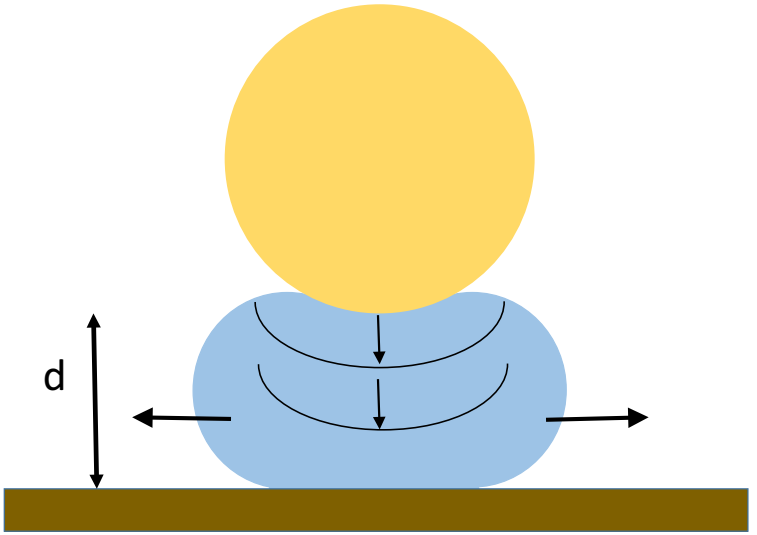
International School for Advanced Studies
(SISSA) Italy

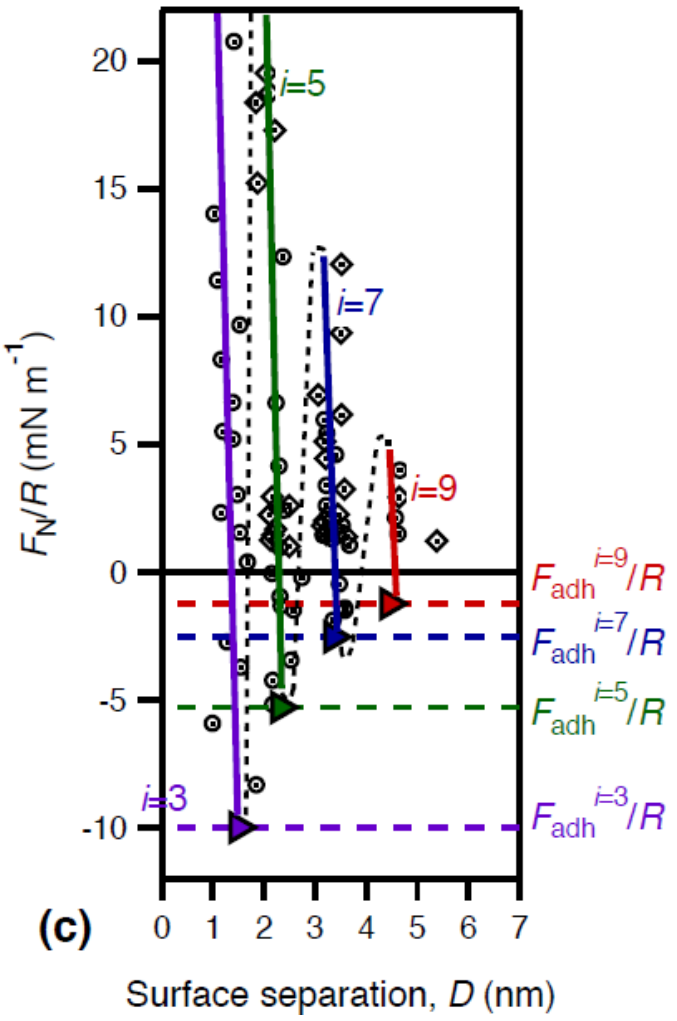
ISTITUTO ITALIANO
DI TECNOLOGIA

Layering, glass formation and entropy evolution during squeezout of a model confined ionic liquid

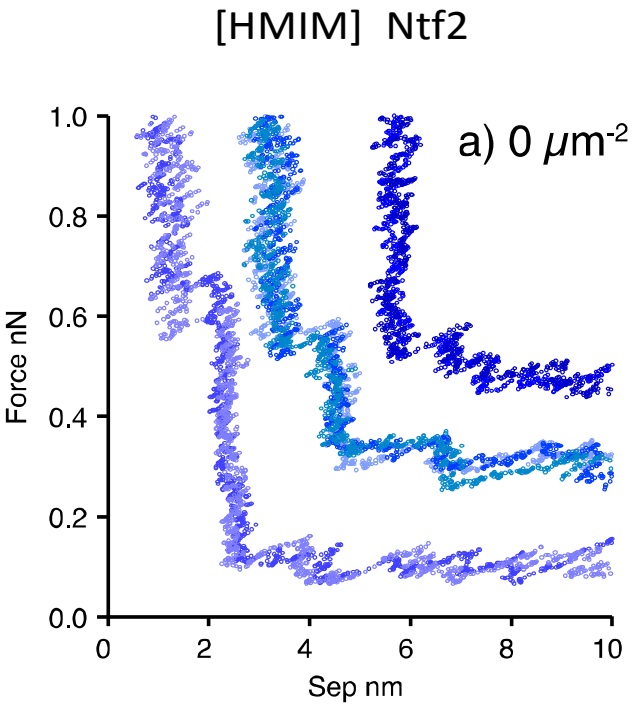


R. Capozza & E. Tosatti

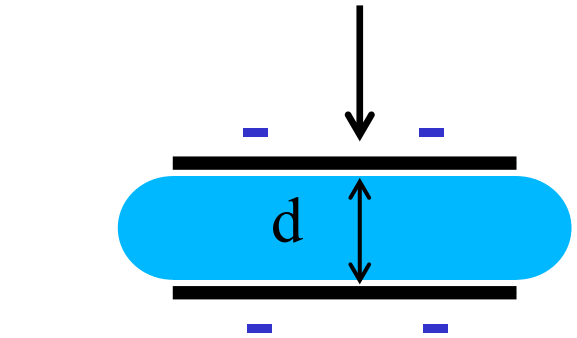
Ionic liquids squeeze out by neutral bilayer

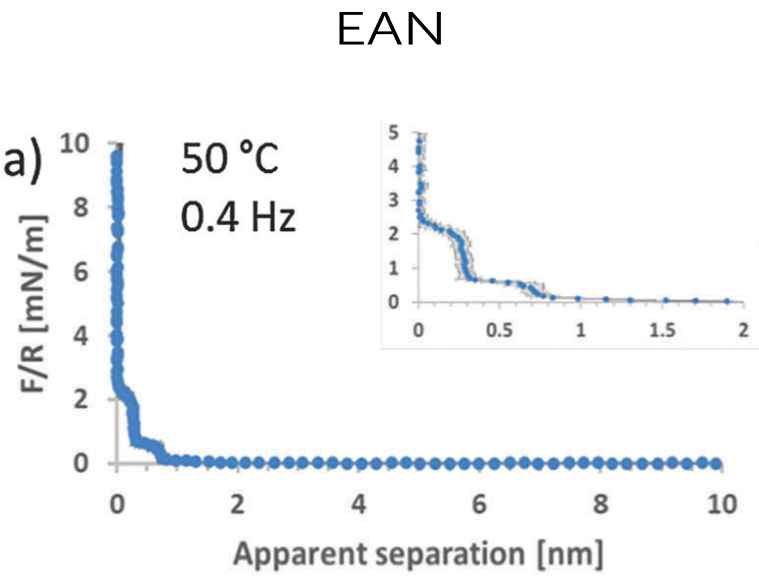


Smith et al. (2016)



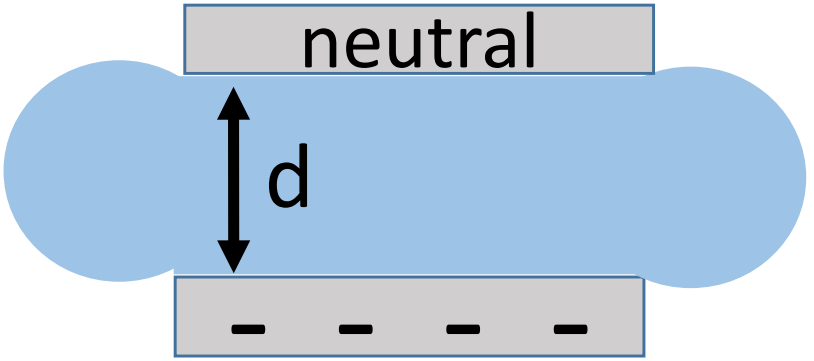
Sheehan et al. (2016)

