The Abdus Salam International Centre for Theoretical Physics

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IAEA International Atomic Energy Agency

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Workshop on Sphere Packing and Amorphous Materials

25 - 29 July 2011

Dialing-in Disorder and Dynamics in Dense Complex Fluids

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Workshop on Sphere Packing and Amorphous Materials
The Abdus Salam International Centre for Theoretical Physics
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Trieste, Italy

Acknowledgements

Former students

J. Mittal (Lehigh)
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G. Goel (IIT Delhi)

Current students

M. Pond (UT Austin)
J. Carmer (UT Austin)

Collaborators

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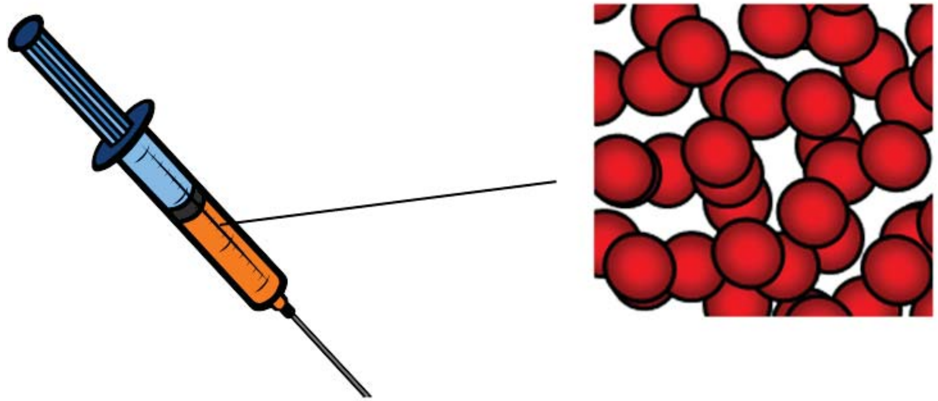
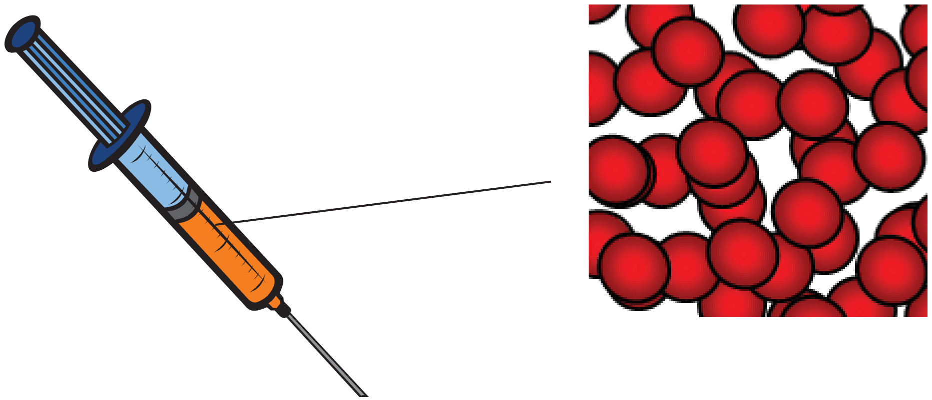
Can one intelligently tune interactions to enhance/decrease transport coefficients?



Dispersions of antibody particles

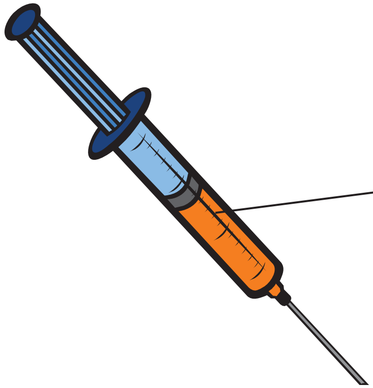
- highly concentrated
- moderate viscosity (syringeable)

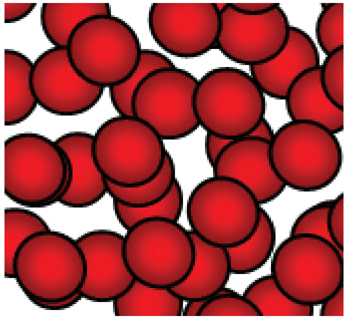


Dispersions of antibody particles

- ~~highly concentrated~~
- moderate viscosity (syringeable)

requires multiple administrations

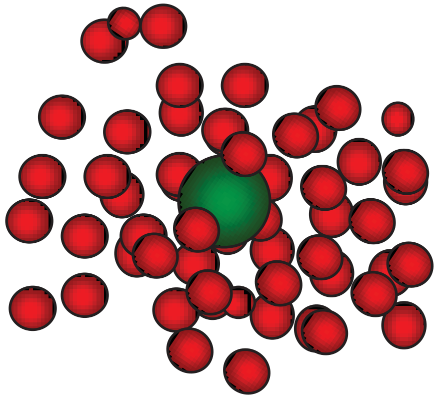




Dispersions of antibody particles

- highly concentrated
- ~~moderate viscosity (syringeable)~~

requires LARGE bore needles



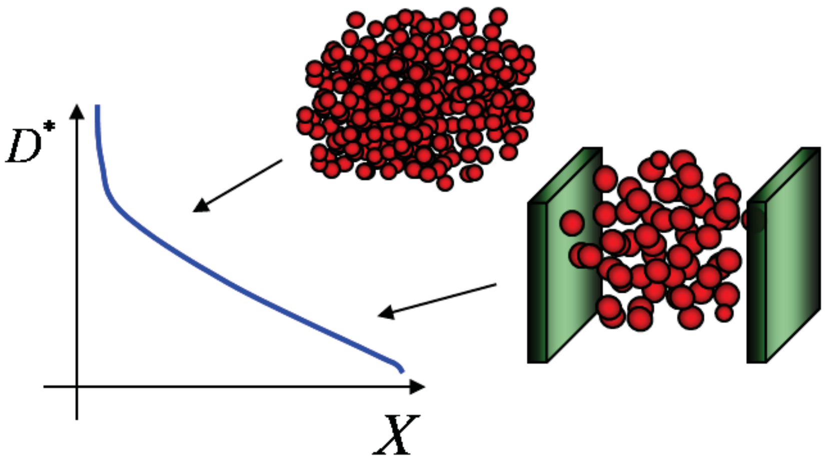
“Tuning” dynamics of a tracer particle by modifying its interactions with its neighbors

Can one intelligently tune interactions to enhance/decrease transport coefficients?

Not easily.

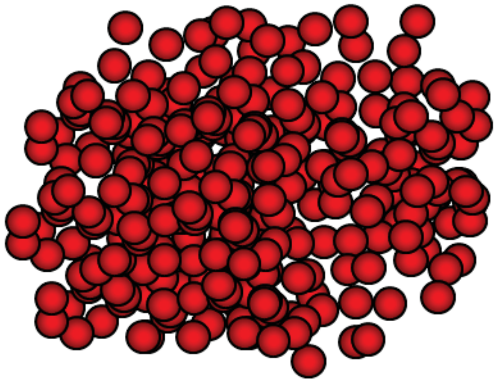
An optimistic hypothesis

Reduced transport coefficients (D^*, η^*, κ^*) are single-valued functions of a static measure X

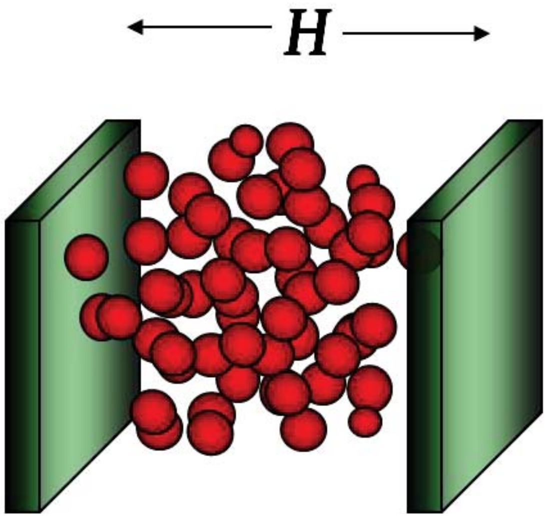


X is "what matters" for dynamics

Could X be density?

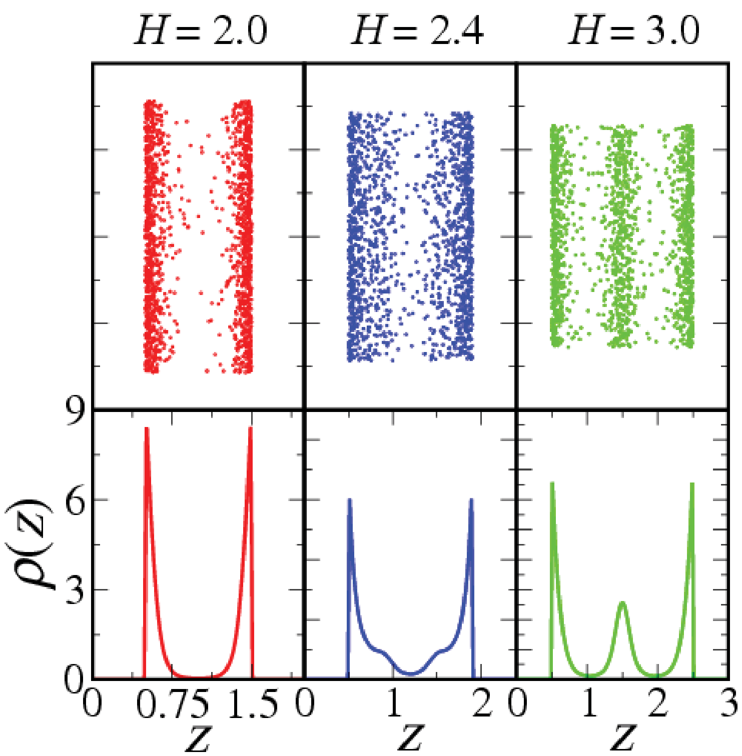


Seems intuitive, connected to available space ...



