Many-Body Correlations Are Non-negligible in Simple Glassformers

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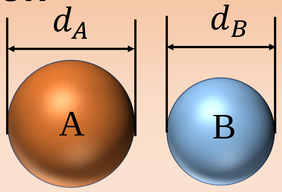
Introduction



Packing fraction : $\varphi = \varphi_A + \varphi_B$
Size ratio : $\delta = \frac{d_B}{d_A}$
Number concentration : $x_B = \frac{N_B}{N_A + N_B}$

Static two-point density correlations are usually assumed to be sufficient to describe the main structural features of simple glassformers. However, recently more and more simulations and experiments show that the higher-order correlations change markedly near the glass transition.

Here we develop a **first-principle theory** that can systematically take **higher-order static and dynamic correlations** into account. We apply it to predict the glass transition of a binary hard-sphere mixture.

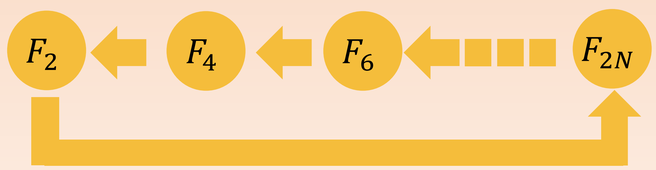
Theory

Input Structures

$S_2 =< \rho\rho >$

$S_3 =< \rho\rho\rho >$

Generalized Mode-Coupling Theory (GMCT)



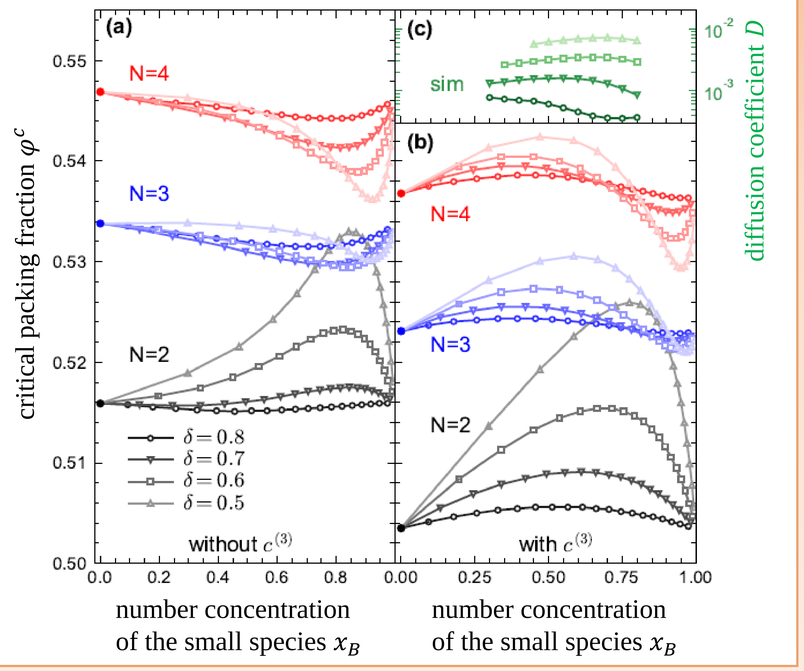
Mean field approximation at level N: $F_{2N} \approx (F_2)^N$

Output Dynamics

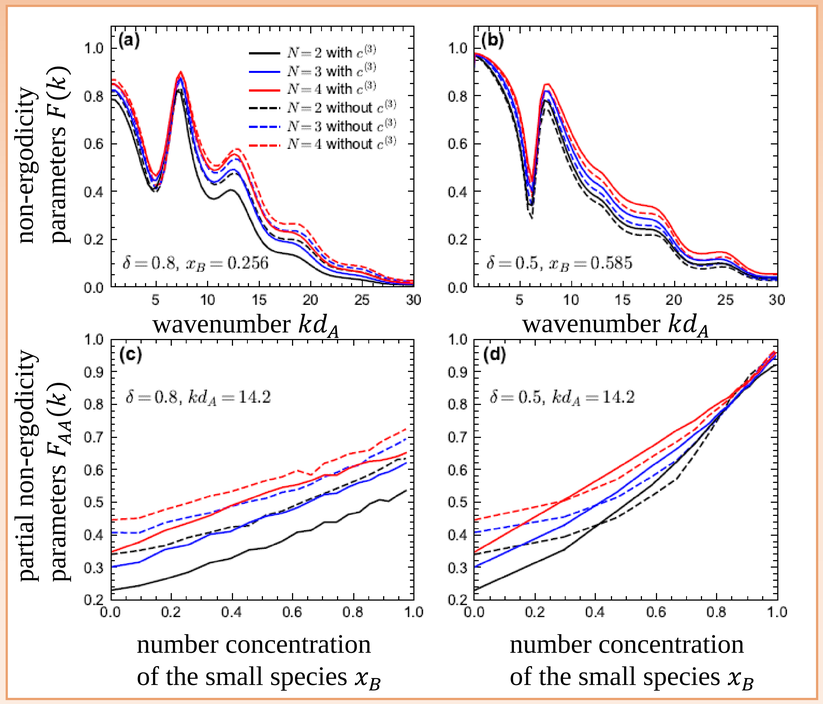
$F_2 =< \rho\rho(t) >$

$F_4 =< \rho\rho\rho(t)\rho(t) >$

Results



- Adding static triplet $c^{(3)}$stabilizes the glass state.
- Including higher level dynamic density correlations stabilizes the liquid state.
- Both static triplet $c^{(3)}$ and dynamic level N qualitatively change the transition curve.



- The non-ergodicity parameters increase as level N increases.
- The effect of the static triplet $c^{(3)}$ on the non-ergodicity parameters is more complex, highly dependent on the number concentration and size ratio.

Conclusion

By studying the liquid-glass transition of a binary hard-sphere mixture within GMCT, we demonstrate that the conventionally neglected static triplet direct correlations, as well as higher-order dynamic correlations, are in fact non-negligible.

We find a non-trivial competition between static triplet correlations that work to stabilize the glass state, and dynamic higher-order correlations which destabilize it.

The reasonable predictions of standard MCT for mixtures, based solely on two-point correlations, should essentially be regarded as a coincidence.

References

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[3] Chengjie Luo and Liesbeth M. C. Janssen. J. Chem. Phys., 153, 214507 (2020)

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