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Simulations of Coarse-Grained Ionomer Melts in an External Electric Field

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Abstract

Ionomers are polymers that contain both electrically neutral and charged chemical groups, and are being investigated as potential solid electrolytes in batteries. Our group has been investigating structure and dynamics in ionomer melts using molecular dynamics simulations. The overall goal is to understand the relationships among polymer architecture, ionic aggregate morphologies, and ion dynamics. Here we apply an external electric field to coarse-grained models of ionomer melts, which have ionic groups placed either in or pendant to the polymer backbone. In the linear response regime, the field does not affect ionic aggregate morphologies but does affect ion dynamics. The applied field allows us to calculate the ion mobilities and hence the conductivity. A comparison of the conductivity with that calculated by the Nernst-Einstein relation reveals a significant amount of ionic correlation.

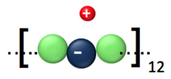
System

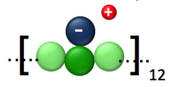
Coarse-grained MD simulations

charged groups in the backbone: "ionene"

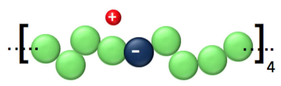
charged groups pendant to the backbone: "pendant"

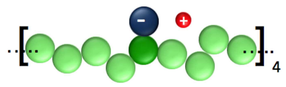
N_{bb} = 3





N_{bb} = 9

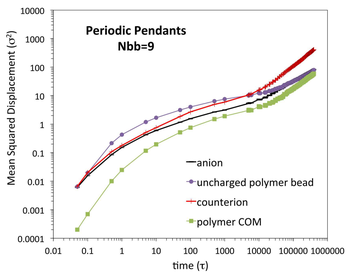




repulsive LJ interactions
+ FENE bonds
+ coulomb interactions: $U(r) = \frac{q_1 q_2}{4\pi\epsilon_0\epsilon r}$
+ Langevin thermostat

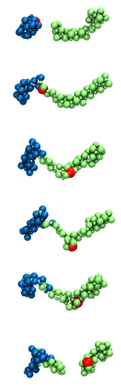
Simulation details:
800 polymers
100% neutralization
bulk dielectric constant = 4
counterion size = 0.5σ
Bjerrum length = 35.7σ

Ion Dynamics



ions move by cluster rearrangment/ collision

time

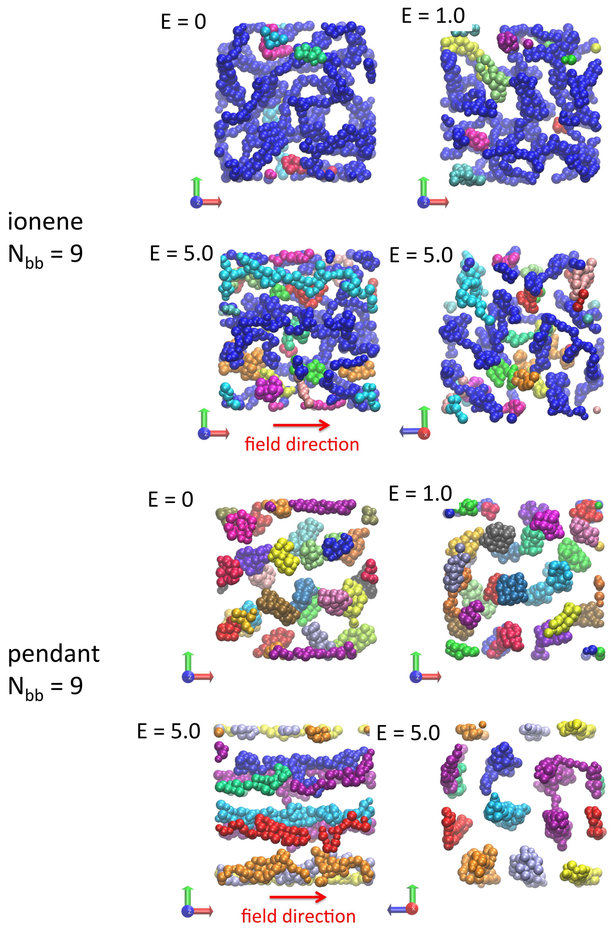


Hall et al., *Macromolecules*, **45**, 8097 (2012)