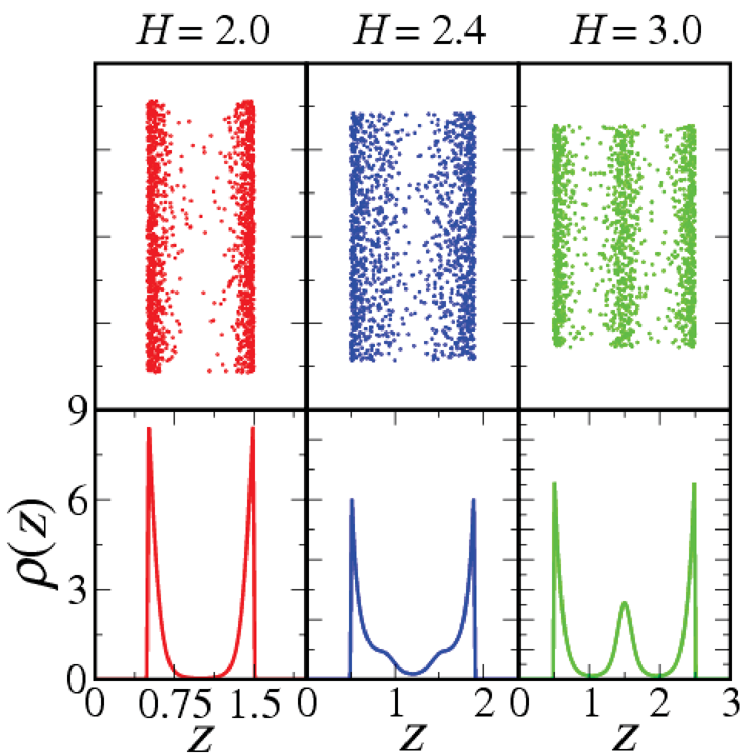
How does confinement affect “hard-sphere” colloids at fixed average particle density?

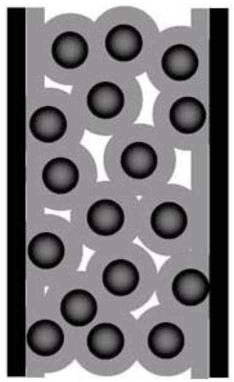
Mittal et. al., *J. Chem. Phys.* (2007)
Goel et al., *J. Stat. Mech.: Theory & Experiment (2009)*



Three examples have the same average density

Mittal et. al., *J. Chem. Phys.* (2007)
Goel et al., *J. Stat. Mech.: Theory & Experiment (2009)*

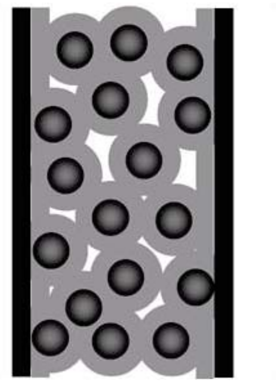


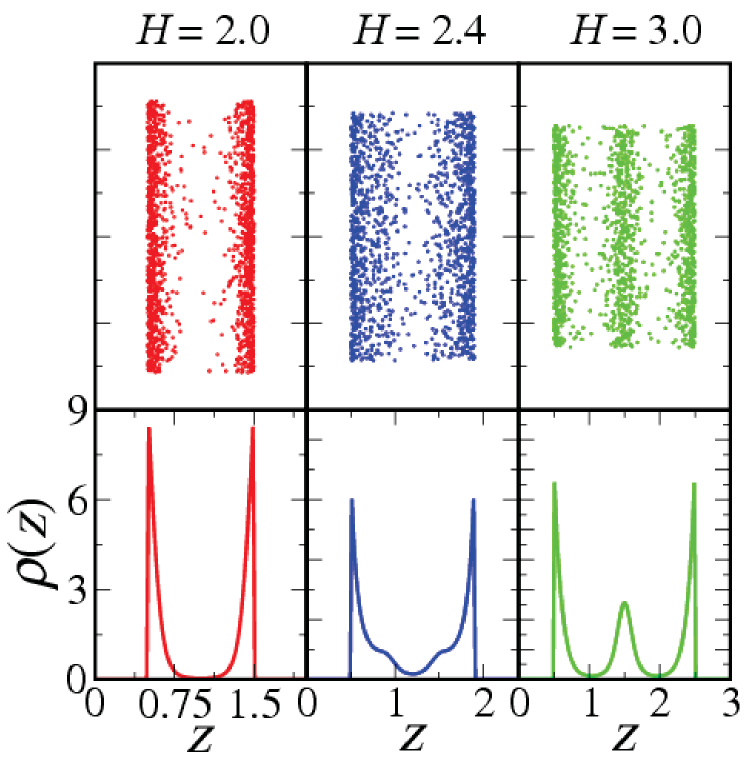


How is available space distributed?

Which has the most available space?

Mittal et. al., *J. Chem. Phys.* (2007)
Goel et al., *J. Stat. Mech.: Theory & Experiment (2009)*



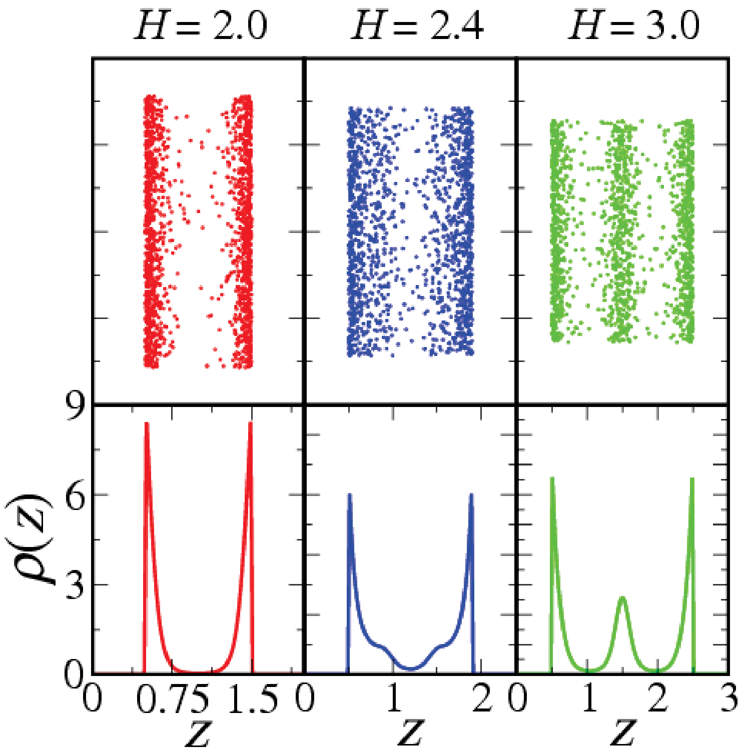


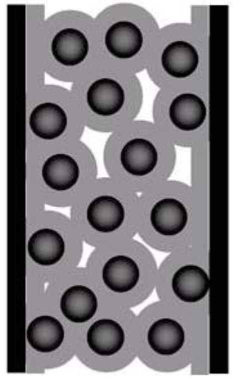
How is available space distributed?

$$p_0(z) = \rho(z)/\xi$$

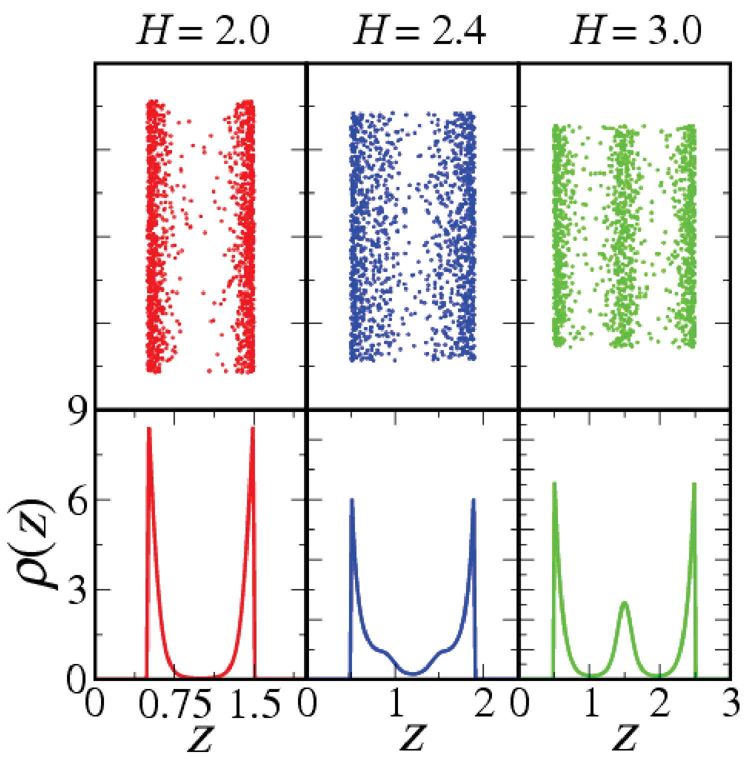
Mittal et. al., *J. Chem. Phys.* (2007)

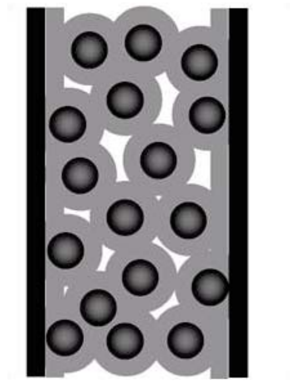
Goel et al., *J. Stat. Mech.: Theory & Experiment (2009)*





Mittal et. al., *J. Chem. Phys.* (2007)
Goel et al., *J. Stat. Mech.: Theory & Experiment (2009)*





