Structure and Dynamics of Interacting Brownian Particles in a Spherical Cavity

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ABSTRACT

Theoretical studies of the structure and dynamics of finite-size particles embedded in confined fluids are often limited by the complexity of modeling many-body hydrodynamic interactions (HI). To overcome the complexity, we have released a computational package, COPSS[2,3], that can perform both deterministic and stochastic simulations of arbitrarily shaped particles under confinement with HI. Here, we report a theoretical study on the diffusion of both pure sphere and cylinder particles confined in a spherical cavity using this technique.

- This study serves to illustrate the effects of both short- and long-range HI, confinement, particle volume (packing) fraction, and particle shape on the equilibrium structure and diffusion behavior of concentrated particles.
- Regardless of HI, particles distribute uniformly in density and orientation along the radial direction of the cavity at low volume fractions (ϕ). As ϕ increases, particles start to aggregate into layers and the corresponding particle density in these layers also increases. To accommodate this layering phenomenon, cylinder particles start to form significant orientational order.
- HI strongly hinder the diffusion of particles and also induce anomalous diffusion behavior at high ϕ. Interestingly, cylinder particles diffuse slower than sphere particles in both short-time and long-time scale at the same ϕ, and the transition between different diffusion regimes happens earlier for cylinder particles.

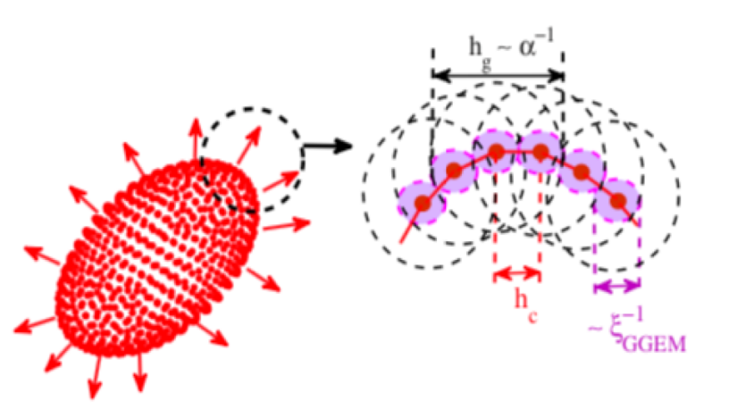
METHODS

- The equation of motion for suspended particles with Brownian motion

$$d\mathbf{R} = \left[\mathbf{U_0} + \mathbf{M}\cdot\mathbf{F} + \frac{\partial}{\partial \mathbf{R}}\cdot\mathbf{D}\right] dt + \sqrt{2}\mathbf{B}\cdot d\mathbf{W}$$

Unperturbed velocity	Perturbed velocity	Brownian drift resulting from the configuration-dependent mobility	Brownian displacement

  - ***M*** is the mobility tensor that depends on configurations of the system
  - ***D*** = $k_B T$ ***M***, is the diffusion tensor
  - ***B*** is related to **D** by $\boldsymbol{B}\cdot\boldsymbol{B}^T = \boldsymbol{D}$, satisfying fluctuation-dissipation theorem
  - ***M*F*** is obtained by solving Stokes equation in confined geometries
- Immersed Boundary method to account for finite-size particles



$$\rho^f_{IB}(\mathbf{x}) = \sum_{\nu=1}^{N_{IB}} \mathbf{f}^C_\nu \delta_{IB}(\mathbf{x}-\mathbf{x}_\nu),$$

