SAND2013-6448C

Li^+ transport in organic solvents: a Green-Kubo study

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Funded through the V & V ASC program.

Motivation: Li^+ Batteries

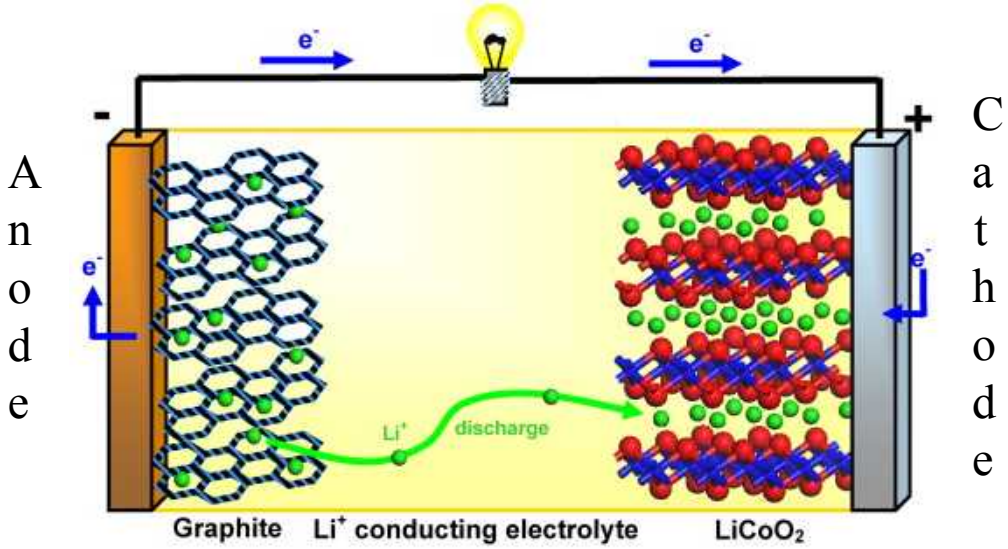


Fig. 1. Schematic representation of a lithium-ion battery. Negative electrode – graphite, positive electrode – $LiCoO_2$, separated by a non-aqueous liquid electrolyte $LiPF_6$ ethylene carbonate/dimethyl carbonate. P.G. Bruce, Solid State Ionics, 179 (2008), pg. 752

- Li+ batteries have become industry standard in personal electronics
- New applications for vehicles and higher energy demand fields
- Electrolytes generally consist of Lithium Salt ($LiBF_4$) and organic solvent (carbonates)
- Transport between anode and cathode can be tuned by electrolyte
- Molecular dynamic (MD) methods can sample a large number of configurations

Transport properties via Green-Kubo

- Technique for calculating macroscopic properties from microscopic properties
- Correlation functions are determined from atom velocities

Fick's law gives

$$J = -D\nabla c$$

Continuity requires

$$\frac{\partial c}{\partial t} + \nabla \cdot J = 0$$

Substitution gives

$$\frac{\partial c(r,t)}{\partial t} = D\nabla^2 c(r,t)$$

Einstein's Derivation (do some math: *r^2 and integrate)

$$\frac{\partial}{\partial t}\int d\vec{r} r^2 c(r,t) = 2dD$$

Transport properties via Green-Kubo

$$\frac{\partial}{\partial t}\int d\vec{r} r^2 c(r,t) = 2dD$$

LHS is average of r^2

$$\frac{\partial}{\partial t}\left\langle r^2(t)\right\rangle = 2dD$$

Or for atomistics

$$\frac{\partial}{\partial t}\left\langle \Delta x(t)^2\right\rangle = 2dD$$

Displacements as velocities

$$\Delta x(t)^2 = \int_0^t dt' v_x(t')$$

Make substitutions and adjust time integrals (left for you!)

$$D = \int_0^\infty d\tau \left\langle v_x(\tau) v_x(0)\right\rangle$$

Transport properties via Green-Kubo

Viscosity

$$\eta = \frac{1}{Vk_BT}\int_0^\infty dt\left\langle \sigma_{xy}(t)\sigma_{xy}(0)\right\rangle$$

