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## Abstracts Invited Talks

All talks are in "Hs 7 Schütte-Lihotzky Hörsaal", TU Wien, Karlsplatz 13, 1040 Vienna

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### Novel entropy-driven phase behaviour in colloidal systems

Laura Filion

Over the last few years increased control over particle synthesis has led to a wide array of new colloidal building blocks. These building blocks, which are typically on the nano-to-micro meter scale, can spontaneously order, i.e. self-assemble, into structured arrangements, leading to astoundingly rich phase behaviour, i.e. solid solutions, liquid crystals, plastic crystals, columnar phases and many more. One of the more intriguing facets of colloidal phase behaviour involves the self-assembly and dynamics of so-called entropy-driven phases, i.e. phases where the entropic contribution to the free energy dominates the phase behaviour. Here, I will discuss a variety of different colloidal systems where the entropy has been found to play a crucial role in determining the phase behaviour resulting in counter-intuitive phenomena. In particular, I will show how entropic effects lead to a surprisingly high vacancy concentration in crystals of hard cube-shaped particles, how they stabilise an interstitial solid solution in binary mixtures of hard spheres, and how they successfully compete with the potential energy to strongly modify the phase behaviour of "patchy" colloidal particles.

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### The curious world of correlated materials

Philipp Hansmann

When electrons in a solid move not independently but correlated materials tend to be i) loaded with interesting physics and ii) notoriously difficult to treat theoretically. The reason for the latter is that the many-body Schrödinger equation is just impossible to solve due to the Coulomb interaction which couples the differential equations of all electrons. One strategy is to look for the best possible effective single particle descriptions: The most famous and successful realization of this strategy, which allows for a parameter-free (i.e. ab-initio) materials calculation, is the conception of density functional theory. A complementary strategy is to give up on being ab-initio and formulate toy models concentrating on microscopic "mechanisms" which might explain certain behaviour of a material: Here, the Hubbard model and its relatives are the most prominent representatives.

In the past 20 years the idea was born and pushed forward to merge the strengths of both strategies and derive low energy Hamiltonians from ab-initio methods. In my talk I will review some of the methods which are used to perform such derivation as well as the subsequent many-body treatment. Moreover, I will highlight different materials and experimental probes which show what can happen when there simply are no independent electrons.

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### The XC in DFT

Georg Madsen

Density Functional Theory and the self-consistent Kohn-Sham equations will be introduced. Local approximations to the exchange-correlation energy will be discussed. It will be explained how the results obtained with different versions of the generalized gradient approximation (GGA) can vary. Recent developments in local functionals including the kinetic energy density, so-called meta-generalized gradient approximations (MGGAs), are described. It is shown how MGGAs can solve the long-standing problem of the cross over between 2D and 3D structure for cationic and anionic gold clusters. The MGGAs stronger tendency towards 3D structures lies their smaller gradient enhancement, but contrary to GGAs with smaller gradient enhancements, MGGAs do not overestimate the atomization energy. Furthermore, it is demonstrated how weak interactions are fingerprinted in the kinetic energy density.

Madsen Phys. Rev. B, 75, p195108 (2007)

Ferrighi, Hammer, Madsen, J. Am. Chem. Soc., 131, p10605 (2009)

Madsen, Ferrighi, Hammer, J. Phys. Chem. Lett., 1, p515 (2010)

Ferrighi, Madsen, Hammer, J. Chem. Phys., 135, p084704 (2011)

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## Time-dependent wavefunction theories of atoms and molecules in intense laser fields

Takeshi Sato

Recent experimental progress in strong field and ultrafast physics makes it possible to directly measure and even control the electron motion in atoms and molecules on their natural time scale, i.e., attosecond. The time-dependent Schrodinger equation (TDSE) provides the rigorous theoretical framework for investigating such electron dynamics. However, direct real-space simulations of TDSE for more-than-two electron systems are extremely difficult. In this talk, I will present an overview of time-dependent wavefunction theories of atoms and molecules for describing multielectron dynamics in intense laser fields. Especially I will discuss how to generalize the time independent quantum chemical techniques to explicitly time-dependent problems.

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## Abstracts Contributed Talks

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### Classical two-dimensional Wigner crystals formed by an equimolar binary mixture

Moritz Antlanger

A classical two-dimensional Wigner crystal is composed of point charges on a uniform neutralizing background. The ground state of such a system is a simple hexagonal crystal [1]. Experimental realizations of this problem include electrons at the surface of liquid helium or in semiconductors. We investigate the ground state structures of an equimolar binary mixture of point charges. By introducing a single parameter, namely the dimensionless ratio  $q$  between the charges, the situation becomes much more complex. We perform theoretical considerations and derive a reference energy based on a phase separation scenario. This allows us to verify the stability of the structures we observe in the range  $0 < q \leq 1$ . All energies are calculated using high-precision Ewald summation techniques [2]. In an effort to identify possible ground state structures, we have employed an optimization tool based on ideas of evolutionary algorithms [3]. For large values of the ratio  $q$ , we observe phase separation; for smaller values of  $q$ , we identify six non-trivial ground states [4].