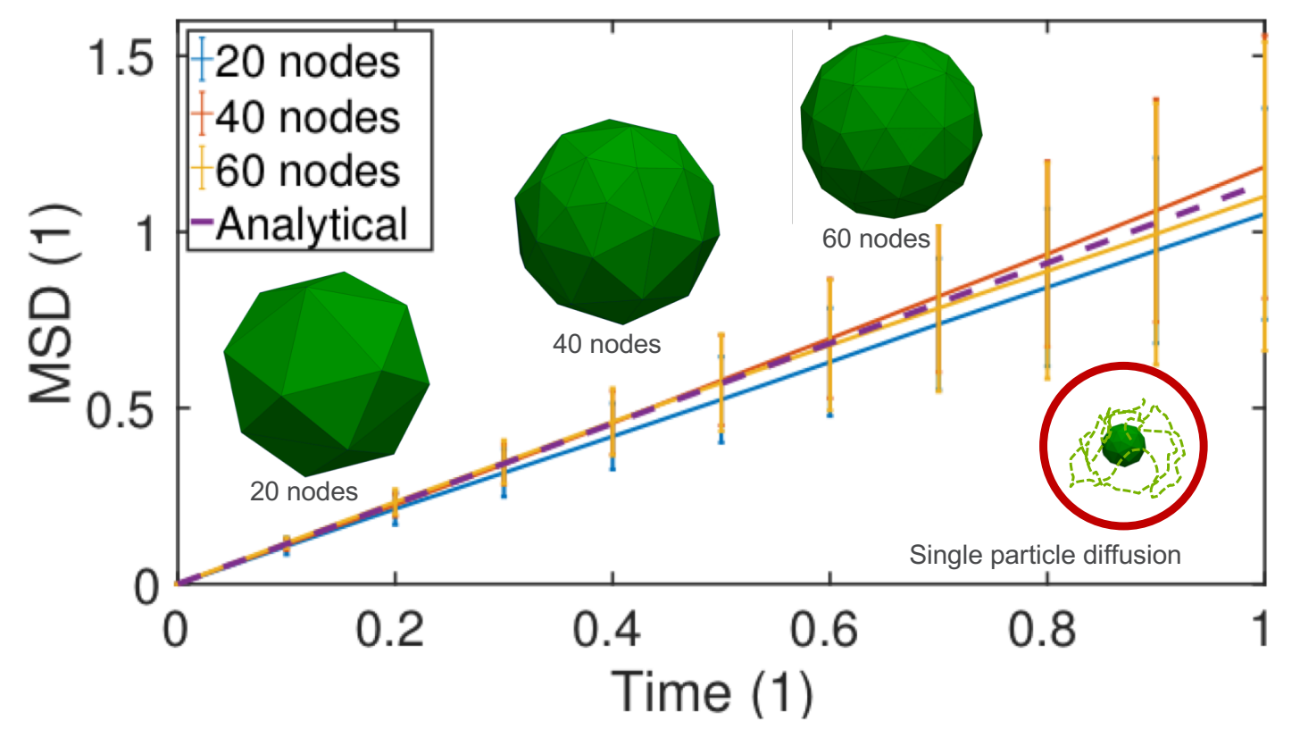


Figure 1. Single particle diffusion

Structural properties (regardless of HI)