Thermal Conductivity

$$\lambda_T = \frac{1}{Vk_BT}\int_0^\infty dt\left\langle j_z^e(t)j_z^e(0)\right\rangle$$

Electrical Conductivity

$$\sigma_e = \frac{1}{Vk_BT}\int_0^\infty dt\left\langle j_x^{el}(t)j_x^{el}(0)\right\rangle$$

CHARMM Potential

$$V = E_b + E_a + E_d + E_i + E_{nb}$$

$$E_b = \sum_{bonds} k_b (b - b_0)^2$$

$$E_a = \sum_{angles} k_\theta (\theta - \theta_0)^2$$

$$E_d = \sum_{dihedrals} k_\varphi [1 + \cos(n\varphi - \delta)]$$

$$E_i = \sum_{impropers} k_\omega (\omega - \omega_0)^2$$

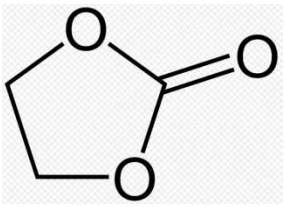
$$E_{nb} = \sum_{nonbonded} \varepsilon_1 \left[\left(\frac{R_{\min ij}}{r_{ij}} \right)^{12} - \left(\frac{R_{\min ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{\varepsilon_2 r_{ij}}$$

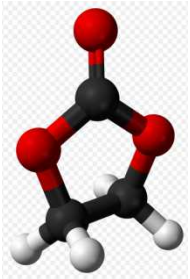
2 cases

a) Flexible carbonates

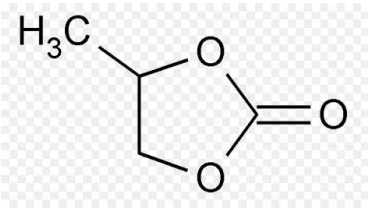
b) Rigid carbonates

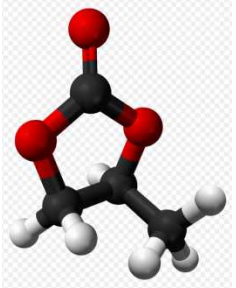
Ethylene Carbonate (EC)



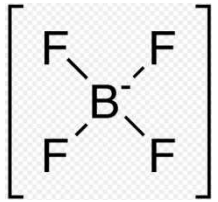


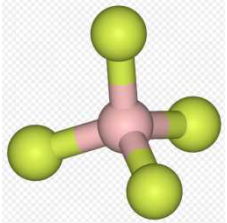
Propylene Carbonate (PC)