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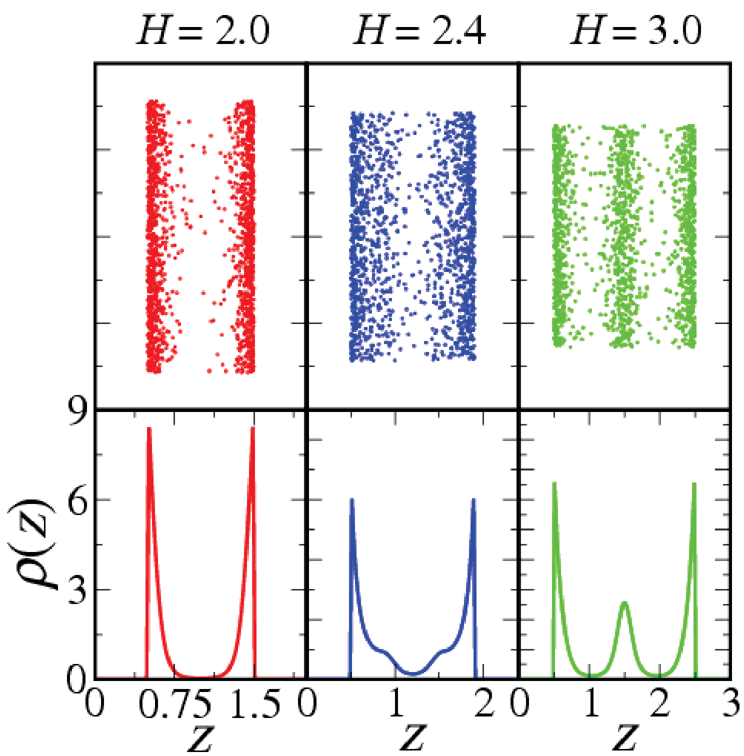
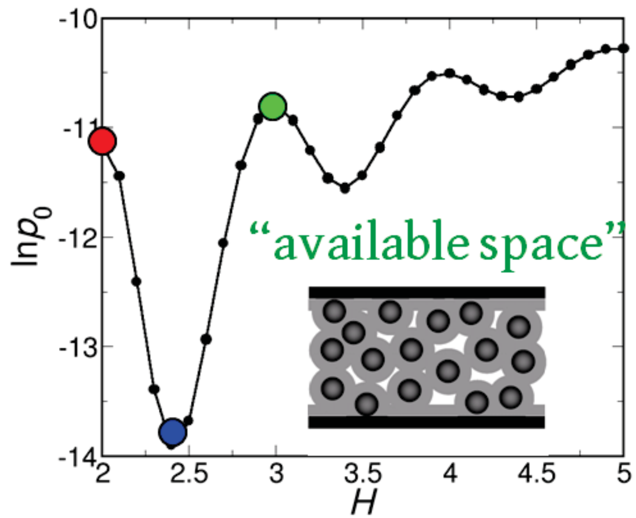
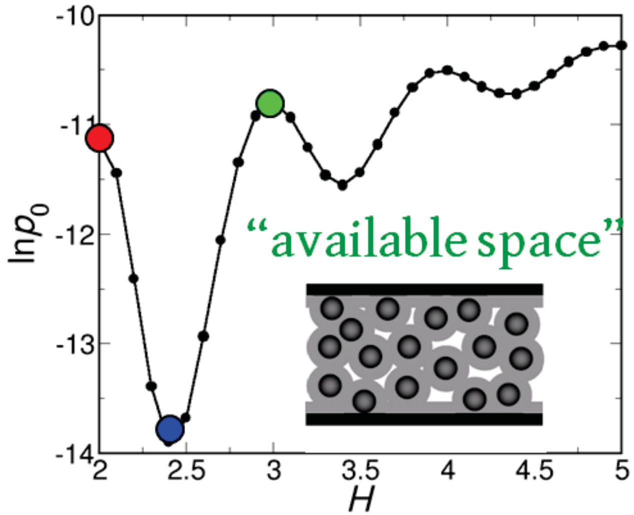


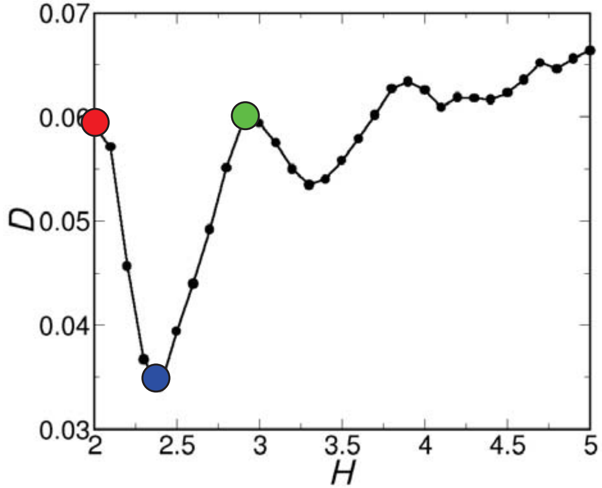


Which has the most available space?

Mittal et. al., *J. Chem. Phys.* (2007)
Goel et al., *J. Stat. Mech.: Theory & Experiment (2009)*

Perhaps $X = p_0$?





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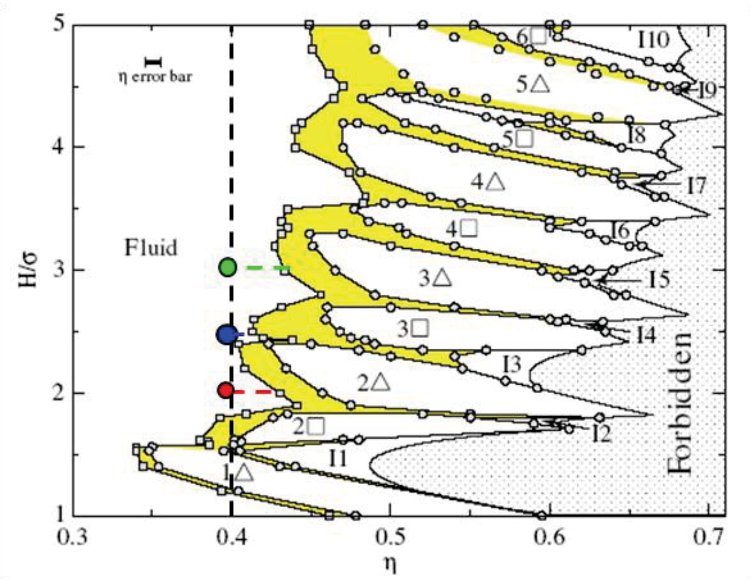
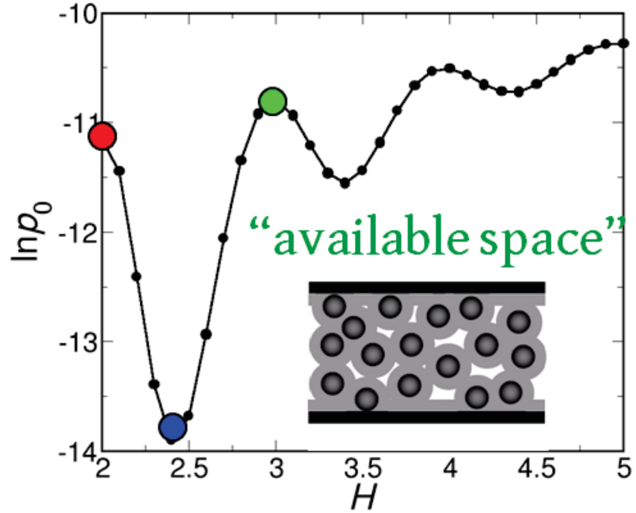
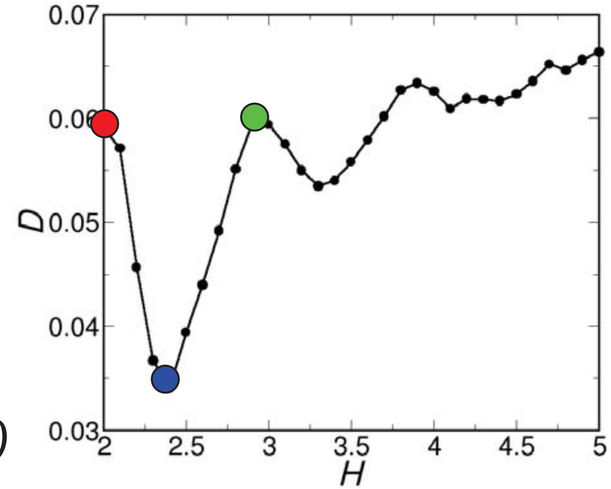


Fortini and Dijkstra, *Europhys. Lett.* (2006)