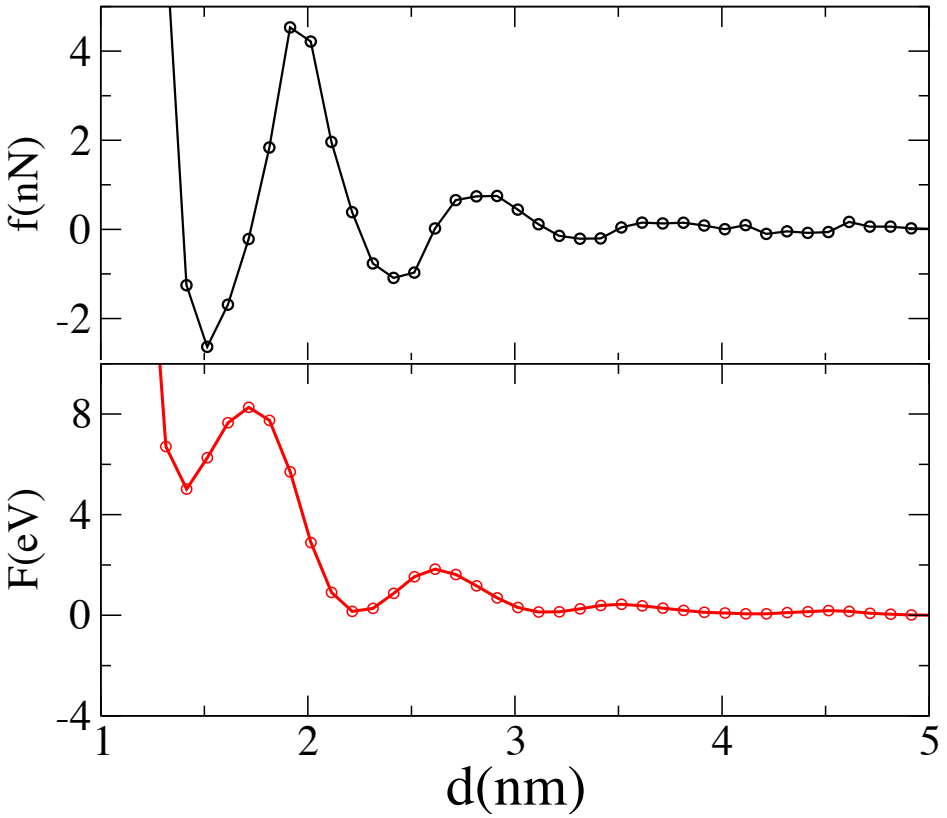




N. Hjalmarsson et al. (2016)

Ionic liquids squeeze out: free energy

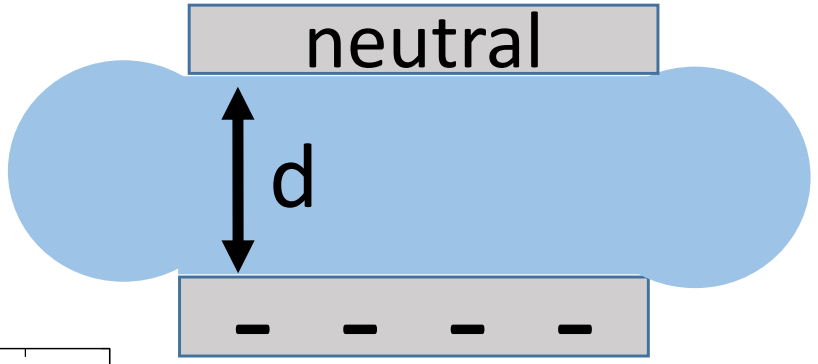


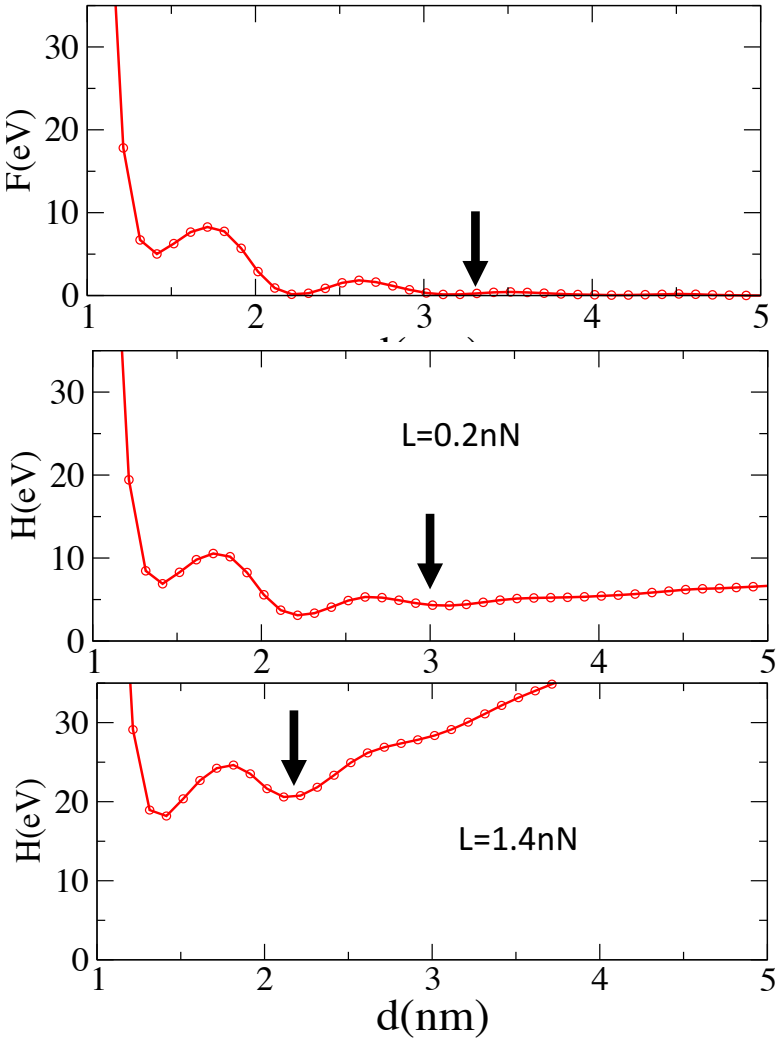


$f(d)$ **Interplate force**

$$F(d) = \int_{\infty}^{d} f(z)\, dz$$ **Free energy**

Ionic liquids squeeze out: enthalpy



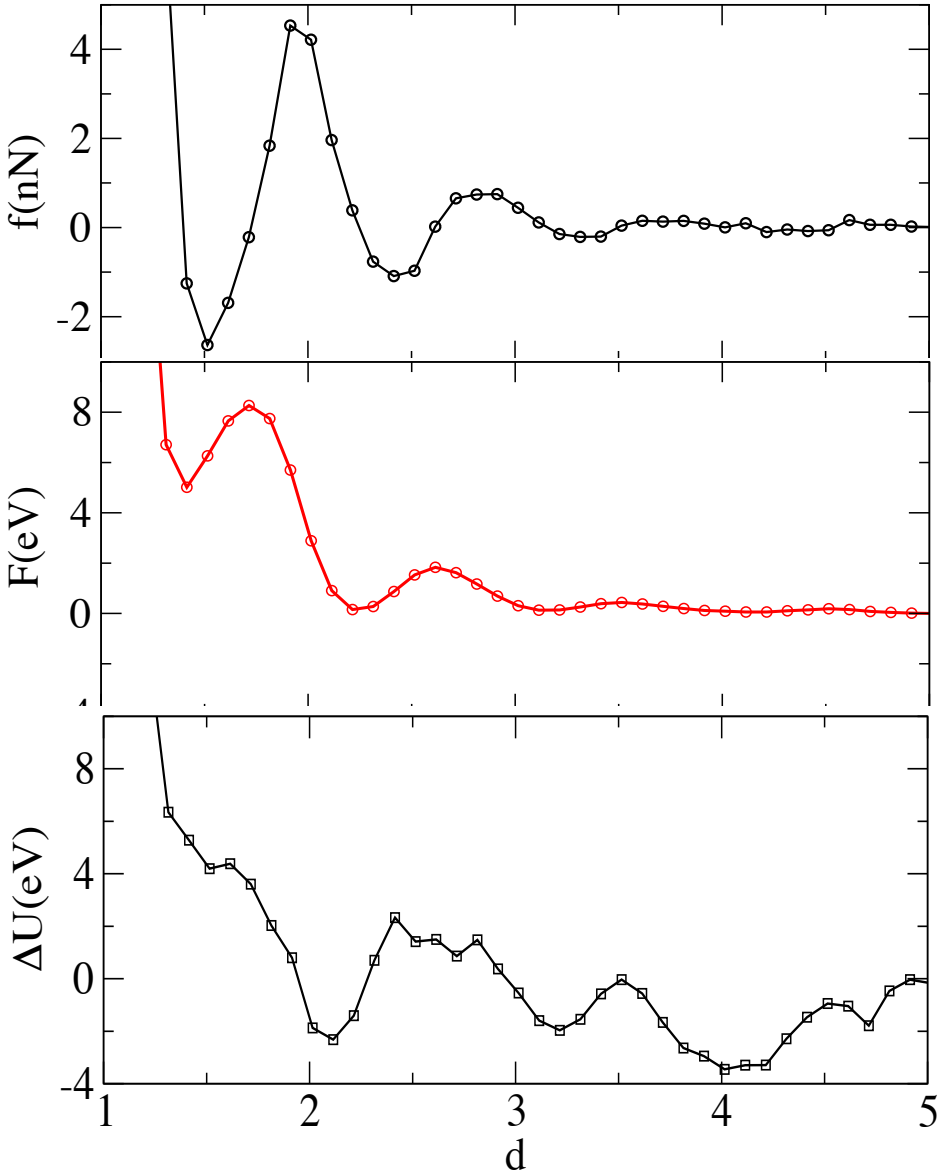


$$H(d) = F(d) + L\,d$$ **Enthalpy**

Load induced jumps

Equilibrium thermodynamics