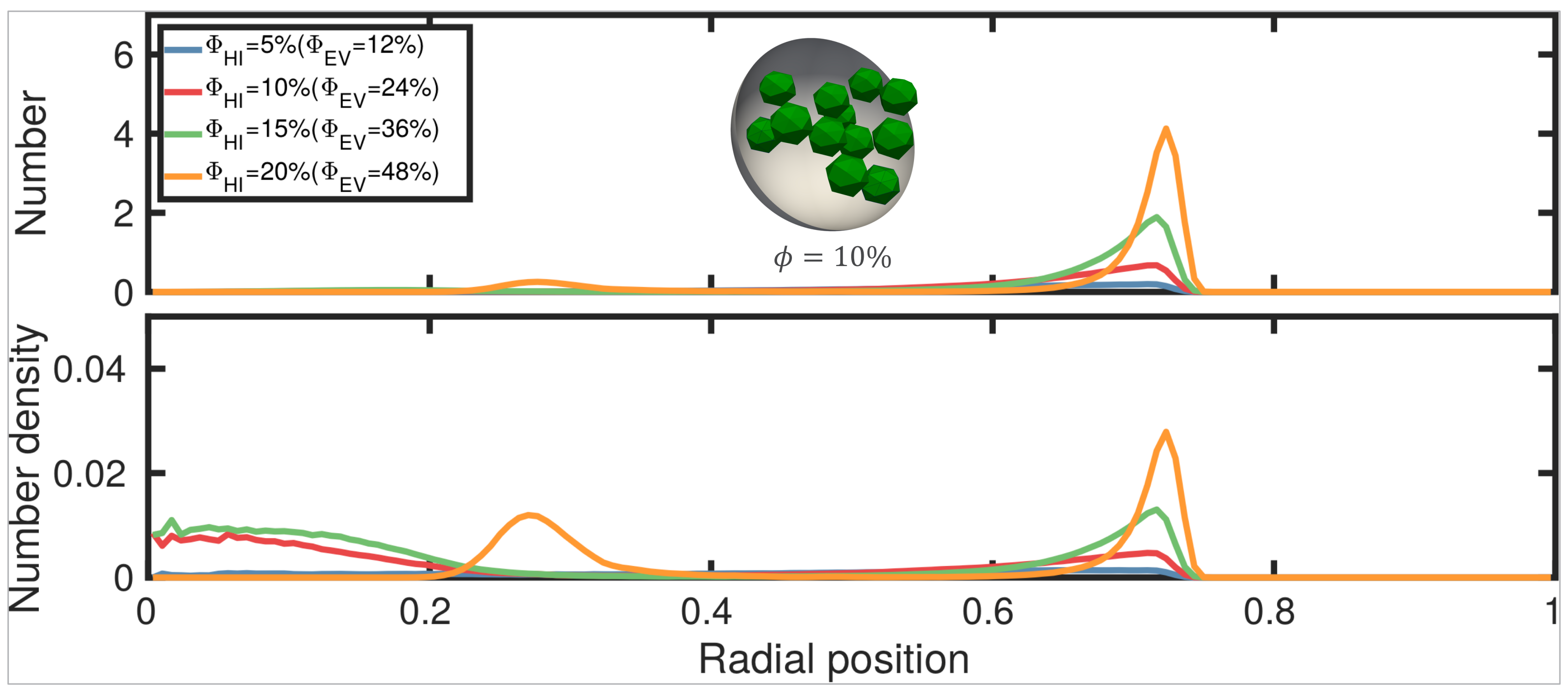


Figure 2: a) Particle (model) count as a function of normalized radial position in a spherical cavity of radius R = 10a. Volume fractions of the systems range from 5% to 20% (b) Particle density as a function of normalized radial position.

