Correlations between hard objects in a continuum: Exact results

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Systems composed of hard objects in a continuum often show a tendency to order as the density is increased, but exact results on such systems are scarce. We consider a system of disks centred on either of two nearby parallel lines, and interacting only through mutual exclusion. Each disk attempts a random displacement on the line, and also exchanges its location between lines, with attempts being successful only if the hard core constraint is respected. The partition function involves both placements on the lines, and displacements along each line. In the constant pressure ensemble, the partition function is evaluated through an exact mapping to an antiferromagnetic Ising model in one dimension, with exchange coupling proportional to the pressure p. The system tends to develop a staggered order involving placements, and corresponding correlation functions can be evaluated. The correlation length diverges exponentially with increasing p. Other systems with hard core interactions between constituents on a continuous line can also be mapped similarly. Interestingly, systems of needle-like objects map onto Ising-like models, whereas if the objects resemble arrow heads, they map onto spin systems with chiral interactions and consequently a different behaviour of correlations. The dynamics of these systems have also been investigated by numerical simulation.
Event-chain Monte Carlo algorithm for hard-sphere systems

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Monte Carlo algorithms for hard spheres have changed little since the 1950s, especially for high densities. In two dimensions, the systems one can equilibrate today are much smaller than for the Ising model or for the XY model, for which powerful cluster algorithms are available. The nature of the melting transition in two-dimensional hard disks is still an open question.

I will present the Event-chain algorithm ¹, a rejection-free Markov-chain Monte Carlo algorithm, where an arbitrarily long chain of particles is displaced. This algorithm outperforms the conventional Metropolis method by two order of magnitude. Moreover, irreversible versions of the Event-chain algorithm accelerate the method even further, which is a telling example of the benefits of breaking detailed balance in Monte Carlo algorithms.

I will then show results of fully converged large-scale simulations which clearly prove the existence of the hexatic phase in between the liquid and the solid ².

Anomalous liquid to vapor nucleation in water
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We have investigated the nucleation of vapor bubbles in water subjected to high amplitude acoustic waves [1]. Measurement of the liquid density just before nucleation is performed with a fiber optic probe hydrophone [2]. The nucleation rate is also measured, and the size of the critical bubble determined with the nucleation theorem [3]. Our results reveal an unexpected nucleation mechanism, for which several explanations are proposed.

2. K. Davitt, A. Arvengas and F. Caupin, to appear in EPL.
Diblock copolymers self-assemble into a variety of periodic nano-structures in the bulk. In contact with a patterned surface, they may either replicate the surface pattern without defects or a more complex reconstruction of the morphology can occur depending on the mismatch between the symmetry and length scale of the surface pattern and bulk morphology. Certain patterns that do not have an analogue in the bulk, can be replicated by adding "defectants" to the copolymer material. These substances – e.g., homopolymers or nanoparticles – that enrich at locations, where the substrate pattern deviates from the bulk morphology, reduce the excess free-energy of these local structures, and thereby permit defect-free replication. This approach, however, requires fine-tuning of the composition and molecular architecture of defectants to the specific pattern. Using computer simulation of a coarse-grained model for supramolecular polymers we investigate the perspectives of quasi-block copolymers (QBCP) assembled on chemically patterned substrates for creating device-oriented nanostructures. QBCP are comprised of AB diblock copolymers and supramolecular B segments that reversibly bond to the B terminus of the diblock and themselves, creating a polydisperse blend of B homopolymers, AB and ABA copolymers. We demonstrate that the same QBCP replicates simultaneously defect-free patterns with perpendicular crossing, differing by up to 50% in their length scales, illustrating the high versatility of QBCP materials. The interplay between pattern geometry and distribution of molecular architectures and the key role of supramolecular associations for replicating patterns with different length scales will be discussed.
Fast Monte Carlo simulation of self-avoiding walks and related models of polymers

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We have developed a new data structure which enables efficient Monte Carlo simulation of polymers with hundreds of millions of monomers. Thus far, we have implemented this data structure for self-avoiding walks, and then used the pivot algorithm to simulate walks on the simple cubic lattice with up to 270 million steps. Consequently we have determined the critical exponents $\nu$ and $\gamma$ to unprecedented precision.