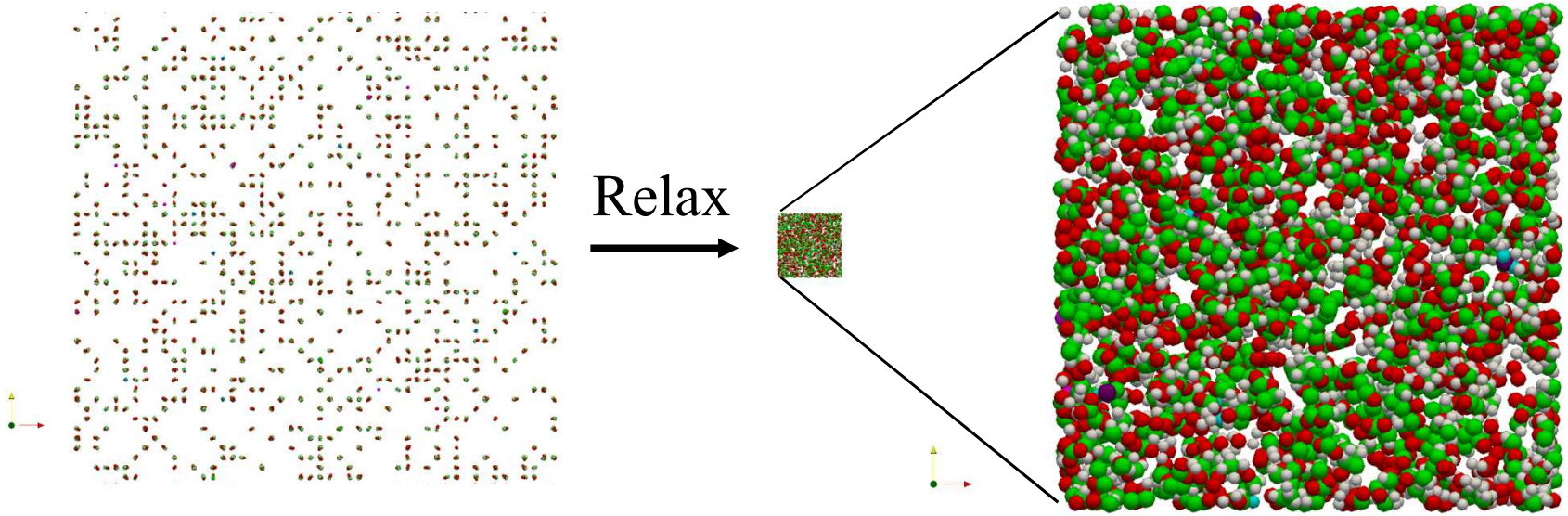


Tetrafluoraborate (BF_4)





Initial configuration



- 3 step initialization process
  - Create sparse distribution of Carbs and separated salts
  - NVE/limit to ensure no atom ejections
  - Relax to desired temperature/pressure for ~0.5 ns

Simulations

- All configurations: ~0.1 M (10 Li^+/1000 carbonates)
- 3 Different carbonate compositions
  - 100% EC
  - 100% PC
  - 50/50 EC/PC (by mass)
- Range of temperatures from 300-500K
- Rigid/flexible molecules
- High pressure and low pressure