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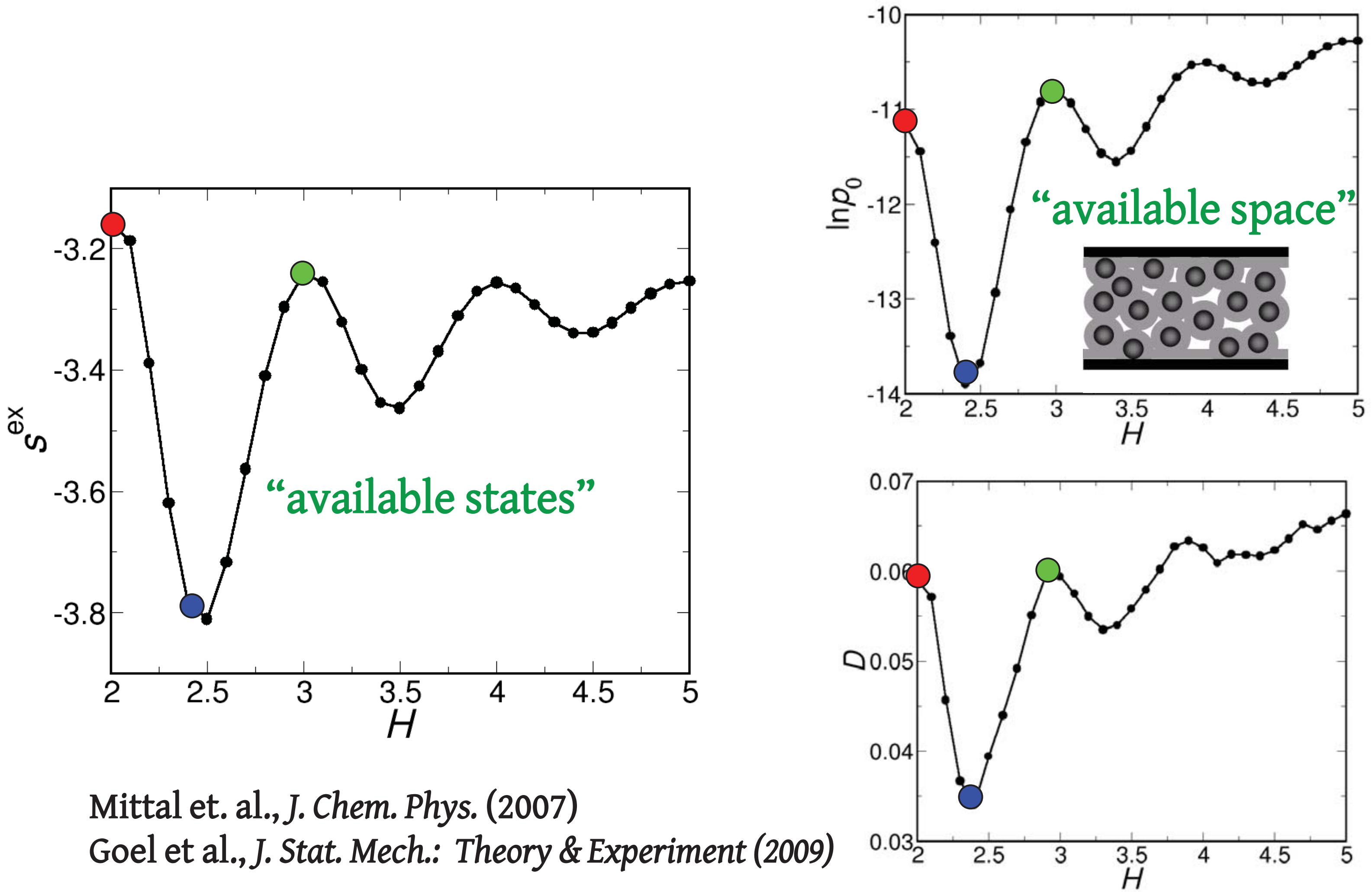


Mittal et. al., *J. Chem. Phys.* (2007)

Goel et al., *J. Stat. Mech.: Theory & Experiment (2009)*

Could X be excess entropy, s^{ex}?

Measures # of states taken away from the fluid due to static interparticle correlations

$$s^{\mathrm{ex}}[T,\rho(\mathbf{r})] = s[T,\rho(\mathbf{r})] - s^{\mathrm{ideal}}[T,\rho(\mathbf{r})]$$

$$0 \le -s^{\mathrm{ex}} < \infty$$

Excess entropy, s^{ex}

Measures # of states taken away from the fluid due to interparticle correlations

$$s^{\mathrm{ex}}[T,\rho(\mathbf{r})] = s[T,\rho(\mathbf{r})] - s^{\mathrm{ideal}}[T,\rho(\mathbf{r})]$$

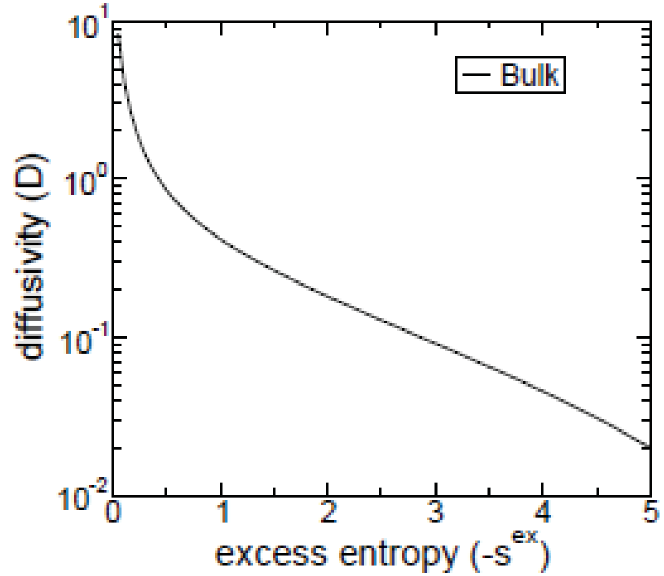
How does it connect to structure?

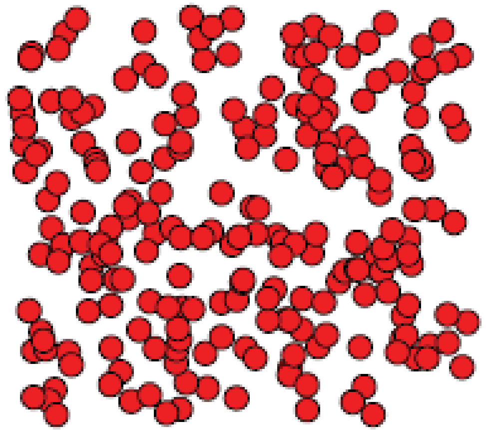
$$s^{\mathrm{ex}} = s_2 + \Delta s_R$$

higher correlations

pair correlations

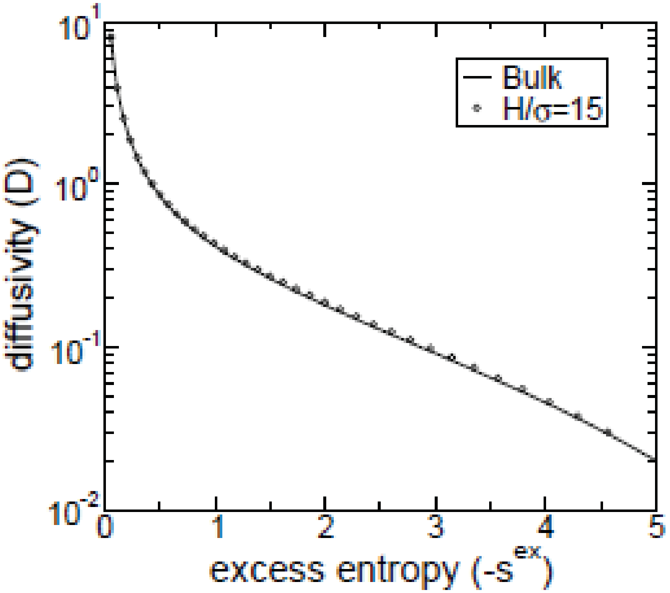
Diffusivity and excess entropy: Confined HS Fluid

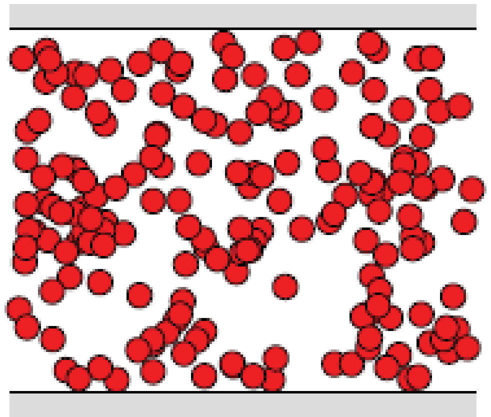




Mittal *et. al. Phys. Rev. Lett.* (2006)

Diffusivity and excess entropy: Confined HS Fluid





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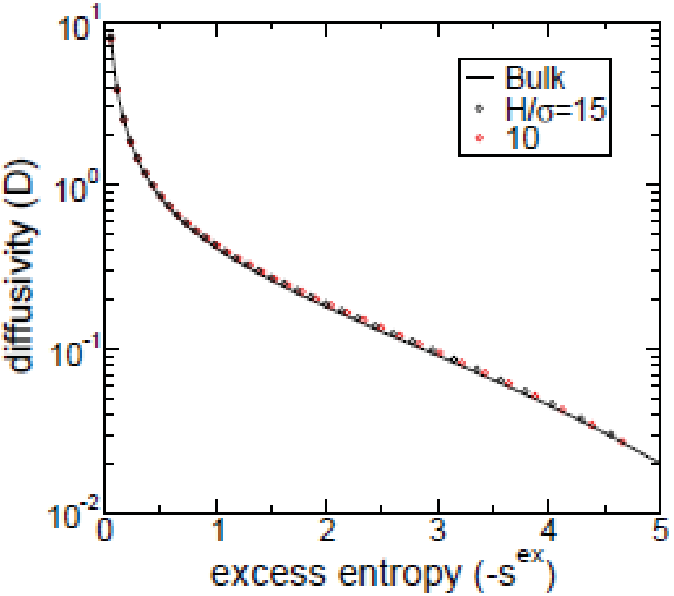

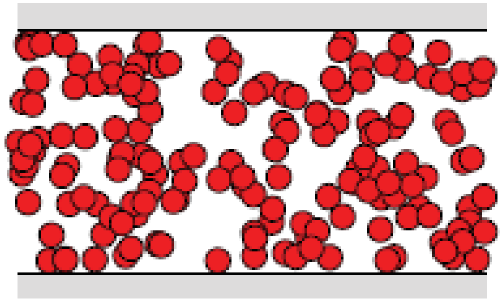

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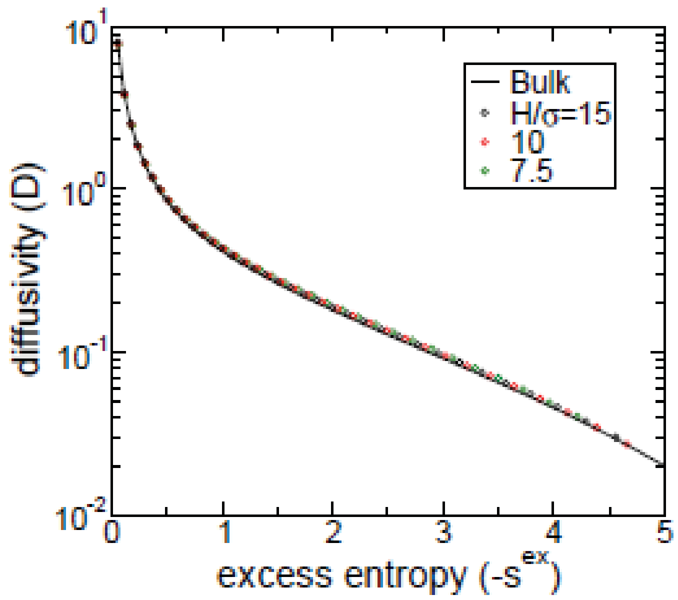