[1] G. Meißner, H. Namaizawa, and M. Voss, Phys. Rev. B 13:1370 (1976)

[2] M. Mazars, Phys. Rep. 500:43 (2011)

[3] D. Gottwald, G. Kahl, and C. Likos, J. Chem. Phys. 122:204503 (2005)

[4] M. Antlanger and G. Kahl, Cond. Matt. Phys. 16:43501 (2013)

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### Gel and solid structures formation with colloidal particles with heterogeneously charged surfaces (IPCs)

Silvano Ferrari

If charged colloidal particles are decorated on their surface by regions of opposite charge (so-called patches), the effective interaction between two such particles is characterized by a complex interplay between anisotropic attractive and repulsive contributions. We consider axially symmetric particles with a spherical, negatively charged core and two positively charged patches located at their poles; such particles are termed in the literature [1] inverse patchy colloids (IPCs). Using a faithful coarse-graining method one can derive for effective interactions of IPCs which faithfully capture both the geometry of the particles as well as the interaction behaviour.

Monte Carlo based investigations carried out so far [2] provide evidence that at low temperatures the system is prone to gel-formation. In an effort to better understand the reasons for this slowing down of the dynamics we have implemented a molecular dynamics simulation code that allows us to model IPCs via three rigidly connected interaction spheres [3]. Recording the particle positions, their velocities and their orientations along extended trajectories, single particle and collective dynamic correlation functions (such as the velocity autocorrelation function, the orientational correlation function, or the intermediate scattering functions) are

evaluated. A detailed analysis of the trajectories allows us to track which IPCs are trapped in the network and which are freely moving.

Our simulation data provide evidence of complex structure formations, with solid planes divided by liquid layers and immersed in a very diluted gas, with an interplay between the spatial and the rotational motion of the particles, in particular when one (or both) components of motion are (nearly) arrested. Additional comparisons of the fluid phase are made against Ornstein-Zernike type integral-equations [4].

[1] E. Bianchi, G. Kahl, C.N. Likos, *Soft Matter* 7, 8313 (2011)

[2] E. Bianchi, C.N. Likos, G. Kahl, *ACS Nano* 7, 4657 (2013)

[3] G. Ciccotti, M. Ferrario, J.-P. Ryckaert, *Mol. Phys.* 47-6, 1253 (1982)

[4] F. Lado, *Mol. Phys.* 47-2, 283 (1982)

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## Defect states at c-Si/a-SiN:H interfaces

Leif Eric Hintzsche

Modern electronic devices are unthinkable without the controlled formation of interfaces at heterostructures. These often involve at least one amorphous material. Modelling such interfaces poses a significant challenge, since a meaningful result can only be expected by using huge models or by drawing from many statistically independent samples. Here we report on the results of high throughput calculations for interfaces between crystalline silicon (c-Si) and amorphous silicon nitride (a-SiN:H), which are omnipresent in commercially available solar cells. The findings reconcile many hardly understood key features. At the interface, many threefold coordinated Si atoms are present. These are caused by the structural mismatch between the amorphous and crystalline part. The local Fermi level of undoped c-Si lies well below that of a-SiN:H. To align the Fermi levels in the device, charge is transferred from the a-SiN:H part to the c-Si part resulting in an abundance of positively charged, threefold coordinated Si atoms. This explains the existence of a positive, fixed charge at the interface that repels holes.

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## Diagrammatic Method to the Second Order Screened Exchange Energy in the Uniform Electron Gas

Felix Hummel

The second order screened exchange (SOSEX) energy is the leading order correction to the random phase approximation (RPA) of the correlation energy. We present a way to evaluate the RPA+SOSEX energy directly using diagrammatic methods without the coupled cluster formalism. The method is applied to the uniform electron gas using Monte Carlo integration to reach the thermodynamic limit. The agreement with QMC results is astonishingly good.

