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Thermodynamics and Vibrational Modes of Hard Sphere Colloidal Systems
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Summary

Colloids are ubiquitous in our everyday experience in various forms and have a wide range applications in foods, petrol, and drug industries. Additionally, colloids have become powerful model systems for scientist because of their relatively large length scales and concomitant long time scales that make it easy to study colloidal systems in real space and time. Colloidal hard sphere system is probably the simplest and the most studied system that mimics the behavior of atomic and molecular systems. Phase behavior of hard spheres is dictated by entropic contributions and is governed by only the volume fraction. The central question that we address in this thesis is the thermodynamics of colloidal hard sphere glasses. Understanding glasses is perhaps the most important unsolved problem in condensed matter physics. The thermodynamics of colloidal hard sphere glasses are directly related to the entropy and the vibrational dynamics of the system. In this thesis, we provide a direct measurement of the entropy and the vibrational modes of colloidal hard sphere glasses and compare them to those of the crystals which have been studied much more extensively.

In chapter 1, we present an introduction about the colloidal crystals and glasses. We then explain how the thermodynamics of hard sphere systems are directly related to their statistical geometry. The traditional cell theory for colloidal crystals is presented and its results for different determinations of the free volume are compared. Furthermore, vibrations in crystalline solids and the Debye behaviour for these systems are compared to the vibrational modes in glasses.

Chapter 2 discusses our experimental techniques in detail. We explain how we prepare our colloidal hard sphere suspensions and then discuss how to determine the particles size using the Dynamic Light Scattering (DLS) technique. The Laser Scanning Confocal Microscopy (LSCM) technique, its resolution in acquiring images and the data acquisition is explained in detail. We then discuss the method that is used to analyse the confocal images and to track the particles positions.

In chapter 3, we present the first measurements of the free energy of a glassy system. The concept of the free energy landscape and its deep minima is central in our current theoretical understanding of glassy systems. However, a direct measurement was so far not possible but has been achieved here. The determination of the free energy reveals the strong spatial and temporal heterogeneity of the free energy and its link to the slow structural relaxation that is the hallmark of glassy behavior. We find that similar to the Gutenberg-Richter law in seismology, the probability of particle rearrangements shows a power law dependence on the free energy changes associated with the rearrangements.

In chapter 4, we present the first experimental evidence that the excess of soft modes is an intrinsic property of glasses and does not arise due to structural disorder in crystals. This conclusion takes advantage of the opportunities offered by hard spheres, in which the crystal and glass phases can be compared at the same volume fraction, and for which a simultaneous measure of disorder and free energy is possible with experiments. We show that, this happens in spite of the observation that the fraction of particles with local six-fold symmetry in the very defected crystals is only slightly larger than in a glassy system. We show that, the vibrational and thermodynamical properties, i.e. the DOS and the entropy, for a defected

crystal are significantly different from those for a supercooled liquid or a glass, implying the different nature of the glass compared to a defected crystal.

In chapter 5, scaling relations with respect to the jamming point are reported for the density of states, the shear modulus, and the mean squared displacement that we measure experimentally. For the density of states, while our results are in great agreement with theoretical results for low frequencies, they are not reliable for high frequencies where experimental noise become very important. We find that both the shear modulus and the MSD show power law dependence on the distance from the maximum volume fraction with almost the same power, in very good agreement with theoretical predictions. The shear modulus increases with increasing the distance from the maximum volume fraction, while the MSD decreases with the distance from the jamming point.

In chapter 6, we investigate the effects of size polydispersity on the thermodynamics and the phase behavior of hard sphere systems. We do so by measuring the free energy for crystals and glasses and find that the free energy of crystal increases with increasing polydispersity however, for disordered systems it decreases with polydispersity. For both crystal and glass the free energy changes quadratically with the polydispersity with a same amplitude for both systems. The phase diagram for polydisperse hard spheres is presented. We show that for volume fractions larger than 0.58 and polydispersity larger than 12%, the system is always in the glassy phase and therefore never crystallizes on the experimental time scales.