CPP 17: Confined Fluids

Time: Tuesday 9:30–12:15 Location: ZEU 160

CPP 17.1 Tue 9:30 ZEU 160

Solid-liquid phase transitions in hard spheres and colloid-polymer mixtures — •Tatyana Zykova-Timan[1], Jürgen Horbach[2], and Kurt Binder[1] — [1]Institut für Physik, Johannes Gutenberg-Universität Mainz, Staudinger Weg 7, 5509 Mainz — [2]Institut für Materialphysik im Weltraum, Deutsches Zentrum für Luft- und Raumfahrt (DLR), 51170 Köln, Germany

We present the results of Monte Carlo (MC) simulations of liquid-to-crystal phase transitions in hard spheres and colloid-polymer mixtures, the latter modeled by the Asakura-Oosawa potential. In the traditional approaches such as thermodynamic integration or phase-switch MC, the coexistence point is computed from the estimates of bulk solid and liquid free energies. These methods are computationally demanding and do not provide any information about crystal growth kinetics.

On the contrary, we considered a direct simulation of solid-liquid coexistence in a slab geometry and obtained the melting point from an analysis of the interface velocity. Using Monte Carlo in the NPT ensemble we determined the coexistence pressures and kinetic growth coefficients. Their dependence on system size is investigated and compared to results reported in the literature. Moreover, the solid-liquid interface properties are studied including a careful analysis of finite size effects in the capillary wave spectrum.

CPP 17.2 Tue 9:45 ZEU 160

Lennard Jones Fluid in the Slit Pore. How Does It Nucleate? A Simulation Study. — •Nadezhda Gribova[1,2], Hamed Maleki[3], Axel Arnold[4], Tanja Schilling[3], and Christian Holm[1] — [1]Institute for Computational Physics, Stuttgart, Germany — [2]Institute for High Pressure Physics, RAS, Troitsk, Moscow Region, Russia — [3]Institute of Physics, Johannes Gutenberg-University, Mainz, Germany — [4]Fraunhofer SCAI, Bonn, Germany

A study of heterogeneous nucleation has practical reasons because it occurs more often in nature then homogeneous. The existing theories describe heterogeneous nucleation mostly phenomenological and are the extensions of classical nucleation theory. When fluids are confined in the pore their properties differ significantly from the bulk. In this work we report a study of one of the simplest models that is still capable to reproduce the thermodynamic behaviour of classical fluids, the Lennard-Jones system. Confining it between the structureless walls and observing layering in the system we ask ourselves: do walls induce heterogeneous nucleation? Does it start from the layers? Is the crystallization a 3D or 2D process? The talk will summarise our current answers to the above questions.

CPP 17.3 Tue 10:00 ZEU 160

Phase transitions of charged colloidal suspensions in slit pores — •Stefan Grandner and Sabine H. L. Klapp — Institut für theoretische Physik, Freie Universität Berlin, D-14195 Berlin, Germany

Employing Monte Carlo simulations in grandcanonical and isobaric ensembles we investigate freezing phenomena in a charged colloidal suspension confined to narrow slit-pores [1]. The macroion interactions are described by the Derjaguin-Landau-Verwey-Overbeek (DLVO) potential, which involves the counter- and salt ions implicitly, supplemented by a repulsive soft-sphere potential. Corresponding to experiments [2] we focus on moderately charged silica particles in solvents of low ionic strengths. The considered densities are too small to drive bulk freezing transitions. However, confining the suspension to sufficiently small pore widths does not only yield the well-known layering but also the formation of crystalline in-plane structures. This capillary freezing is consistent with ground-state calculations [3]. Furthermore, varying the parallel pressure at given surface separation we found a solid-solid transition from two-layer to three-layer systems with different in-plane order as found for uncharged spheres [4]. Finally, we consider the influence of wall charges including the possibility of charge-induced freezing.

[1] S. Grandner and S. H. L. Klapp, J. Chem. Phys., *accepted*.
[2] S. H. L. Klapp, D. Qu, and R. v. Klitzing, J. Phys. Chem. B **111**, 1296 (2007); S. H. L. Klapp, Y. Zeng, D. Qu, and R. v. Klitzing, Phys. Rev. Lett. **100**, 118303 (2008).
[3] R. Messina and H. Löwen, Phys. Rev. Lett. **91**, 146101 (2003).
[4] A. Fortini and M. Dijkstra, J. Phys.: Cond. Matter **18**, L371 (2006).