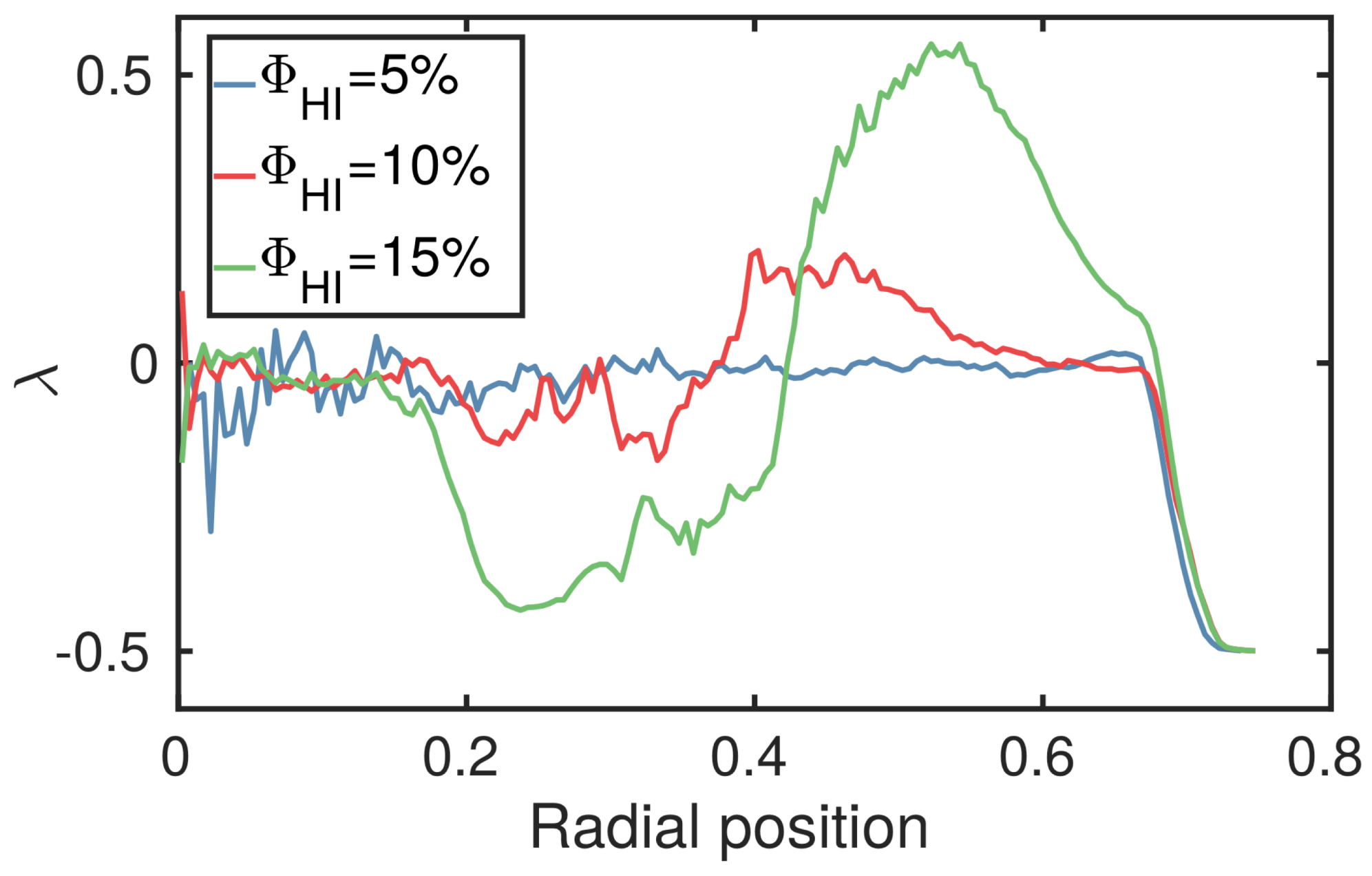