For $N$-step self-avoiding walks our implementation performs pivot moves in average case time $O(\log N)$, which is dramatically faster than previous methods. For simulations of walks of 1000 steps on the simple cubic lattice our method is at least a factor of 4 faster than previous implementations, whereas for walks of $10^6$ steps our method is more than 300 times as fast.

We will describe this new data structure, and give heuristic arguments as to why it is so effective. We will discuss how to implement a wide range of global moves, such as pivots, in time $O(\log N)$ or better, and show how to adapt the data structure to other models of polymers with short-range interactions, on the lattice and in the continuum.

In the near future we will release our implementation as an open source software library which promises to be widely useful in the field of polymer simulation.
Metastable liquid water: Four theories in one

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Four scenarios have been proposed for the supercooled liquid water, each predicting different thermodynamics. As there is no definitive experimental test, it is still unclear which of the scenarios best describes water. Here, by combining mean field calculations and Monte Carlo simulations for a coarse-grained model, we show that a common physical mechanism underlies each of the four scenarios, and that two key physical quantities determine which scenario describes water: (i) the strength of the directional component of the hydrogen bond and (ii) the strength of the cooperative component of the hydrogen bond. We argue that our conclusions are model-independent and that experimental parameters support the existence of a liquid–liquid critical point at positive pressure [1].

A possible transition scenario between the two liquid phases in SnI₄

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From in situ synchrotron x-ray diffraction measurements on liquid tin tetraiodide, we have established that the liquid forms existing above and below a break point pressure of ∼ 1.5 GPa, where the slope of the melting curve of the solid phase changes abruptly, have different structures. This discovery offers evidence of thermodynamically stable polyamorphism in general compounds as well as in elements such as phosphorus. The vertex-to-face orientation between the nearest molecules with regular tetrahedral symmetry plays a key role in the transition from the low-pressure to the high-pressure liquid phase.

Four scenarios have been hitherto proposed regarding the polyamorphic transitions in water. Among them, the liquid – liquid critical point (LLCP) scenario, which presumes the existence of a critical point associated with the liquid – liquid phase transition, seems to be naturally applicable to describe the aspect observed in SnI₄. Indeed, the LLCP scenario can consistently explain all our findings. Our recent experimental investigation suggests that the LLCP is, if it exists, located close to the break point on the melting curve. We found by mean-field treatments for the scenario 20 JK⁻¹mol⁻¹ and −3.7 × 10⁻⁶ m³mol⁻¹ for differences in the molar entropy and volume, respectively, between the two liquid phases. Although the former is about 5 times larger than the one between the two amorphous states in ice, the latter is quite comparable with that of ice, implying that the value represents a specific volume contraction upon collapsing a tetrahedral open network structure.
Inhomogeneous flow and fracture of glassy materials

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The fracture mechanism of amorphous materials, which are of crucial importance in various fields of engineering, remains a long-standing fundamental problem of science despite intensive efforts over the years. On the basis of a novel rheological model of fracture, we demonstrate that nonlinear behavior associated with fracture is a consequence of the coupling between density fluctuations and deformation fields: shear-induced enhancement of density fluctuations is self-amplified by the resulting enhancement of dynamic and elastic asymmetry between denser and less-dense regions. This positive feedback may be the origin of fracture. We propose novel criteria for the onset of mechanical instability, extending from ductile to brittle fracture. Their validity is checked by comparing them with numerical solutions of our model and existing experimental results of metallic and polymeric glass formers. The criteria enable us to predict and design fracture behavior of materials from the pressure dependence of their viscoelastic properties.
Phase diagram and structural information within a simple model of patchy colloids

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We report on a computer simulation and integral equation study of a simple model of patchy spheres, each of whose surfaces is decorated with two opposite attractive caps, as a function of the fraction $\chi$ of covered attractive surface. The simple model explored — the Kern-Frenkel model — interpolates between a square-well ($\chi = 1$) and a hard-sphere potential ($\chi = 0$) on changing the coverage.

Both the one and two-patches cases are discussed. We show that integral equation theory provides quantitative predictions in the entire explored region of temperatures and densities from the square-well limit down to a significantly small $\chi$ whose value depends upon the number of patches.