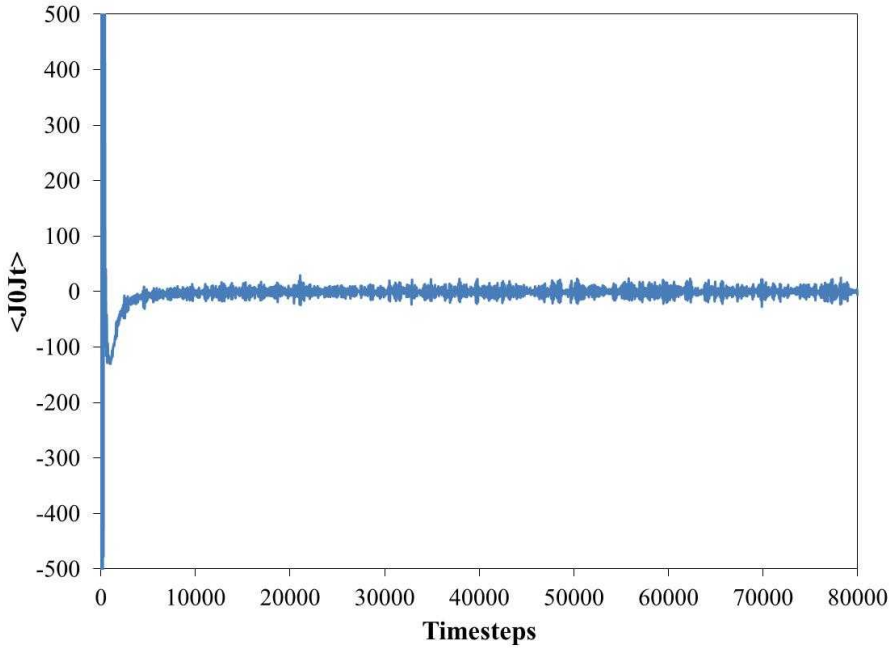
fix ave/correlate command

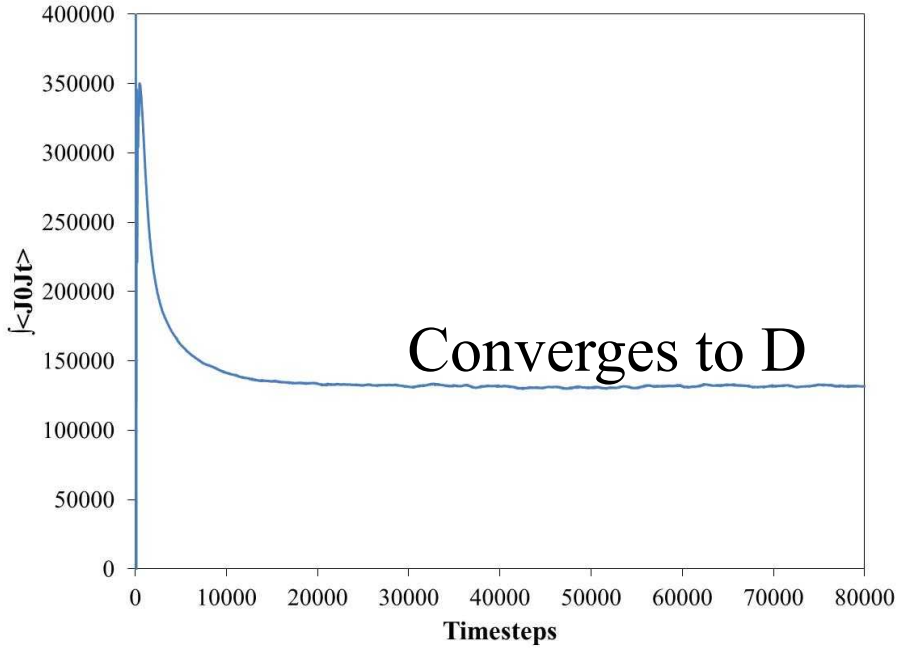
Fix ID group-ID ave/correlate Nevery Nrepeat Nfreq value1 value2 ... Keyword args …

- ID, group-ID are dcumented in fix command
- ave/correlate = style name of this fix command
- Nevery = use input values every this many timestep
- Nrepeat = # of correlation time windows to accumulate
- Nfreq = calculate time window averages every this many timesteps
- One or more input values can be listed
- Value = c_ID, c_ID[N], f_ID, f_ID[N], v_name
- Zero or more keywords/arg pairs may be appended
- Keyword = *type* or *ave* or *start* or *prefactor* or *file* or *overwrite* or *title1* or *title2* or *title3*

fix J0Jt_Li Li ave/correlate 10 8000 10000000 c_J_Li[1] type auto/upper file J0Jt_Li.dat ave running