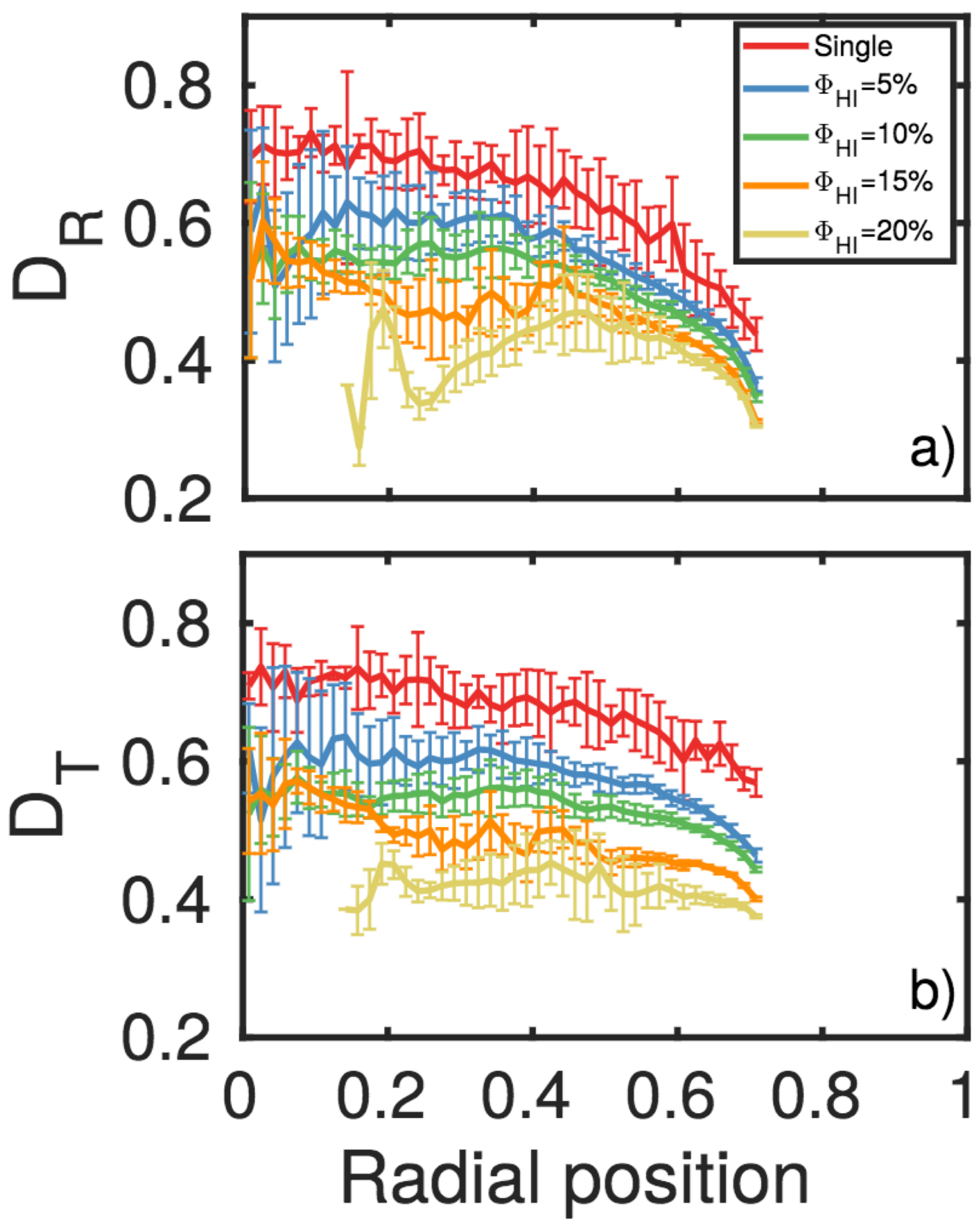


