{\mathrm{elastic}} \sim r^{-3}$ could yield similar effects.

Polymers

- Conductivity $\leftrightarrow$ VTF behavior
  VTF temperature $T(x) \nearrow$ as $x \nearrow \Leftarrow$ cross-linking,
  configurational entropy argument.
- Further coarse-graining:
  Mapping of ion diffusion onto dynamic percolation.