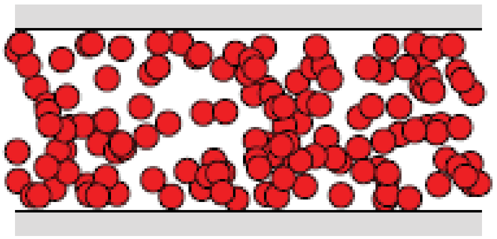

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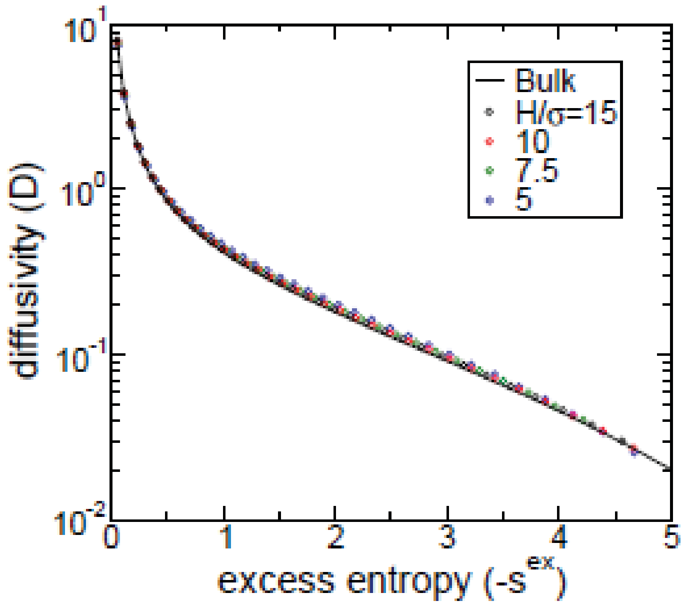
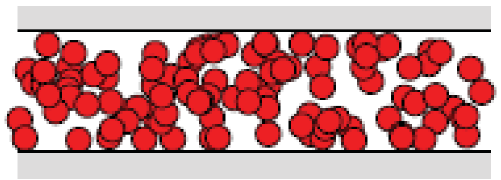
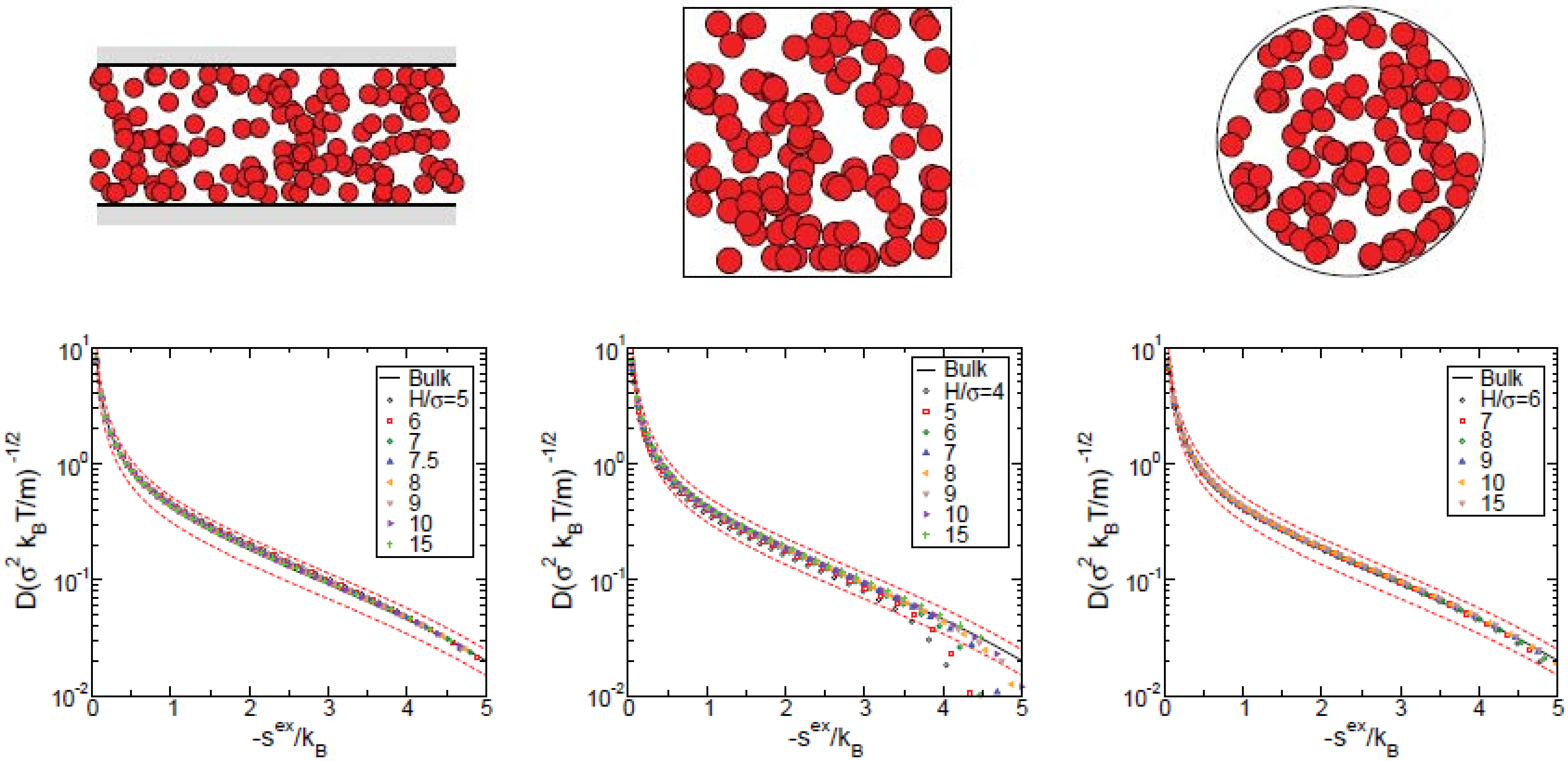




Mittal *et. al. Phys. Rev. Lett.* (2006)

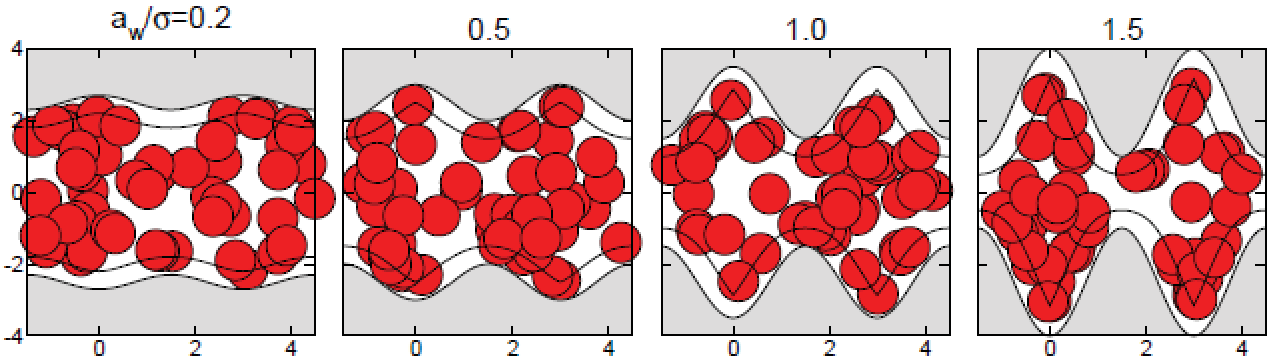
Diffusivity and excess entropy: The effect of geometry



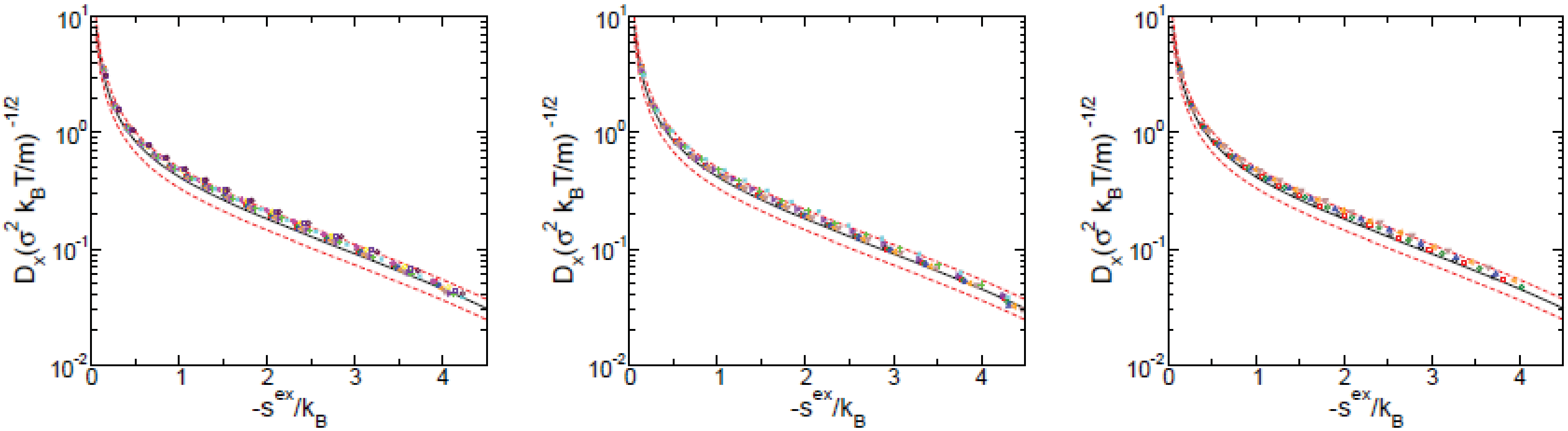
Goel *et. al. J. Stat. Mech.*: Theory & Experiment (2009)