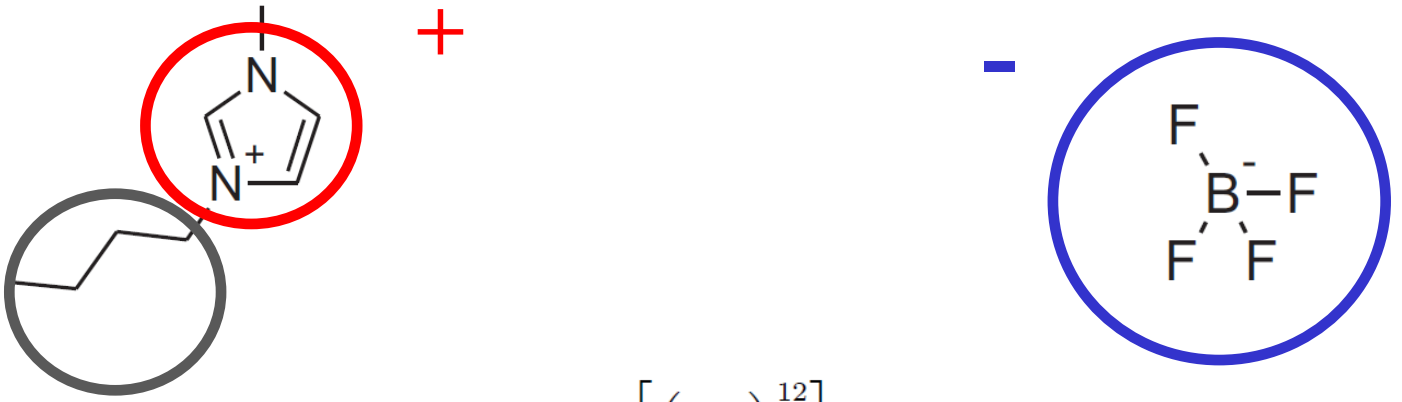
$$F(d) = \Delta U(d) - T\Delta S(d)$$



Which role plays the **entropy**?...simulations

Coarse grained model of IL

TM “tailed” model (Capozza et al. 2015)

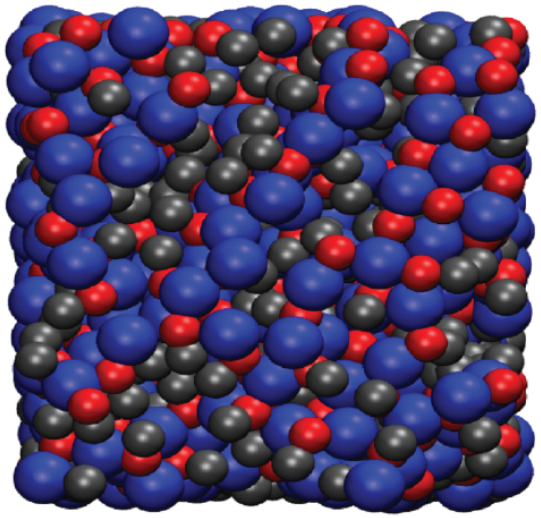


$$V^T(r_{lT}) = 4\epsilon_{lT}\left[\left(\frac{\sigma_{lT}}{r_{lT}}\right)^{12}\right]$$

$$V(r_{ij}) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{e_i e_j}{4\pi\epsilon_0\epsilon_r r_{ij}}$$