Figure 3: Orientational order parameter λ of cylindrical particles as a function of radial position. Order parameter is defined as $\lambda = \frac{1}{2}\langle 3\,cos^2\theta - 1\rangle$, where θ is the angle between the cylinder centerline and the normal director from cavity center to cylinder center.

Dynamics (Diffusion behavior)



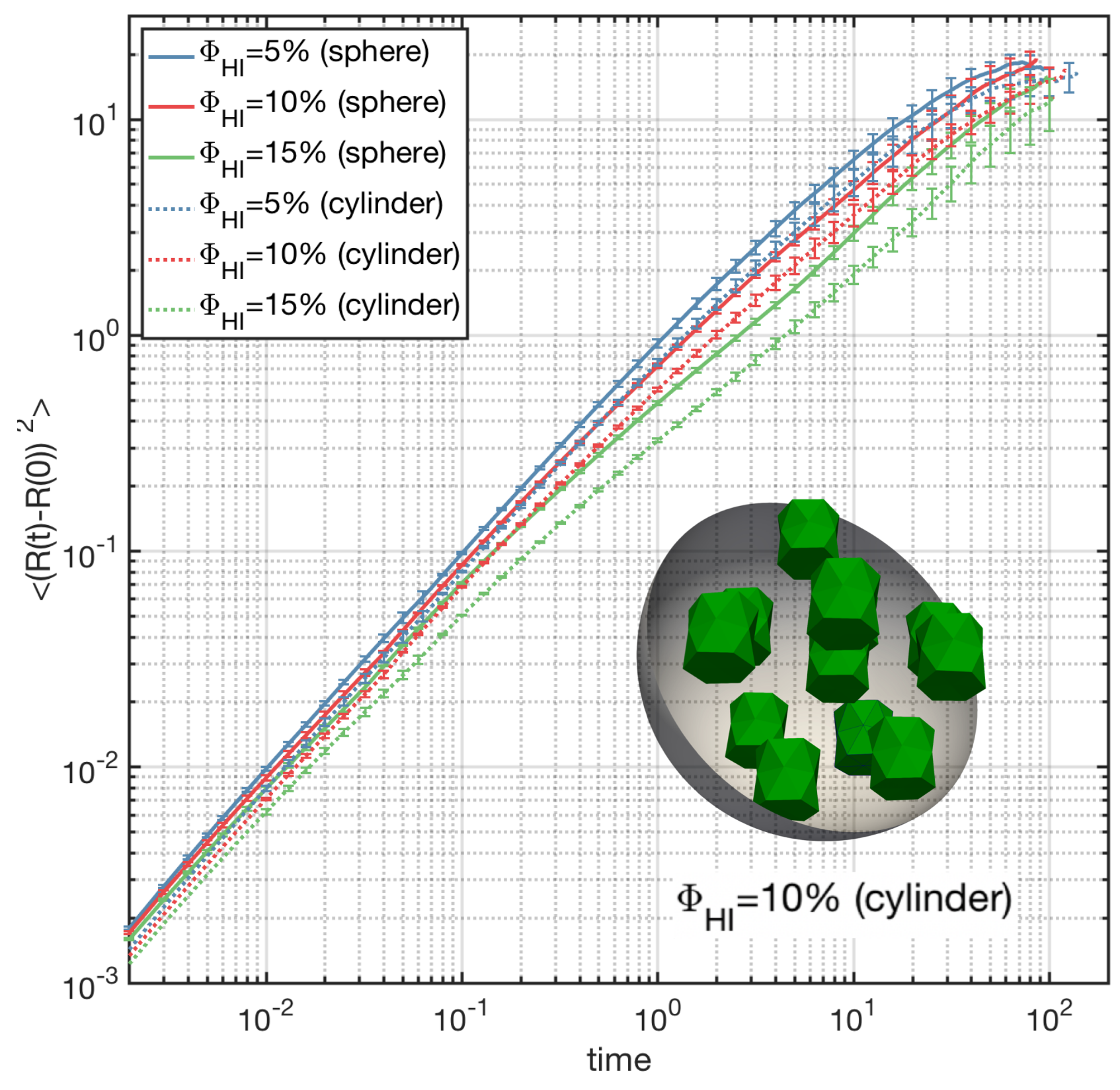


Figure 4

Figure 5

Figure 4. Short time diffusion calculated by COPSS for spherical particles. (a) Short-time diffusivity along the radial direction of the cavity. (b) Short-time diffusivity in the tangential direction to the cavity wall. Particle volume fractions are from 5% to 20%.

Figure 5. Comparison of long time mean square displacement for spherical and cylinder particles. Cylinders show similar transitions as spheres, but there are two key differences: 1) cylinders diffuse slower than spheres at the same volume fraction; 2) cylinders enter sub-diffusive regime (due to crowding) earlier than spheres.

CONCLUSIONS

- We have simulated the Brownian motions of sphere and cylinder particles confined in spherical cavity with the consideration of many-body HI using an O(N) method in COPSS.
- This work is the first attempt to simulate the Brownian motions of arbitrary shaped particles embedded in highly confined fluid and the results are fundamental to understanding the structure and dynamics of hydrodynamically interacting Brownian particles under confinement in a wide variety of physical, chemical and biological processes.

FUTURE WORK

- Apply our simulation technique to mixtures of spheres and cylinders and analyze the transitions between diffusion regimes for different system to fully understand the effects of particle shapes on the diffusion behavior.

REFERENCES

[1] J. Li, *et al.* to be submitted (2018)

[2] X. Zhao, J. Li, X. Jiang, et al. JCP, 2017.

[3] Code available at http://ime-code.uchicago.edu

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