# Glass transition in confinement

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The effect of confinement on the dynamical and thermodynamical behavior of liquids is a problem of uttermost importance from the theoretical point of view as well as for the interest in technological applications and biology. In particular the phenomena related to the glass transition are yet not well understood in the case of liquids in confined geometries. We present an extensive Molecular Dynamics study on the behavior of a liquid Lennard Jones binary mixture confined in a random matrix of soft spheres to model a xerogel at high porosity. A snapshot of the simulated system is reported in Fig. 1.

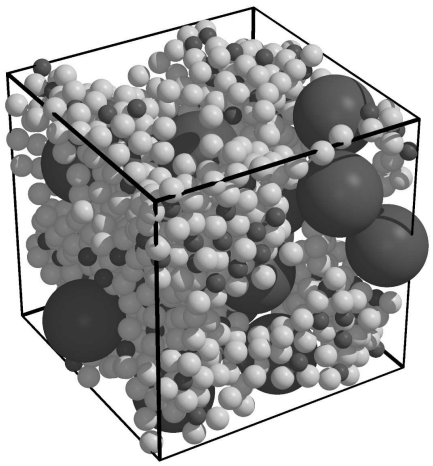

Figure 1: Snapshot of the model studied. The large dark spheres are the soft spheres which form the confining matrix. The small spheres represent the Lennard-Jones mixture of A (gray) and B (black) particles.

The confined system is found to display a behaviour in agreement with the Mode Coupling theory as the bulk system [1]. A quantitative comparison at equivalent thermodynamical conditions of bulk and confined dynamical properties show that important modifications are induced by the confinement in particular for what concerns hopping phenomena [2].

A study of the thermodynamical properties via inherent structure analysis is performed. The liquid entropy is computed by means of a thermodynamical integration procedure. It is shown that the free energy of the liquid can be decoupled also in confinement in the configurational and the vibrational part. The vibrational contribution can be calculated in the harmonic approximation. The structural entropy $S_{liq}$ can obtained after subtracting a term due to confinement. $S_{liq}$ is shown in Fig. 2 together with the entropy of the disordered solid ($S_{DS}$) calculated in the harmonic approximation. The crossing

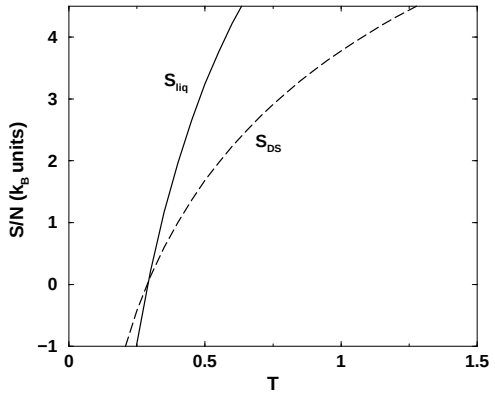


Figure 2: Configurational entropy of the confined liquid (full line) and entropy of the disordered solid (dashed curve) as function of temperature. The entropies are per particle and in units of $k_B$. The temperature is in reduced Lennard-Jones units.

point determines the Kauzmann temperature $T_K$ of the confined system. While $S_{liq}$ vs. $T$ has a different slope with respect to the configurational entropy of the bulk mixture, only a slight decrease of $T_K$ is detected upon confinement. Our results confirm the connection between dynamics and the thermodynamics energy landscape sampling as a function of temperature [3].

# References

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[3] A. Attili, P. Gallo and M. Rovere, Phys. Rev. E **71**, 031204 (2005).