Diffusivity and excess entropy: The effect of geometry

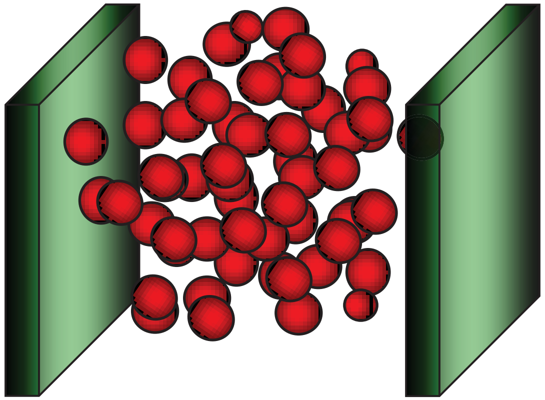
D_x



$h/\sigma = 5.0,\ \lambda/\sigma = 3.0$ $h/\sigma = 7.5,\ \lambda/\sigma = 3.0$ $h/\sigma = 10.0,\ \lambda/\sigma = 3.0$



Krekelberg et al.., in preparation

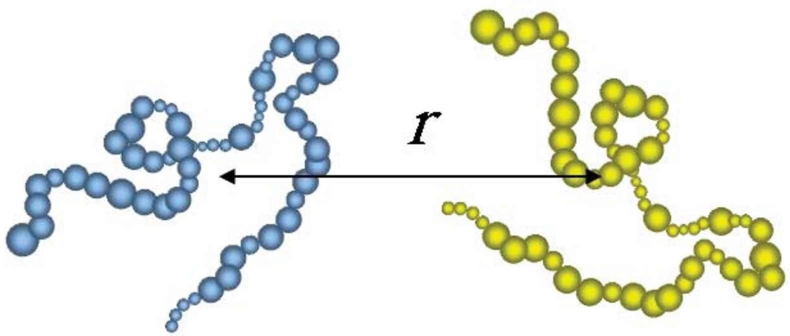


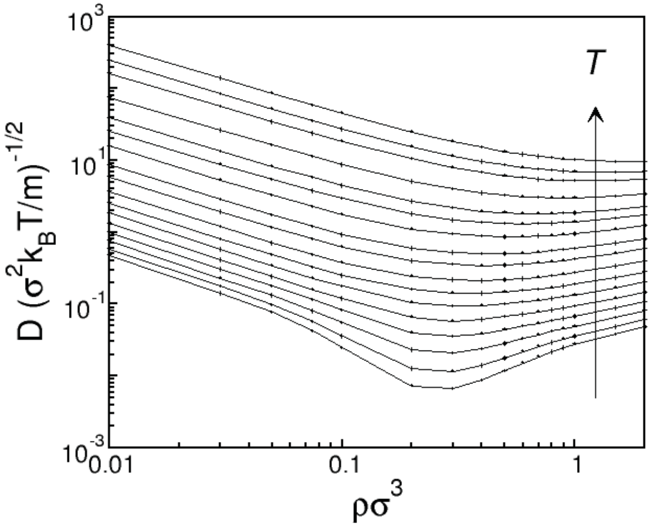
Goel et al., *Phys. Rev. Lett.* (2008)

“Tuning” dynamics of a confined fluid by modifying its interactions with boundaries

Fluids with density anomalies

Gaussian-core model

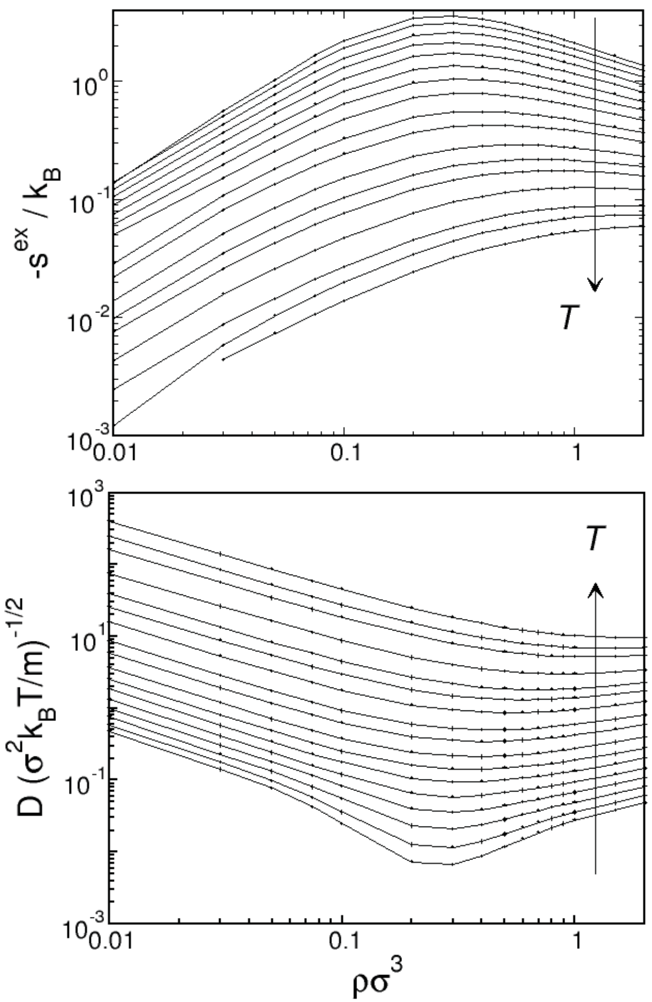




Krekelberg *et. al. Phys. Rev. E* (2009)

Fluids with density anomalies

Gaussian-core model



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Fluids with density anomalies

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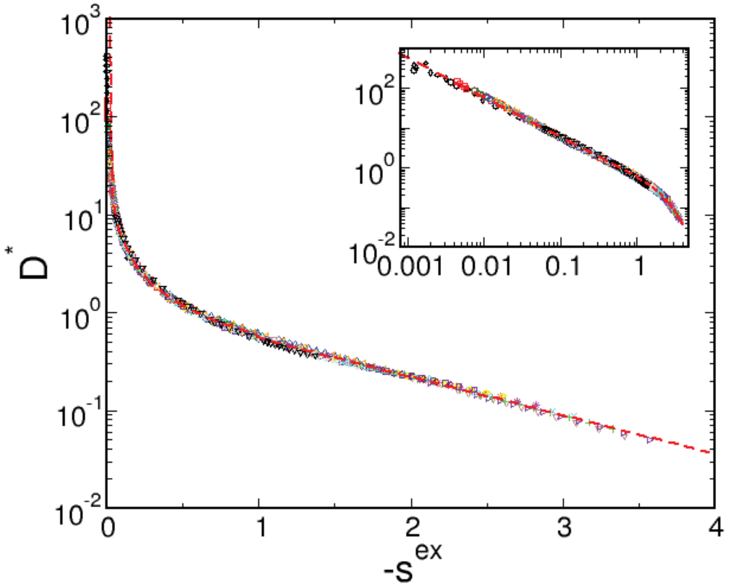
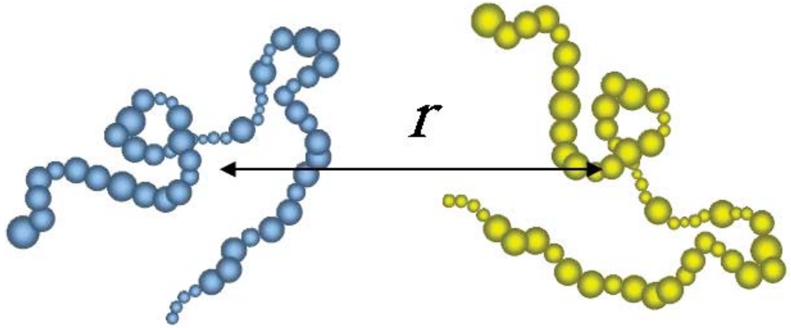


Krekelberg *et. al. Phys. Rev. E* (2009)