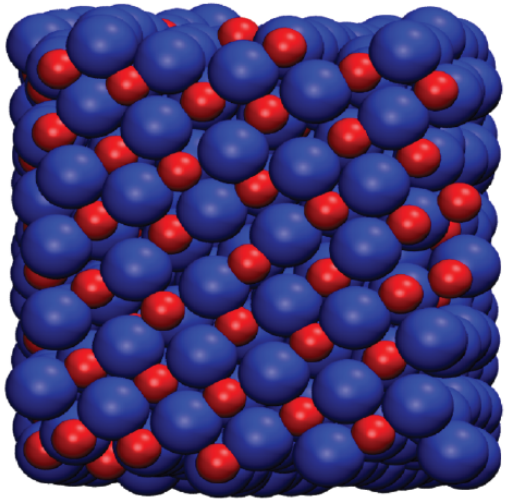
Bulk melting and solidification

TM model



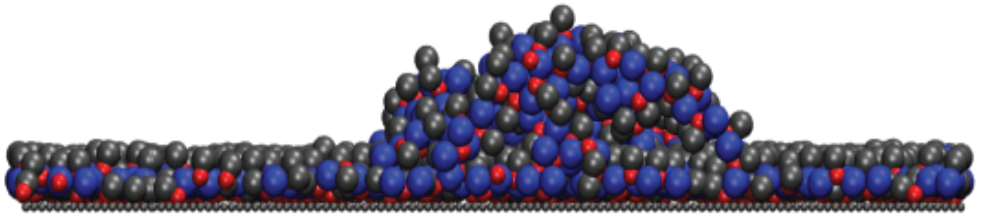
$T<T_m$

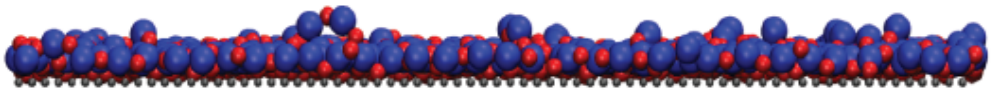
SM model



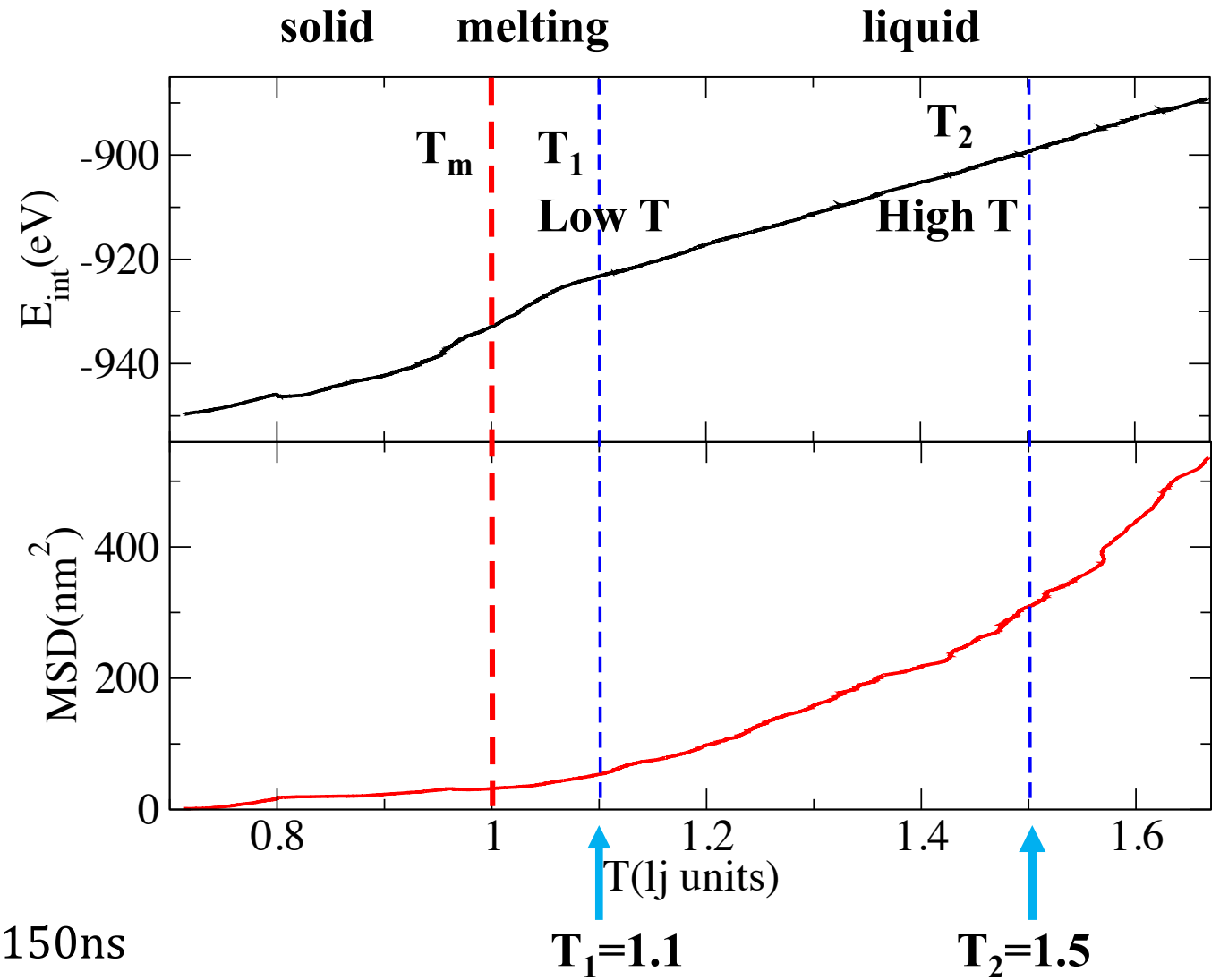
$T<T_m$

Wetting Behavior





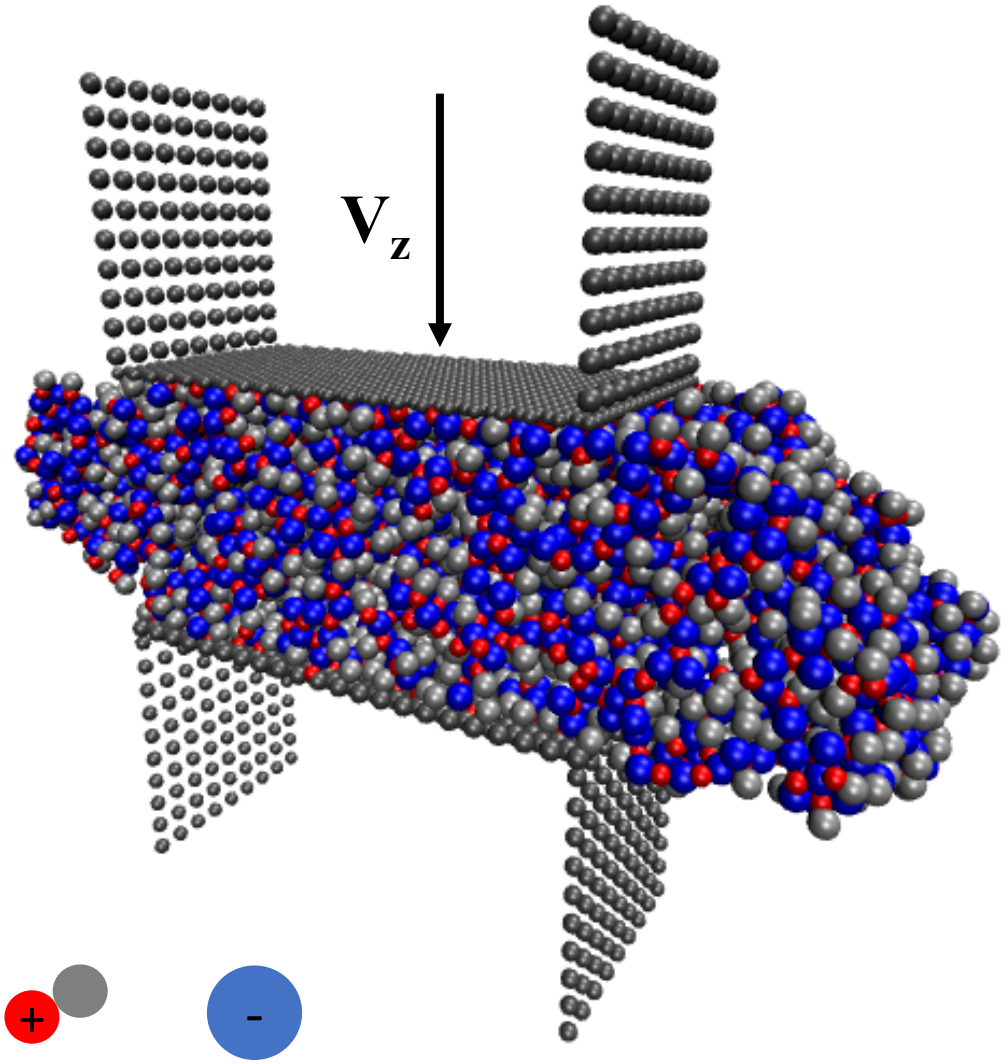
Tailed model melting point by bulk simulations