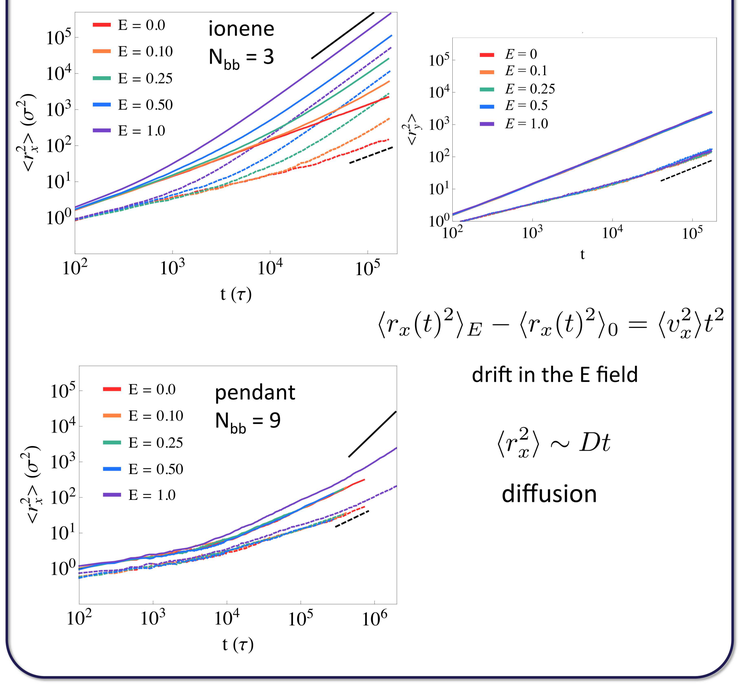
External Electric Field

add force $F_x = qE_x$ to each atom

Aggregate morphologies



MSDs



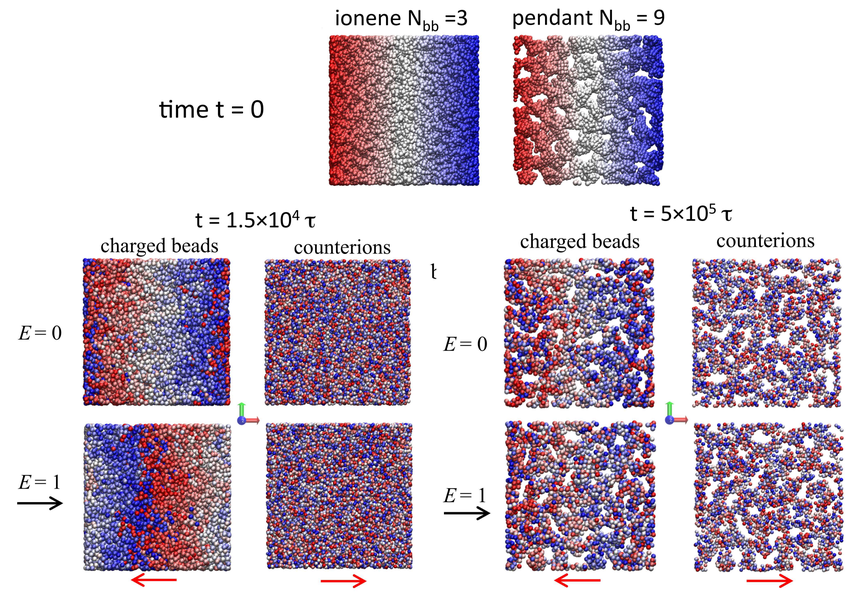
$$\langle r_x(t)^2\rangle_E - \langle r_x(t)^2\rangle_0 = \langle v_x^2\rangle t^2$$

drift in the E field

$$\langle r_x^2\rangle \sim Dt$$

diffusion

Ion Motion in the Field



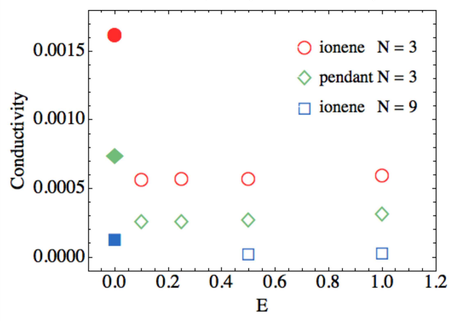
Collective Properties

Nernst-Einstein

$$\lambda^{NE} = \rho e^2(D_{cb} + D_{ci})$$

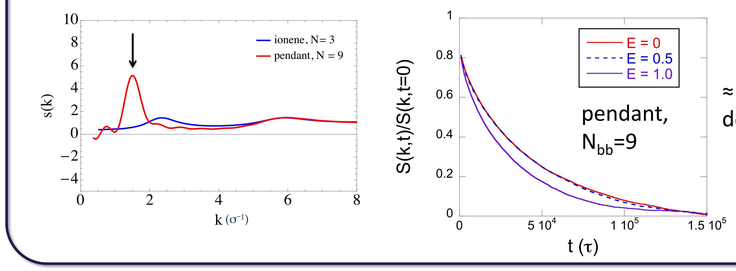
conductivity in field

$$\mu = \langle v_x\rangle / E \qquad \lambda = \rho e(\mu_{ci} - \mu_{cb})$$



system	$\alpha = \lambda/\lambda^{NE}$
ionene N = 3	0.35
ionene N = 9	0.15
pendant N = 3	0.37

dynamic structure factor for counterions



≈ exponential decay

Conclusions

- field does not affect structure in linear response regime
- field speeds up ion motion
- cation, anion motions are correlated

C. L. Ting, M. J. Stevens, and A. L. Frischknecht, manuscript in preparation

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