CPP 17.4 Tue 10:15 ZEU 160

Molecular dynamics simulation of evaporation processes of fluid bridges confined in slit-like pore — •Katarzyna Bucior, Leonid Yelash, and Kurt Binder — Institute of Physics, Johannes-Gutenberg University of Mainz, Mainz, Germany

We study a simple fluid, described by point-like particles interacting via the Lennard-Jones potential, under confinement in a slit geometry between two walls at distance L_z apart for densities inside the vapor-liquid coexistence curve. Equilibrium then requires the coexistence of a liquid “bridge” between the two walls, and vapor in the remaining pore volume. We study this equilibrium for several choices of the wall-fluid interaction (corresponding to the full range from complete wetting to complete drying, for a macroscopically thick film), and consider also the kinetics of state changes in such a system. In particular, we study how this equilibrium is established by diffusion processes, when a liquid is inserted into an initially empty capillary (partial or complete evaporation into vacuum), or when the volume available for the vapor phase increases. We compare the diffusion constants describing the rates of these processes in such inhomogeneous systems to the diffusion constants in the corresponding bulk liquid and vapor phases.

CPP 17.5 Tue 10:30 ZEU 160

Condensation of single drops. — •Mordechai Sokuler, Günter K. Auernhammer, and Hans-Jürgen Butt — Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz

Water condensation on surfaces, or growth of breath figures, is an important and common natural process with applications ranging from heat transfer to dew collection. Many works have detailed the growth of breath figures and their simulation. However, what has yet to be addressed comprehensively is the growth of individual, isolated droplets. Existing theory predicts drop volume increases linearly with time, between nucleation and the merging stage. We show the volumetric growth of isolated drops is much faster than predicted. Thus, the spacing of the drops becomes an important factor. And the distinction needs to be made between the growth of individual drops compared to tightly packed groups of drops. We use calculation of the concentration profiles of the two cases to predict the packing density required for each type of behaviour.

15 min. break

CPP 17.6 Tue 11:00 ZEU 160

Critical Casimir Forces in the presence of varying surface fields — •Ursula Nellen, Laurent Helden, and Clemens Bechinger — 2. Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, 70550 Stuttgart

In 1978 Fisher and de Gennes predicted that the confinement of critical fluctuations in a binary liquid leads to so-called Critical Casimir Forces. Direct experimental measurements of such forces has been only obtained recently. The amplitude of the Critical Casimir Force has been demonstrated to scale with the reduced temperature whereas a variation of the surface field from symmetric to antisymmetric boundary conditions changes the sign of the interaction from attraction to repulsion. Here we report first measurements where the amplitude of the surface field is systematically varied by controlling the surface properties of the confining surfaces. The Critical Casimir Forces are measured with total internal reflection microcopy between a single colloidal particle and a flat surface in a water - 2,6-lutidine mixture.

CPP 17.7 Tue 11:15 ZEU 160

Crystallization of soft crystals — •Max Wolff[1,2,3], Andreas Magerl[4], and Hartmut Zabel[1] — [1]Institute for Solid State Physics/EP IV, Ruhr-University Bochum, Germany. — [2]Insitute Laue-Langevin, Grenoble, France. — [3]Materials Physics, Uppsala University, Sweden. — [4]Crystallography and Structural Physics, University Erlangen-Nürnberg, Erlangen, Germany

The crystallization of metals or ionic crystals either propagates throughout the melt starting from a single seed or small grains grow and develop simultaneously at different locations. In the first case, a single crystal is formed, and the second case results in a polycrystal, which may show pronounced texture. The driving force is the ionic or metallic interaction with binding energies on the order of 100 kBT at room temperature. Inert gas crystals form as a result of much weaker van der Waals forces, and regarding the spherical shape of atoms, in most cases an fcc structure. Soft matter is also characterized by relatively weak binding energies of hydrogen bonds, entropic forces, or hydrophobic interaction.

The crystallization of micelles formed by surfactant F127 solvated by 20 % in water was investigated in the vicinity of a hydrophilic interface. Upon entering the crystalline phase from low temperature, a large correlation length develops without preferential texture. Upon heating, the correlation length decreases and Oswald ripening is observed with crystallites orienting with respect to each other while retaining long-range and textured correlation [1].