$\Delta t \sim 150ns$

$T = a\,t$

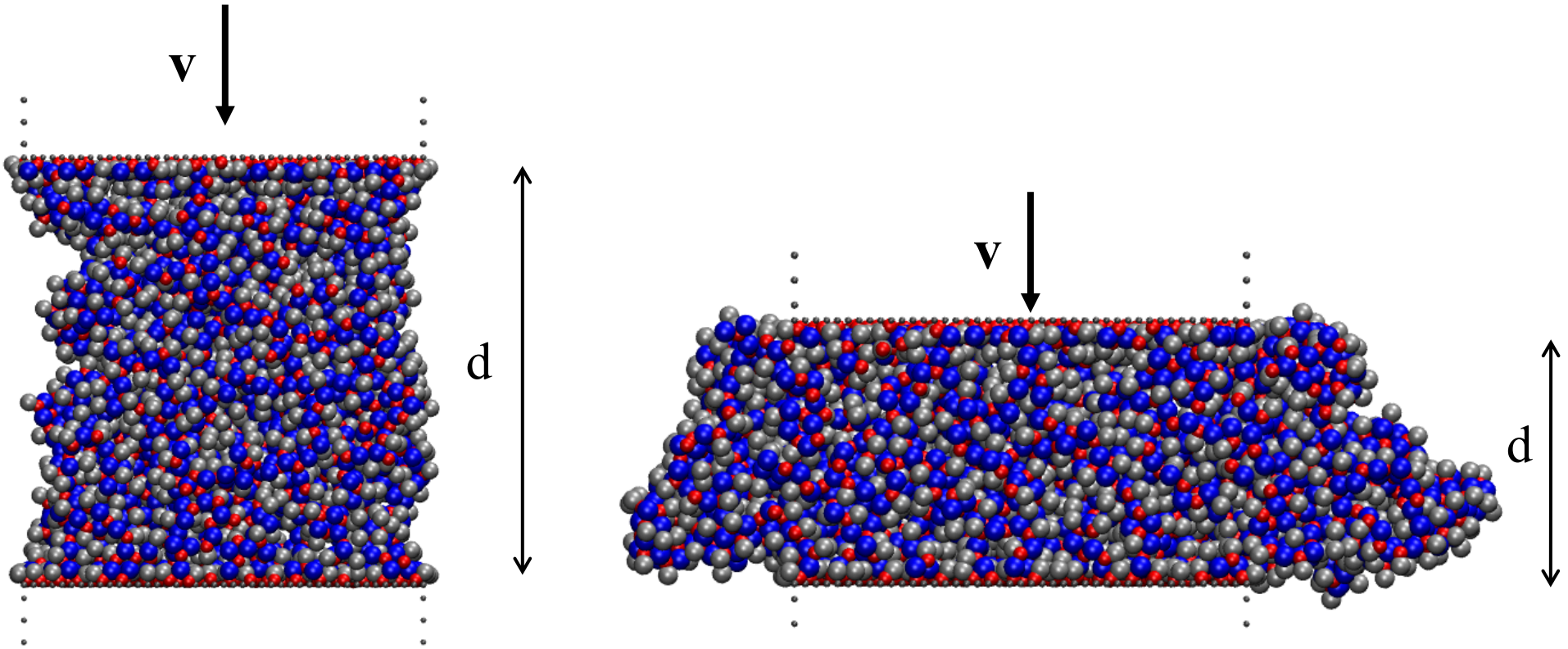
Squeezout simulations



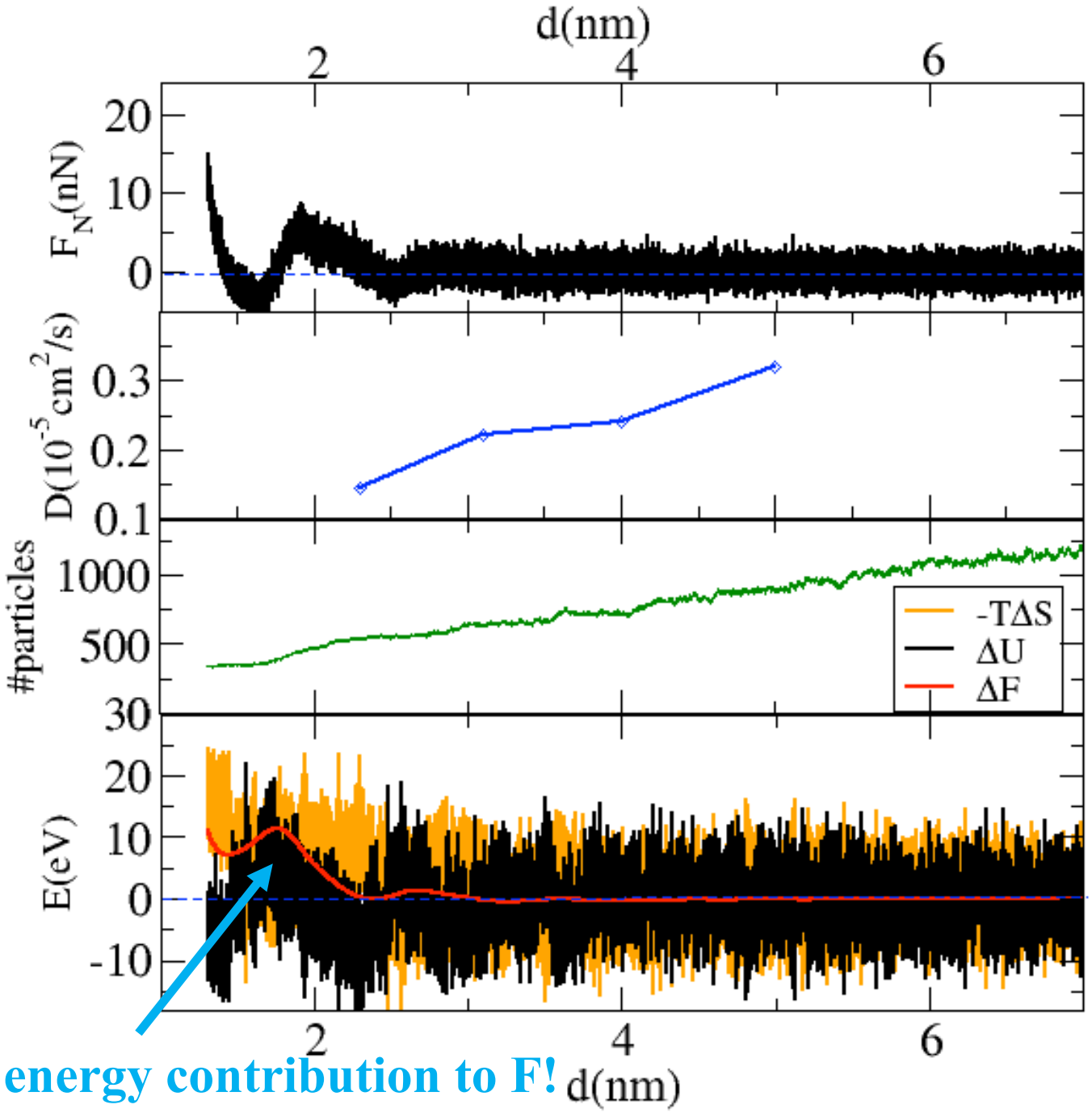
- Mica geometry for plates
- Open boundary conditions
- Negative charge on bottom plate
- Top plate neutral/weakly charge

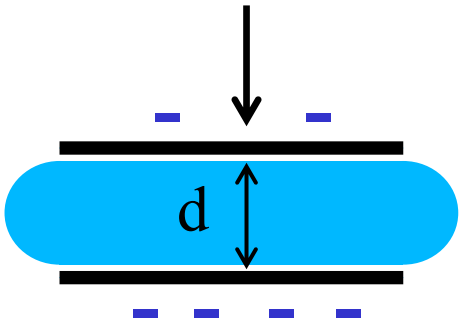
Lateral reservoir

Squeezout simulations – v=3cm/s



High T=1.5 simulation data – v=3cm/s

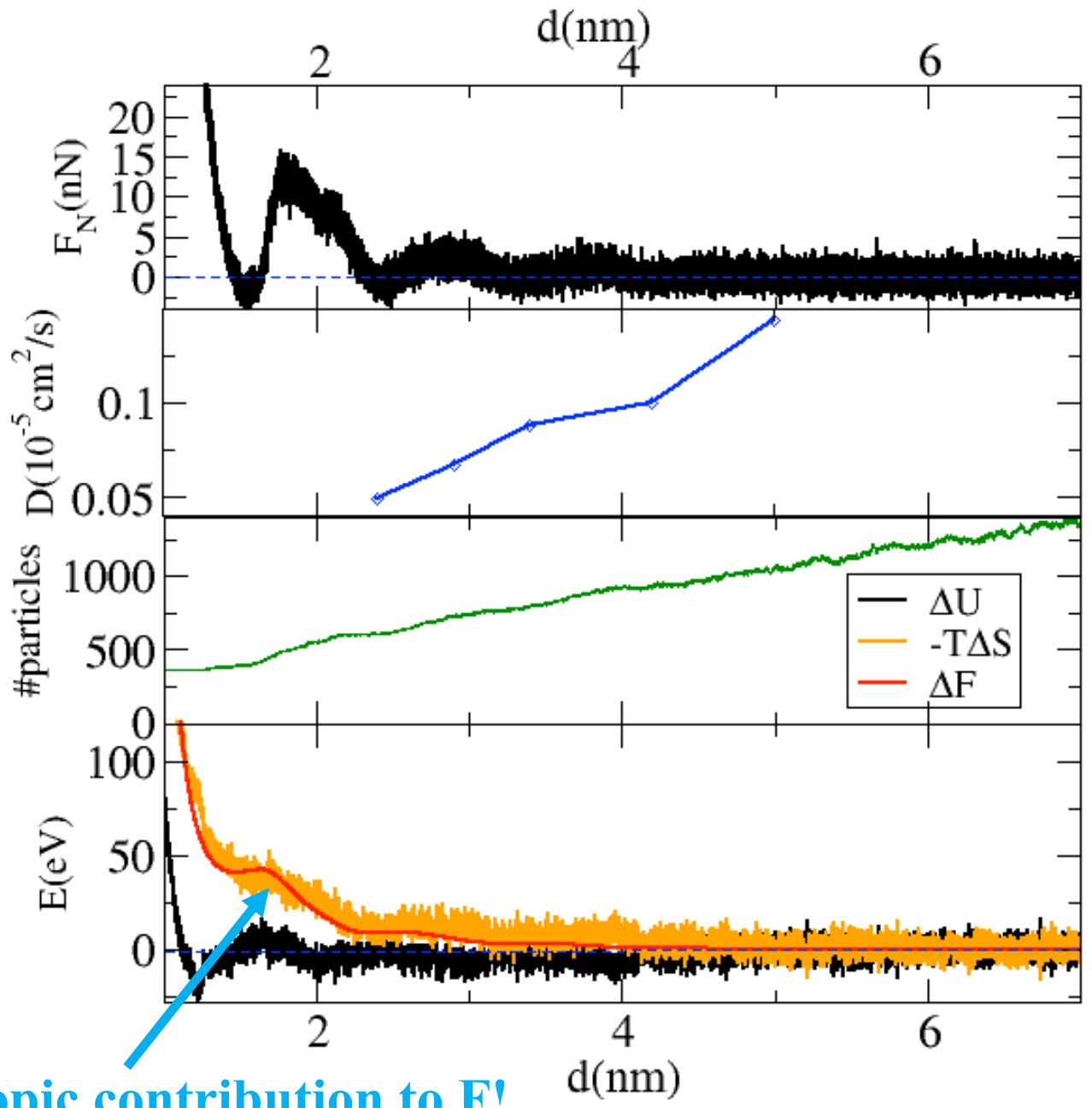


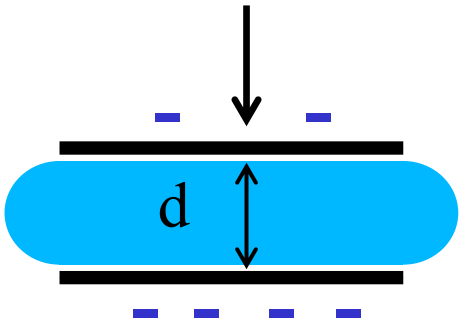


$$F(d) = \Delta U(d) - T\Delta S(d)$$

Int. energy contribution to F!