Binary Gaussian-core fluid

$$v_{ij}(r) = \epsilon_{ij}\exp\left[-\left(r/\sigma_{ij}\right)^2\right]$$

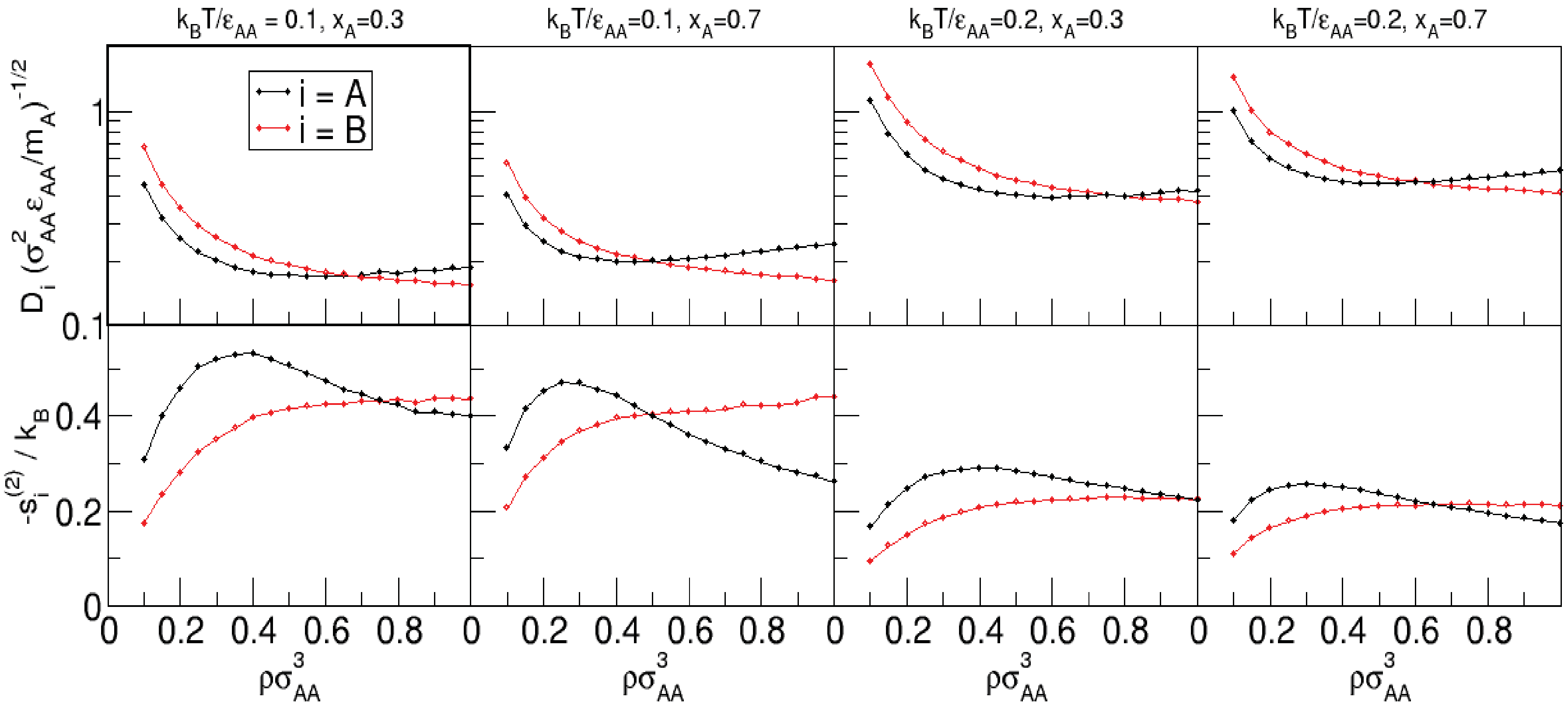


$$\sigma_{BB} = 0.665\sigma_{AA} \qquad \varepsilon_{BB} = \varepsilon_{AA}$$

$$\sigma_{AB} = \sqrt{0.5(\sigma_{AA}^2 + \sigma_{BB}^2)} \qquad \varepsilon_{AB} = 0.944\varepsilon_{AA}$$

Archer and Evans, Phys. Rev. E, 2001., "Mixture of self-avoiding polymers"

Binary Gaussian-core fluid



Pond et al., J. Chem. Phys. (2009)

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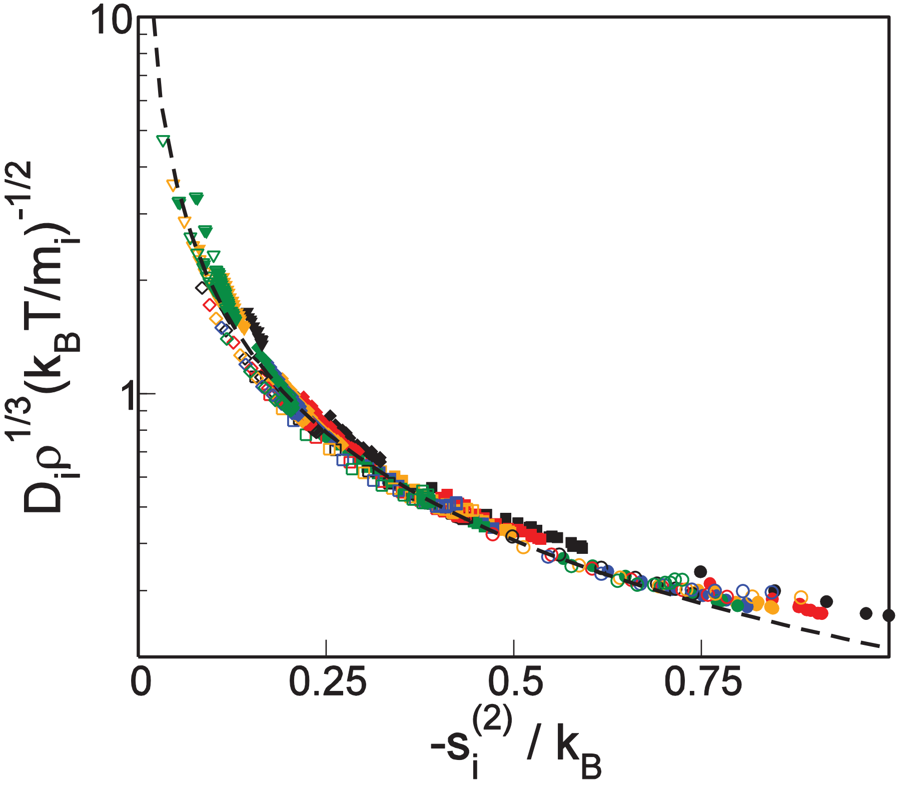
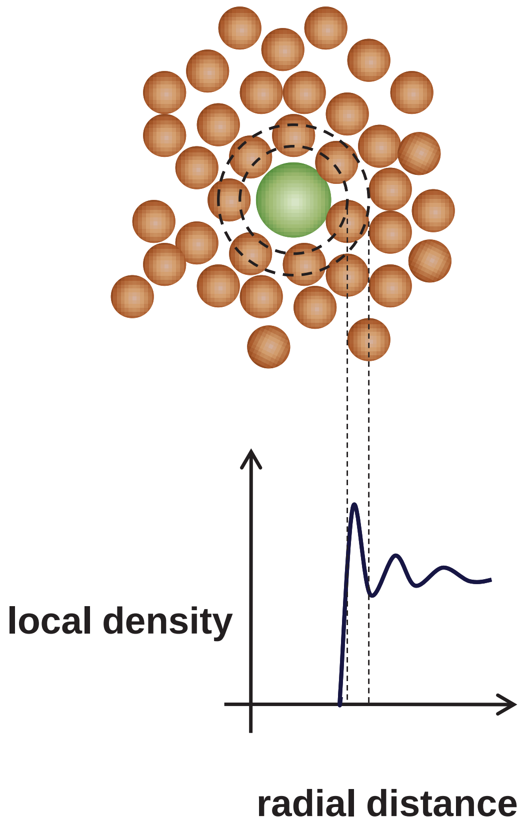


Pond et al., J. Chem. Phys. (2009)