[1] M. Wolff et al.: Langmuir (Letter) doi: 10.1021/la803015t.

CPP 17.8 Tue 11:30 ZEU 160

Deformation of nanoporous materials during the sorption process — •Gerrit Günther and Martin Schoen — Stranski-Laboratorium für Physikalische und Theoretische Chemie, Sekretariat C7, Technische Universität Berlin, Straße des 17. Juni 135, D-10623 Berlin, Germany

Several experiments point at deformations of nanopores due to the sorption of confined fluids. To investigate such strains and their influence on phase behavior of the confined fluid we use the grand canonical ensemble Monte Carlo method (GCEMC). We consider a simple fluid between two plane parallel walls which themselves consist of single wall particles. Wall and fluid particles are of the same type and are interacting via Lennard-Jones(12,6) potentials. The wall particles are not fixed to their lattice sites but bound to them by harmonic potentials. Thus we are able to control the softness of the wall via the force constant of this harmonic potential from an almost rigid structure to more flexible walls. Flexible means that the wall atoms can move from their equilibrium positions to react to the fluid. Despite a shift of fluid phase transition flexible pores reveal a typical sequence of pore deformations during the sorption process even in the critical regime. It is remarkable that strains of our slit pore model are in good agreement with experimental results of cylindrical pores. [1] This suggests that dispersion forces rather than curvature effects are responsible for pore deformation.

[1] G. Günther, J. Prass, O. Paris, and M. Schoen, Phys. Rev. Lett. 101 (2008), 086104.

CPP 17.9 Tue 11:45 ZEU 160

Modelling pore lattice deformations during sorption and capillary condensation of fluids in ordered mesoporous silica — •Dirk Müter, Johannes Prass, and Oskar Paris — Max Planck Institute of Colloids and Interfaces, 14476 Potsdam, Germany

Sorption and capillary condensation of fluids in nanoporous silica materials like SBA-15 and MCM-41 can cause considerable deformations on the pore lattice[1]. Since these materials are promissing candidates for a wide range of applications (e.g. catalysts and filters) their deformation behaviour and mechanical stability are important fields of current interest. While the fundamental physical effects can be understood and modelled with simple pore models using Monte Carlo[1] or Molecular Dynamics simulations, the complex mechanical response of the whole pore lattice is not covered by these models. In this talk, the deformations of model crystallites under external and internal loads are calculated using the Finite-Elements-Method and their dependence on the porosity is analysed. The Finite-Element results are used to produce scattering curves which are compared to small angle x-ray scattering data from in-situ sorption experiments.

[1] Günther et al., Phys. Rev. Lett., 101 (2008)

CPP 17.10 Tue 12:00 ZEU 160

Analysis of sorption strains in ordered mesoporous materials by in-situ x-ray diffraction — •Johannes Prass, Dirk Müter, and Oskar Paris — Department of Biomaterials, Max Planck Institute of Colloids and Interfaces, D - 14424 Potsdam, Germany

Sorption and condensation of fluids create stresses in nanoporous materials. These induce strains in the porous matrix. The details of the solid matrix deformation, and how far in turn a strained matrix affects the sorption process are not well understood. In order to elucidate the extend of these interactions, we apply in-situ x-ray diffraction in ordered mesoporous materials during fluid sorption and condensation. Diffraction data provide not only valuable information on the pore structure and the fluid sorption behaviour [1]. Also "strain isotherms" - i.e. the strain of the pore lattice as a function of the fluid vapour pressure - are extractable from these experiments [2]. We investigated several different materials with 2D hexagonal pore ordering, and thereby varied the material, the porosity and the pore size. In addition we varied the fluid-solid interactions by using different fluids. We demonstrate that an "elastic modulus" can be extracted from the strain isotherms. This modulus cannot be directly related to the Young's modulus or the Bulk modulus due to the peculiar loading conditions which act within the porous body. We use simple analytical considerations and finite element analysis to better understand the relationship between measured strains and elastic properties of the porous solid.

[1] G. A. Zickler et al. (2006). Phys. Rev. B 73, 184109
[2] G. Günther et al. (2008). Phys. Rev. Lett. 101, 086104