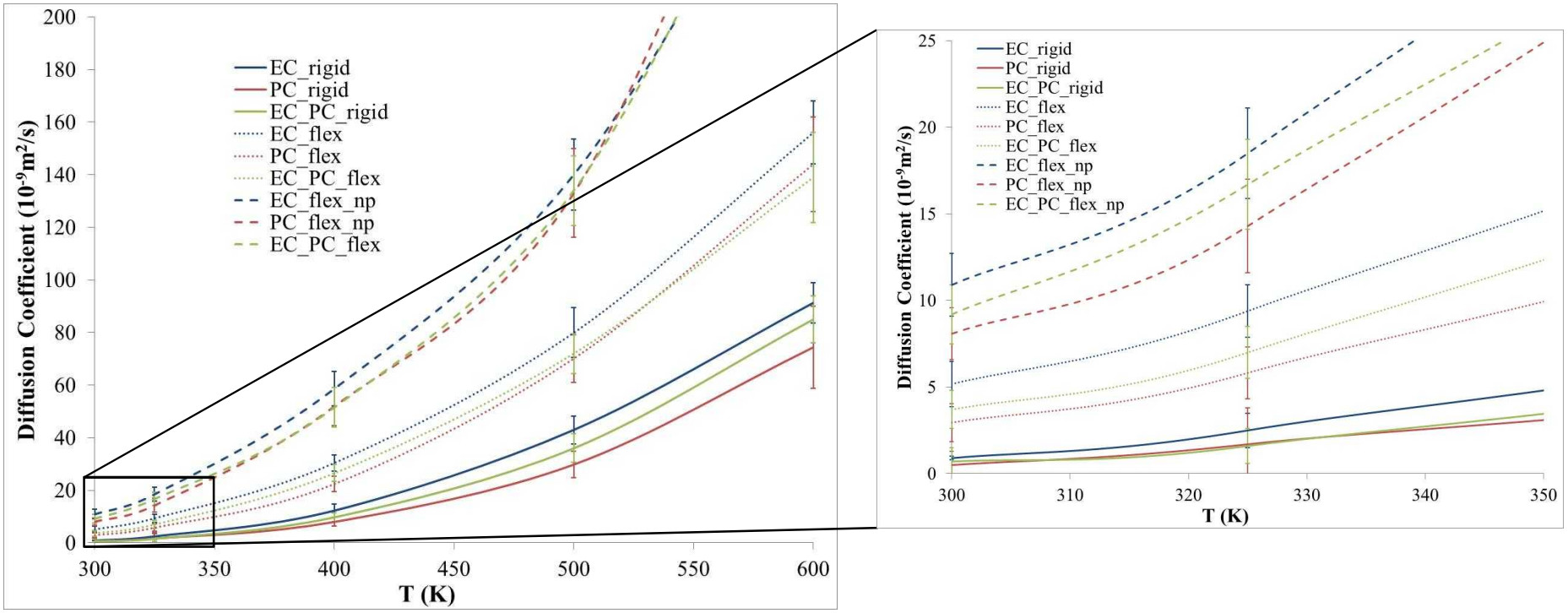
Correlation Functions





- Each correlation is the average of 10 different initial configurations
- Also averaged over the 3-dimensions due to homogeneity

Diffusion Coefficients



- Large discrepancies between potential times
- EC tends to have higher diffusion coefficient
- Problems around T_g of potentials

Model vs. Experiment

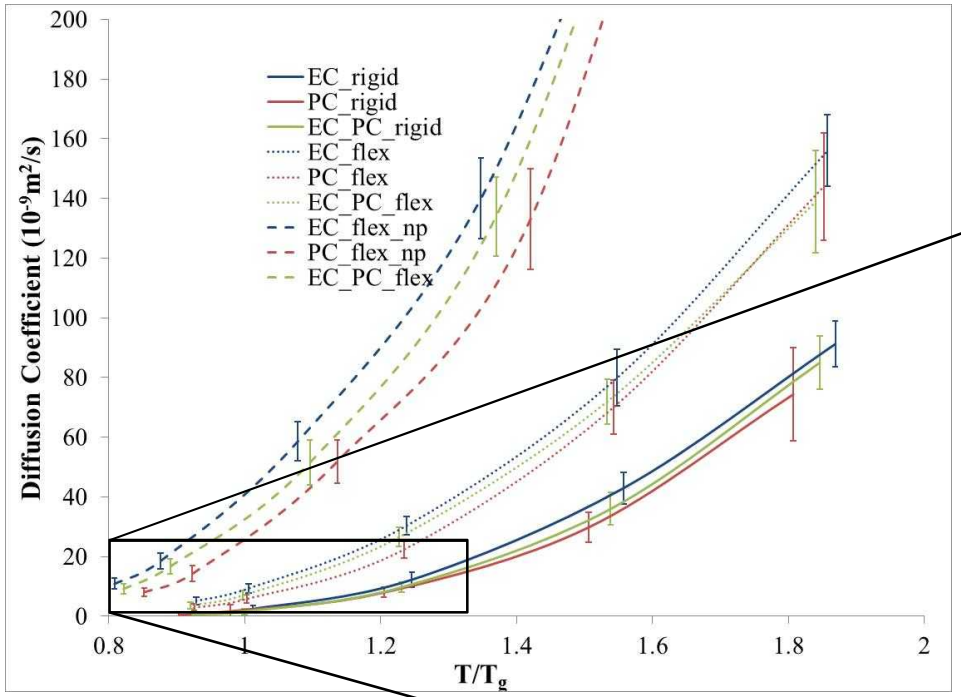
	Rigid	Flex	Flex (np)	Exp.
EC Density (g/cm^3)	1.36	1.28	1.23	1.32
T_g (K)	321	323	371	310
Li^+ diff @ 300K ($10^{-10}m^2/s$)	0.9	5.2	10.9	NA
PC Density (g/cm^3)	1.27	1.22	1.15	1.20
T_g (K)	332	324	352	225
Li^+ diff @ 300K($10^{-10}m^2/s$)	0.5	3.0	8.1	0.2

- None of the potentials studied capture both EC and PC properties.
- Rigid potential does a good job representing EC but misses the very important component of differing T_g.