Low T=1.1 simulation data – v=3cm/s



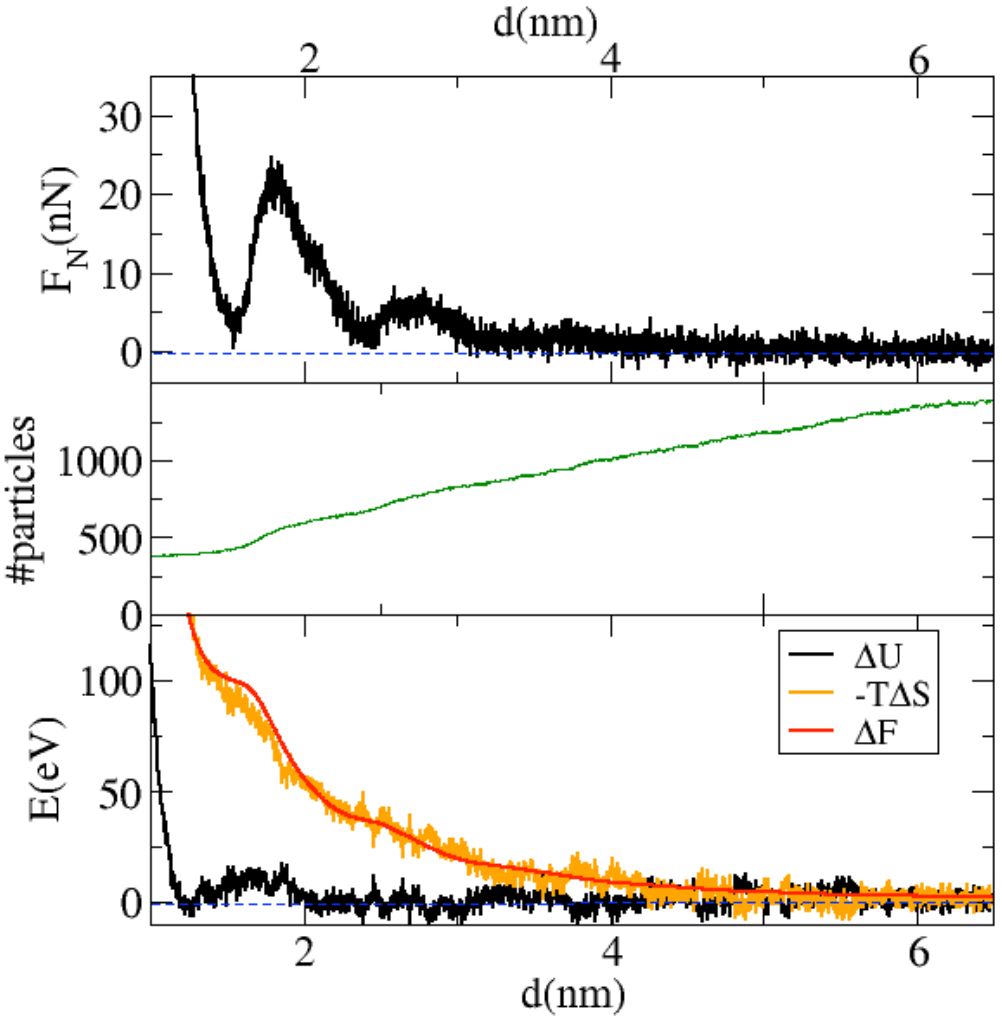


$$F(d) = \Delta U(d) - T\Delta S(d)$$

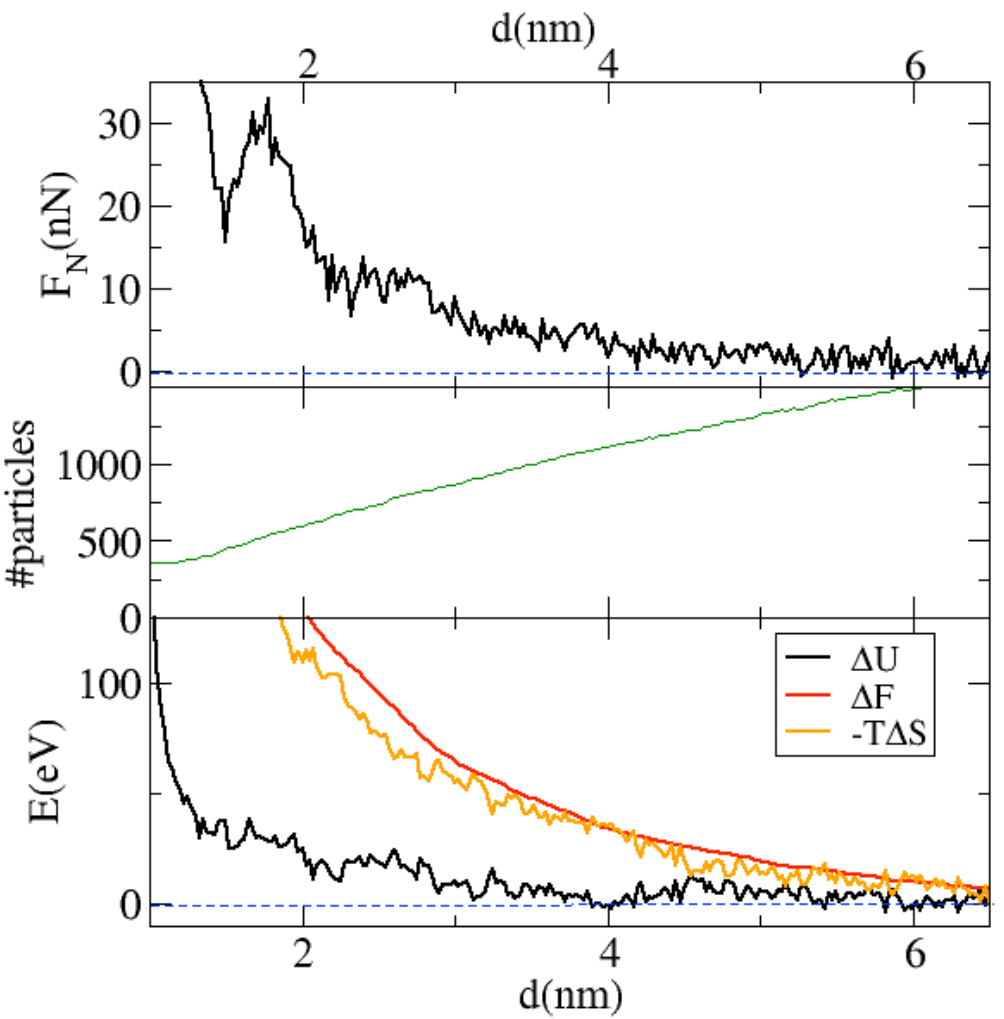
Entropic contribution to F!