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## The role of one-body Green functions in electron transfer processes at Semiconductor-molecule interfaces

Emanuele Maggio

We have derived [1] an expression for the rate of non-adiabatic electron transfer between a semiconductor and a redox centre connected to the semiconductor via a molecular bridge. In this expression we explicitly consider the electron propagation across the bridge moiety, thus the relevant one-body Green function is evaluated. This model is particularly useful to study unwanted charge transfer process in technologically relevant systems such as dye-sensitized solar cells, where the dye is often connected to the semiconductor by a conjugated bridge. This formalism, designed to be coupled with density functional theory electronic structure calculations, can be used to explore the effect of changing the bridge on the rate of interfacial electron transfer. As an example, we have evaluated the charge recombination rate for a series of systems that differ in the bridge length. We have subsequently developed [2] a strategy to hinder the charge recombination processes in analogy with similar approaches to modulate charge transport across nanostructures. If a cross-conjugated fragment is present in the bridge it is possible to suppress the charge

recombination by negative interference of the possible tunnelling paths. Calculations carried out on realistic molecules show how the recombination lifetime can be modulated by changing the chemical structure for groups connected to the cross-conjugated bridge.

[1] E. Maggio and A. Troisi, *Philos. Trans. A. Math. Phys. Eng. Sci.*, 2014, 372, 20130011.

[2] E. Maggio, G. C. Solomon and A. Troisi, *ACS Nano*, 2014, 8, 4092-418.

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## Ultrasoft, cluster-forming systems under compression

Marta Montes Saralegui

We study the response of two-dimensional ultra-soft cluster crystals [1] under the influence of an external pressure- and temperature-reservoir. Using molecular dynamics simulations, the system is in contact with a combined baro- and thermostat which is realized via an ensemble of ideal gas particles [2]: pressure and temperature are triggered via the number of the particles and their velocities. Starting from a fluid state the system is compressed until it solidifies in an ordered hexagonal cluster lattice. Upon further increasing the pressure, the volume decreases while the lattice constant remains (essentially) constant. This is achieved by a merging process of neighbouring clusters. The mutual repulsion of the particles within these clusters leads, in turn, to activated hopping processes of individual particles which start to migrate through the system. After some time, the processes of cluster merging and particle hopping lead to an equilibrated state [3]. By tracing the particle positions we study this complex interplay of the two processes at different temperature and compression rates.

Our setup also allows to extract the equation-of-state of the system (i.e. the density as a function of pressure at some given temperature) via a combined compression-annealing experiment [4]. Due to the finite compression rate of our barostat we first obtain metastable states of our system along the compression line; launching expansion processes at selected pressure values leads to hysteresis loops. Now we take at given pressure value states along these hystereses and heat the corresponding configurations until they melt. Cooling these states subsequently down to the desired temperature leads via an annealing process to an equilibrium state at this particular pressure value, specified by an essentially ideal hexagonal arrangement of the clusters. Performing this annealing procedure for different pressure values leads to the equation of state.

[1] B. Mladek et al, *PRL* 96, 045701 (2006)

[2] M. GrÅEnwald and C. Dellago, *Mol. Phys.* 104,3709 (2006)

[3] M. Montes-Saralegui et al, submitted to *JPCM*

[4] M. Montes-Saralegui et al, submitted to *Soft Matter*

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## Magnetic field effects on the current fluctuations of a Kondo quantum dot out of equilibrium

Sarah Müller

The non-equilibrium electron transport through mesoscopic systems dominated by spin fluctuations is affected by the relaxation and decoherence processes resulting from the coupling of the spin to its environment. The understanding of their origin and their impact on the transport properties is of fundamental importance. We here study the finite-frequency noise of a quantum dot coupled to two non-interacting leads at different chemical potentials. Using the real-time renormalisation group, we determine the relaxation and decoherence rates characterizing the non-equilibrium transport in the Kondo regime. We show that while all resonances in the ac conductance are broadened by the transverse spin relaxation rate, in presence of a magnetic field the noise involves also the longitudinal rate as well as additional contributions characterised by the absence of any decay rate resulting in sharp kinks and singular derivatives. Our results provide a consistent theoretical description of recent experimental data for the emission noise at zero magnetic field, and present a detailed prediction for an extension to finite magnetic fields.

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## Computing the rate along a reaction coordinate with a bias potential

Ulf R. Pederson

A strength of computational condensed matter physics is its ability to compute rates along reaction coordinates. Time-scales that are accessible in a straight forward computer simulation, however, can be too short to study the event directly. Thus, special tools have been devised to compute the rate of rare events. We suggest to compute the rate from a computation where configurations are pinned to a certain part of the reaction path by adding an harmonic energy coupling to an order-parameter. The rate can then be computed from terminal exponential relaxation of the order-parameter assuming that dynamics along the reaction coordinate follow Smolokowski dynamics. Thus, the widely used umbrella sampling method is not only a way of computing free energies but also rates. To exemplify the general use of this method, we will investigate the solid-liquid transition. For the sake of simplicity we will only focus on the crystal growth part of the crystal nucleation event. We will refer to this as the interface pinning for computing crystal growth rates. Reference on interface pinning: [J. Chem. Phys. 139, 104102 (2013)].