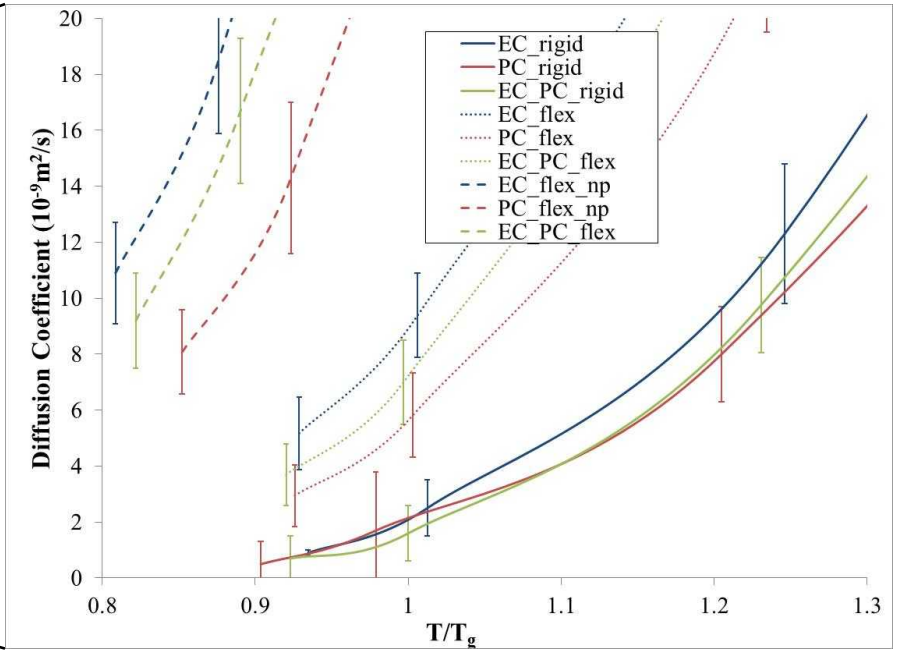
Summary

- Green-Kubo techniques are a method for extracting macroscopic transport properties from microscopic quantities.
- "fix ave/correlate" can be used to determine the correlation functions necessary for Green-Kubo calculations
- Performed simulations on different configurations of EC/PC electrolytes with $LiBF_4$.
- Potentials examined do not sufficiently distinguish between EC and PC.
- Rigid potential does a reasonable job of predicting properties.

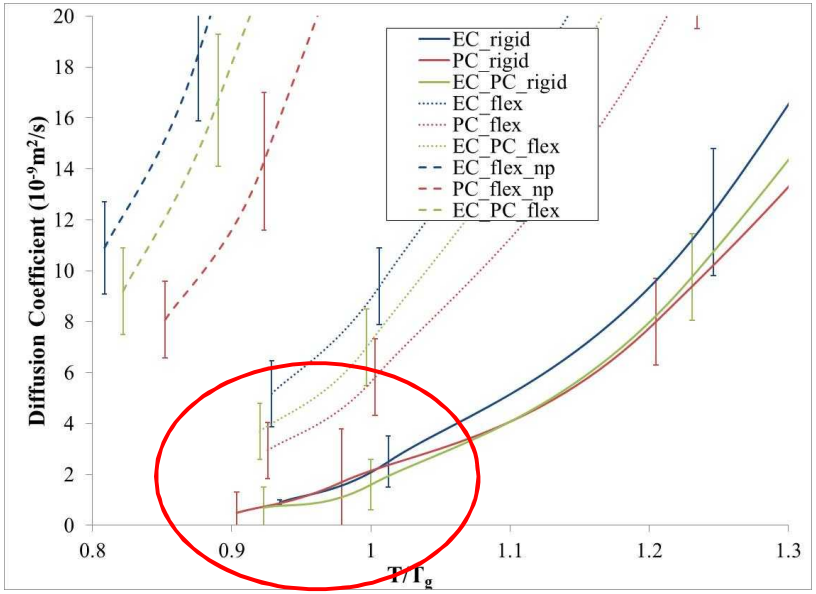
Diffusion Coefficients



EC solvents have higher diffusion coefficients



Large discrepancies between potential times



- Generally EC has higher D than other compositions
- Rigid molecules actually have D nearest to