Velocity dependence – T=1.1

v=30cm/s

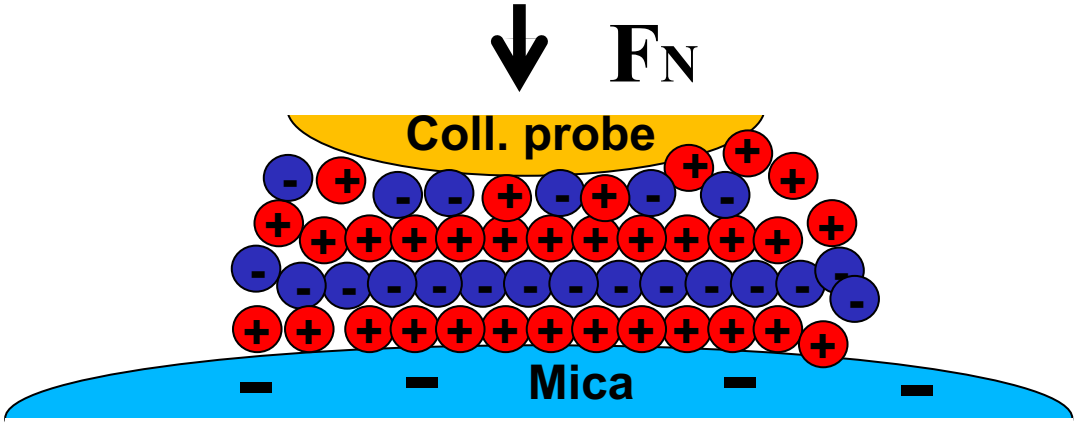


v=300cm/s

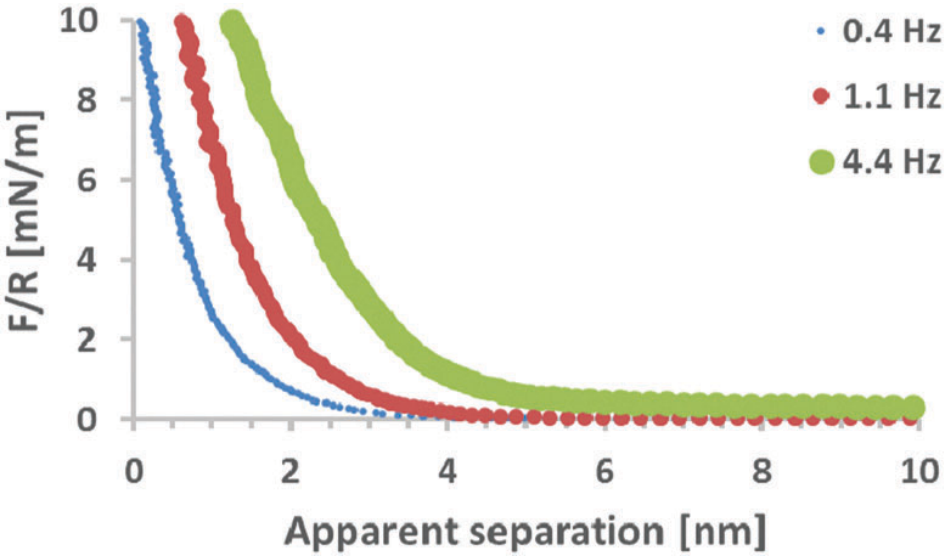


Longer repulsion at low T

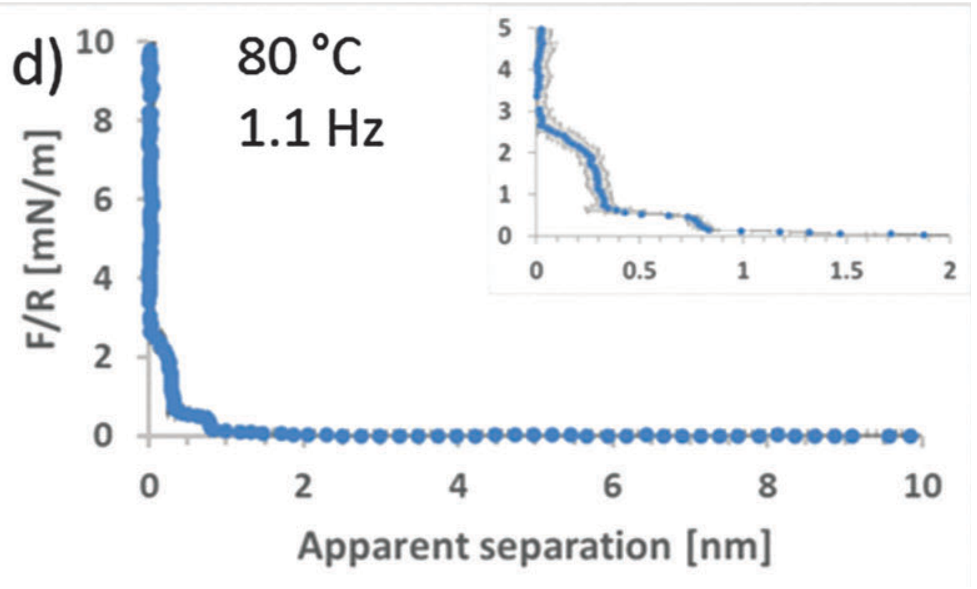
Ionic liquids squeeze out



T= 25^0 C



T= 80^0 C

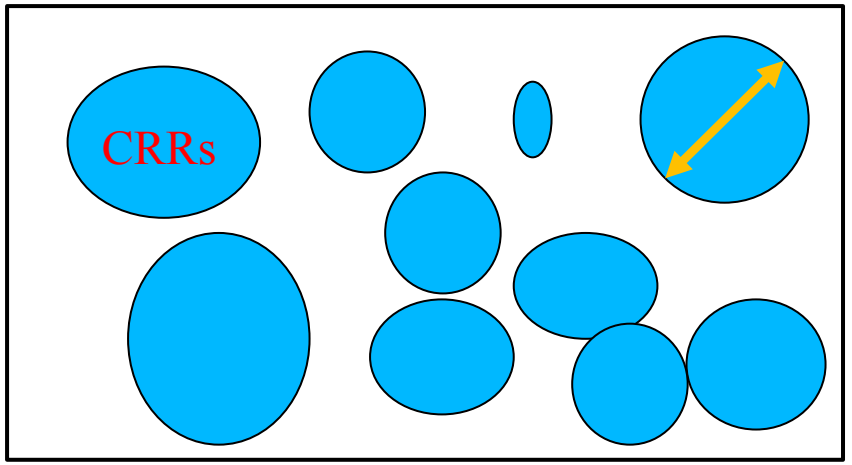


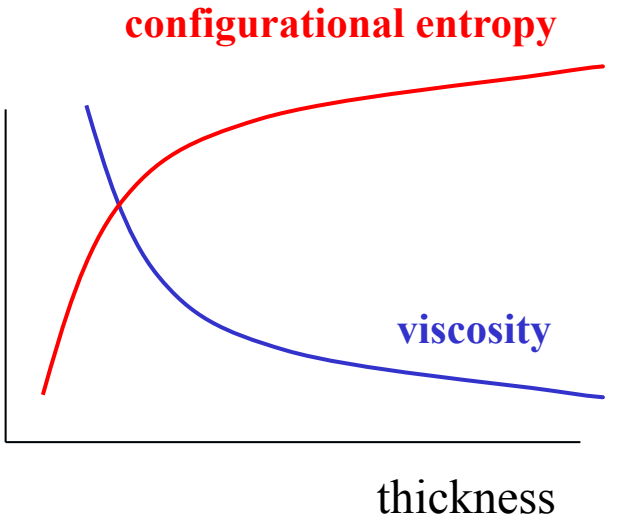
N. Hjalmarsson et al.,Phys. Chem. Chem. Phys., 2016, 18, 9232--9239

Adam-Gibbs

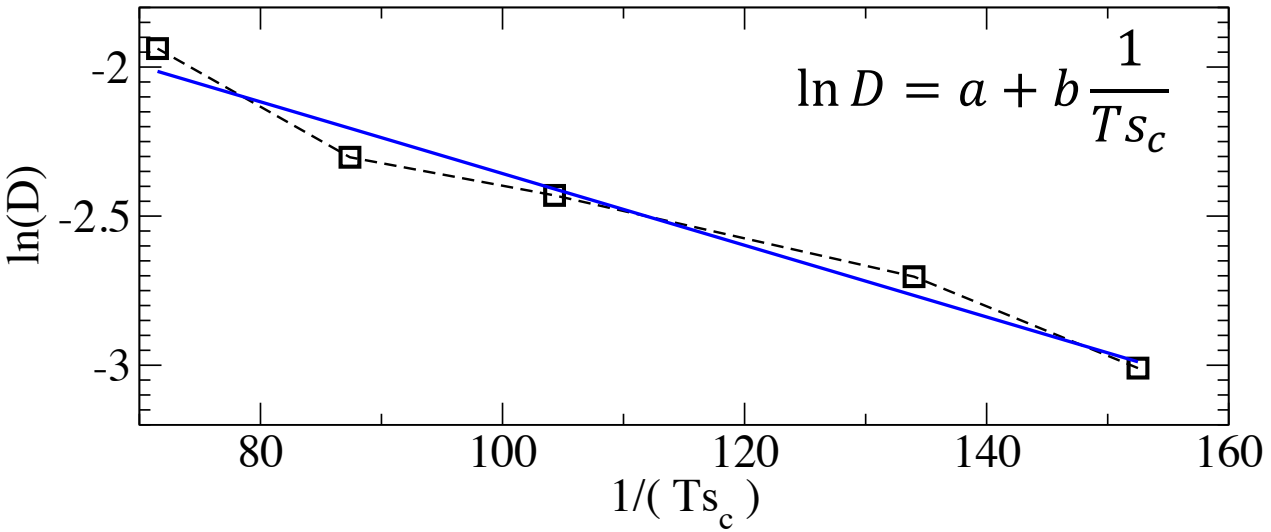
$$\eta = \eta_0 \exp(C/Ts_c)$$

"Cooperatively rearranging regions"