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## The Structure of Ground States in 2d-Cubic Systems

Paolo Piovano

In this talk the fundamental crystallization problem of analytically explaining why particles at low temperature arrange in periodic lattices will be considered. At low temperatures particle interactions are expected to be essentially determined by particle positions. Cubic systems in two dimensions will be the main reference setting. More precisely, the problem consists in verifying the periodicity of the ground states of a suitable configurational energy that accounts for two- and three-body short-ranged interactions (see [1]). It will be first shown that every ground state is a connected subset of the square lattice and that the ground-state energy can be exactly quantified in terms of the number of particles. Furthermore, as the energy favors particle bonding and 'boundary' particles have in general less bonds, ground states can be intuitively expected to have minimal 'perimeter', or maximal 'area'. This intuition will be verified by introducing a suitable notion of perimeter and area of configurations, and by showing that ground states are characterized as those configurations which realize equality in a discrete isoperimetric inequality. Finally, the emergence of a square macroscopic Wulff shape as the number of particles grows will be shown. Specifically, it will be established that ground states differ at most by  $O(n^{3/4})$  particles from the ideal (square) Wulff shape configuration. This result nicely reflects the inherent multiscale nature of the crystallization phenomenon.

[1] Mainini E., Piovano P., Stefanelli U., Finite crystallization in the square lattice. Nonlinearity 27 (2014), 717-737.

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## Interfacial free energies in the FeCu<sub>1-x</sub> system from Monte Carlo simulations

Alice Redermeier

In the present work, we present an efficient method, based on the Monte Carlo technique, to study the curvature and temperature dependence of the interfacial energy of small precipitates in the Fe-Cu system. In our approach, we describe the interaction energies between atoms with pair potentials, which are dependent on the local chemical environment. These energies serve as parameters to perform variance-constrained semi-grand-canonical Monte Carlo simulations. The results of the Monte Carlo simulations are used to calculate the interfacial energies in Fe-Cu alloys. Our MC-results on the curvature and temperature dependence of the interfacial energy are in qualitatively good accordance with results obtained from continuum-mechanical approaches.

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## **Divergent precursors of the Mott metal-insulator transition in dynamical mean field theory and beyond**

Thomas Schäfer

Bulk electronic correlated systems can be often successfully studied by dynamical mean field theory (DMFT), which is able to properly describe the intrinsically non-perturbative phenomenon of the Mott-Hubbard metalto-

insulator transition (MIT). Recently it has been shown that the first hallmarks of the MIT can already be identified well inside the metallic regime in terms of divergences of the two-particle irreducible vertex [1]. Specifically, the strong enhancements and the sign changes of the irreducible vertex functions, which mark this precursor of the MIT, stem from enhanced local scattering processes and can be traced in the high temperature regime up to the atomic limit. This talk explores the nonperturbative region of the Hubbard model's phase diagram beyond the first precursor line towards the MIT in more detail and discusses the effects of the inclusion of short-ranged spatial correlations [2,3].

[1] T. Schäfer, G. Rohringer, O. Gunnarsson, S. Ciuchi, G. Sangiovanni and A. Toschi, Phys. Rev. Lett. 110 246405 (2013)

[2] T. Schäfer, M. Wallerberger, P. Thunström, G. Rohringer, G. Sangiovanni, A. Toschi, in preparation.

[3] J. LeBlanc, E. Gull, T. Schäfer, O. Gunnarsson, G. Sangiovanni, A. Toschi, in preparation.

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## **Electron rescattering at metal nanotips induced by ultrashort laser pulses**

Georg Wachter

The interaction of metal nanotips with near-infrared few-cycle laser pulses provides a unique testing ground for strong field physics in a confined solid-state environment. Due to the sharp tip apex, the laser field is locally enhanced triggering coherent electron emission from a nanoscale emission area at field strength well below the damage threshold. Electron spectra show signatures of strong-field physics, such as multi-photon peaks, carrier-envelope phase dependence, and plateau and cutoff structures [1,2]. We present theoretical studies encompassing the electrodynamics of the laser pulse near the tip apex as well as the quantum surface dynamics leading to electron emission, the latter treated with time-dependent density functional theory. Combined theoretical and experimental investigations allow us to link the observed spectra to the recollision of photoemitted electrons with surface atoms [3,4]. We discuss similarities and differences to rescattering at atomic targets, and the sensitivity of electron spectra to the spatio-temporal shape of the local electric field on the nanometer length and femtosecond time scale.

[1] M Schenk et al, Phys. Rev. Lett. 105, 257601 (2010)

[2] M Krüger et al, Nature 475, 78 (2011)

[3] G Wachter et al, Phys. Rev. B 86, 035402 (2012)

[4] M Krüger et al, New J. Phys. 14, 085019 (2012)