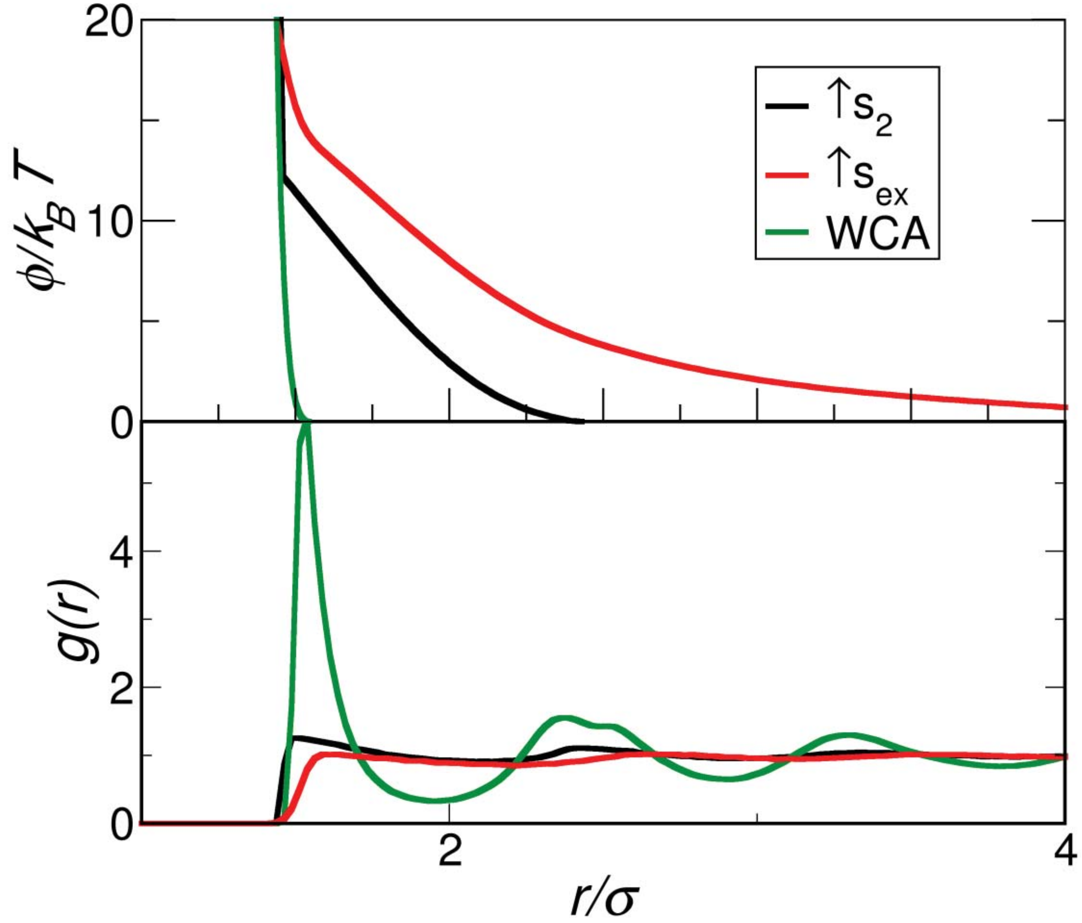
Tuning the dynamics of a tracer



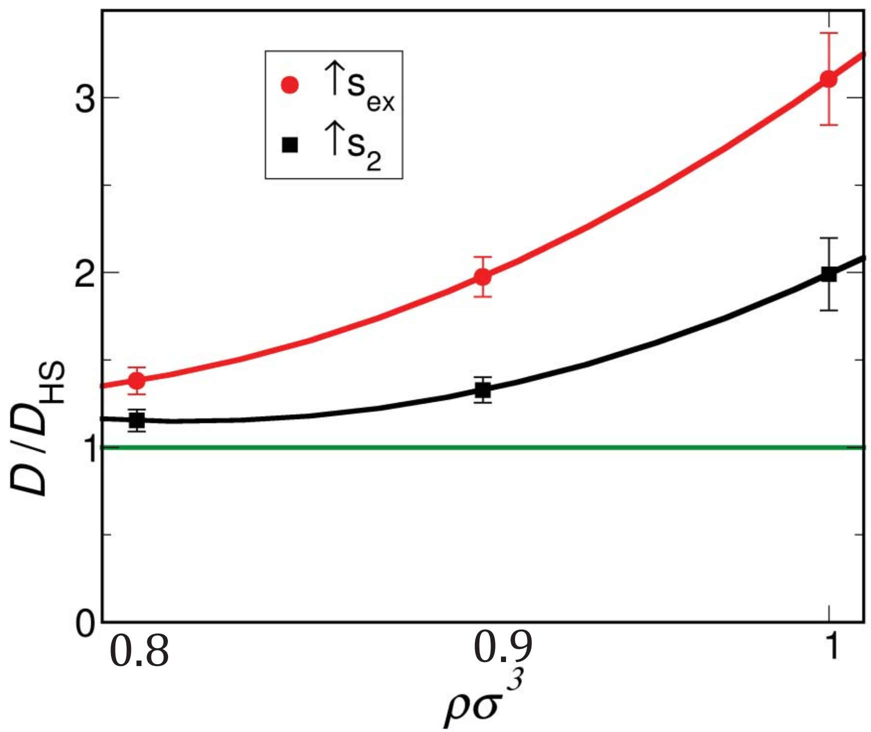
$$-\frac{s_2}{k_B} = \frac{\rho}{2}\int [g(r)\ln g(r) - g(r) + 1]\mathrm{d}\vec{r}$$

$$-s_t^{ex}/k_B = \beta\mu_t^{ex} - \beta e_t^{ex} - \beta P\nu_t + 1$$

Tuning the dynamics of a tracer

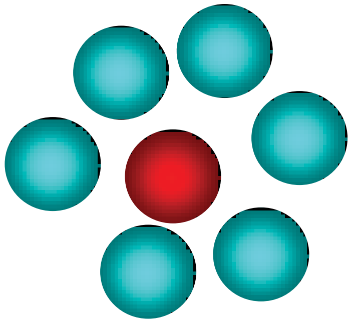


Tuning the dynamics of a tracer

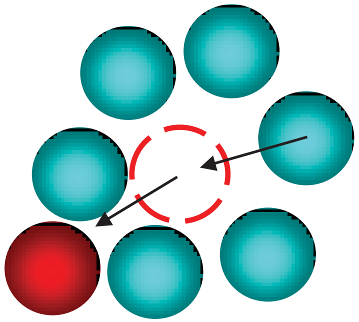


"Dynamic heterogeneities"

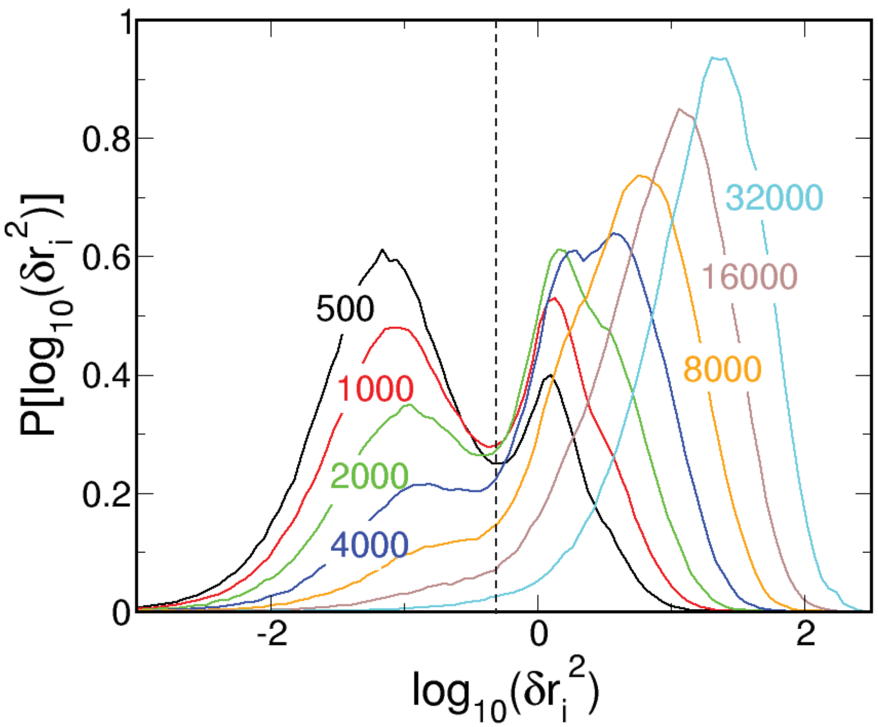
Near Tg, on finite time scales, bimodal distribution of displacements emerge...



Slow, "caged" particles ...



Faster particles "hop", facilitating motion of neighbors



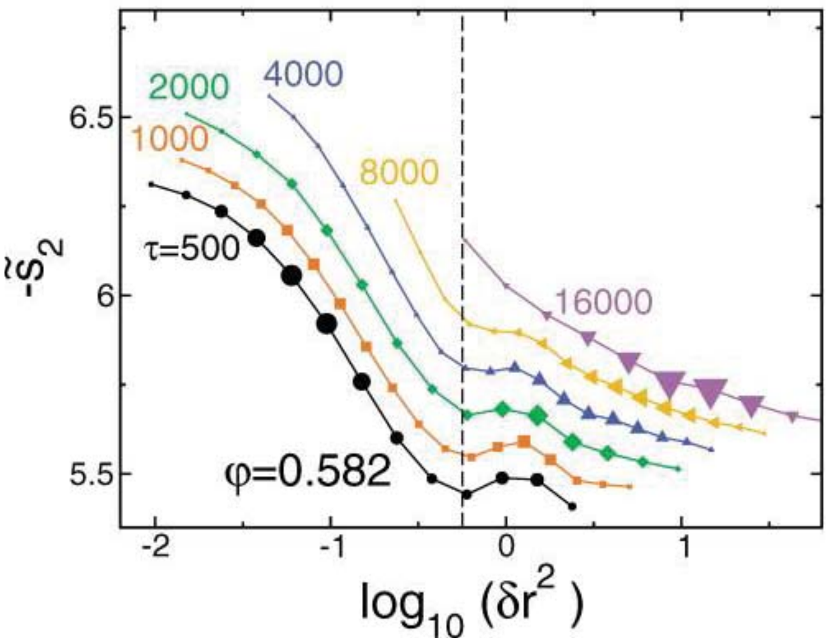
Krekelberg et al., J. Chem. Phys. (2010)

Structuring and dynamic heterogeneity

(i) Strong connection between local disorder and displacement

(ii) Sustained disorder correlated with cage-breaking / hopping

(iii) Local reordering occurs after cage-breaking



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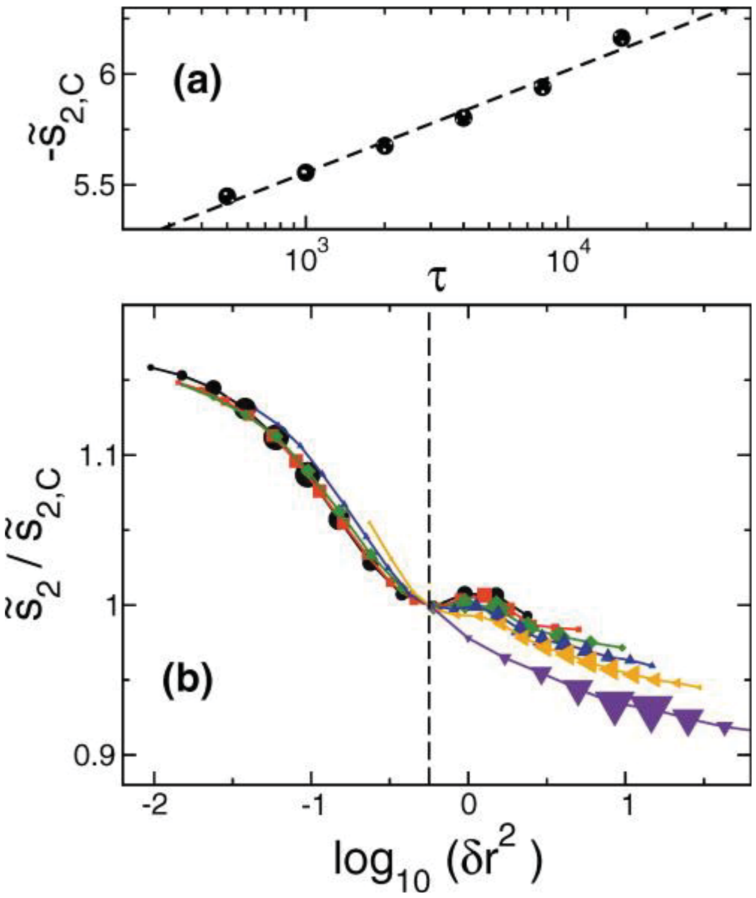

Krekelberg et al., J. Chem. Phys. (2010)

Conclusion

Transport coefficients of complex fluid systems obey an empirical scaling law with excess entropy.

This allows prediction and tuning of dynamics via interactions between the particles.