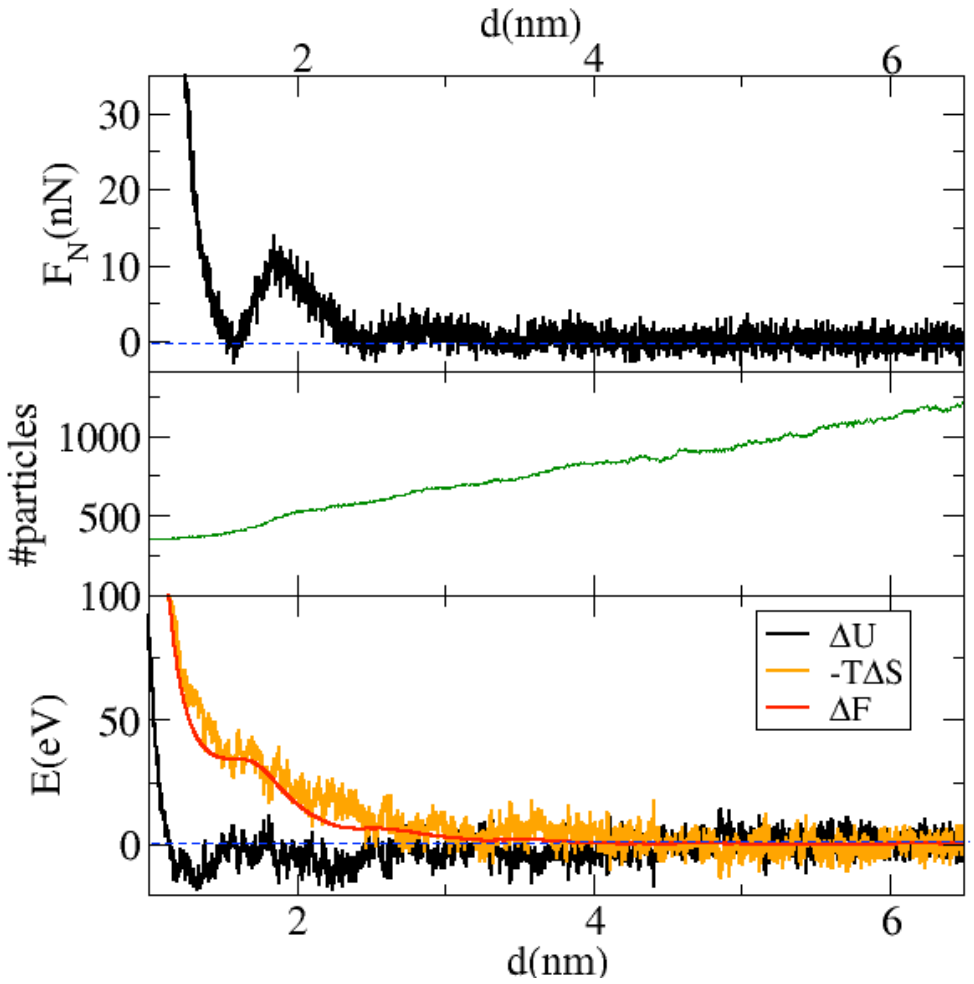
T=1.1, v=3cm/s



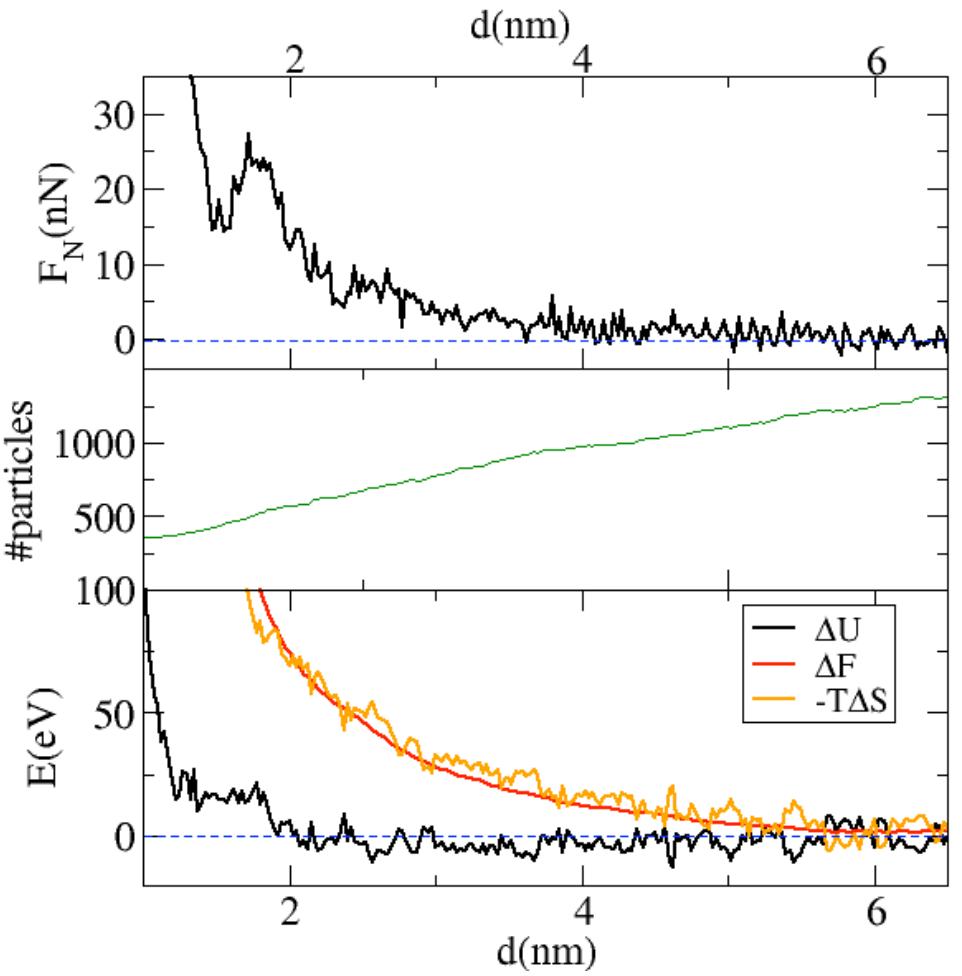
Confinement induced glass!

Velocity dependence – T=1.5

v=30cm/s



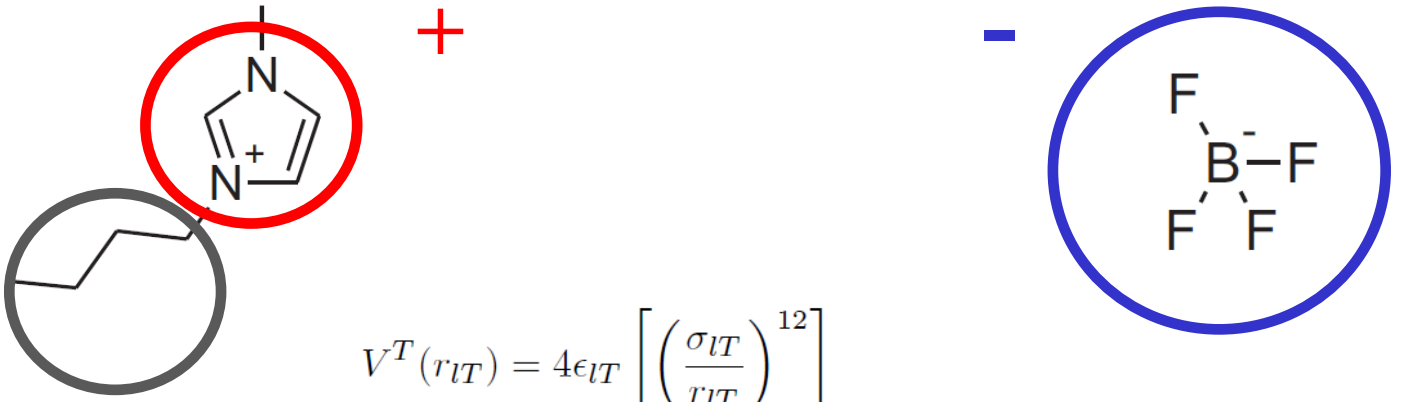
v=300cm/s



Long range entropic force

Adam-Gibbs: Connection between viscosity and entropy

TM model ("tailed" model)



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$$V(r_{ij}) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{e_i e_j}{4\pi\epsilon_0\epsilon_r r_{ij}}$$

SM model ("salt-like" model)