A detailed study of thermodynamics and structural quantities is performed with special attention on the effect of patch size and location. It is shown that for sufficiently small $\chi$ crystallization prevents the possibility of observing the evolution of the line of critical points, providing the angular analog of the disappearance of the liquid as an equilibrium phase on decreasing the range for spherical potentials.

Other interesting structures (micelles, lamellae, chains etc) are also observed at extremely low coverages.

Structural search, packing and assembly of binary spherical nanoparticles

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The packing of binary hard spheres has a long history due to its relevance to alloys and colloidal crystals and more recently the designed self-assembly of nanoparticles. Until recently, dense structures have been found by design or experiment. We have applied a range of stochastic structural search methods to the problem. These include data mining from a database of inorganic crystals, and simulated annealing within reduced-dimension structure-type configuration spaces. We reproduce all known dense packed structures, and additionally find a number of novel structures which exceed the packing fraction of segregated close packed spheres. We examine the consequences for phase diagrams for the self-assembly of such hard spheres. Some of our packings occur outside the previously identified range of stability in terms of the ratio between particle radii. The structures show a wide variety of compositions (AB, A2B, A3B, A13B) and motifs (including nanowires, layered structures and near-icosahedral clusters).
Effect of solvent quality on the dynamics of dilute dendrimer solutions

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Dendrimers represent a special class of hyper-branched polymers. In this work, the dynamics of dilute solutions of dendrimers are studied using Brownian dynamics simulations of coarse-grained bead-spring chain models. Both intra-molecular hydrodynamic and excluded volume interactions are incorporated. The effect of molecular topology on the structural and dynamic properties of dendrimers with different generation numbers and molecular weights is studied in solvents of varying solvent quality, and compared with the behaviour of linear polymer chains of similar molecular weights. The successive fine graining technique is applied to obtain parameter free predictions of properties as a function of solvent quality. In particular, it is shown that with a suitable definition of the solvent quality parameter, the swelling of dendrimers with increasing solvent quality can be collapsed on to a single master curve for chains with the same molecular topology. Swelling of dendrimers is found to cause a decrease in the translational diffusivity, and a shift in the characteristic maximum in intrinsic viscosity with molecular mass to higher generation numbers. Ratios of the radius of gyration to the hydrodynamic and viscometric radii differ for dendrimers with differing generation numbers, but converge to constant values for dendrimers with a fixed degree of branching.
Ion effects on the phase transition in aqueous mixtures and related topics

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Even a small amount of salt can strongly affect phase separation in aqueous mixtures due to preferential solvation. (i) Hydrophilic and hydrophobic ions behave antagonistically around water-oil interfaces, reducing the surface tension and leading to mesophases, as observed in recent experiments. (ii) With hydrophilic ions, we predict precipitation of salted water domains even outside the coexistence curve as in Fig.1. This effect gives heterogeneities (typically 10 nm) detected by many dynamic scattering experiments. This water precipitation mechanism also produces strong attraction among charged particles due to composition heterogeneities as in Fig.2 and a number of dramatic effects of wetting of salted water.

Figure 1: Compositions $\phi_\alpha$ in precipitates and $\phi_\beta$ outside them vs interaction parameter $\chi$ with fixed density $\bar{n}$ of hydrophilic ions (left). Volume fraction of precipitates $\gamma_\alpha$ and their salt density $n_\alpha$ (right).

Figure 2: Free energy vs separation $D$ between two charged particles. Its negative slope implies attraction.
We investigated the response of an oil droplet floating in an aqueous solution while subjected to laser irradiation. Four distinct modes in the motion of the droplet were observed: oscillation, translation, budding, and splitting. Switching between these modes was achieved by altering the laser intensity. We found that the mechanism of the mode selection is determined by the interplay between thermal convection and capillary effects. This new scheme can be useful for constructing and controlling optical devices, such as the ‘total-optical-lab-on-a-chip’.
A maximum-entropy closure for predicting slow dynamics near the coil-stretch transition in dilute polymer solutions

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Recent simulations and experiments have verified the existence of the coil-stretch transition [P. G. De Gennes, J. Chem. Phys., 60:5030-5042 (1974)] in extensional flows of dilute solutions of flexible homopolymers. In a window of extensional rates close to the transition, balance between opposing elastic and hydrodynamic forces on an individual polymer molecule is achieved at two different configurational states. Thermal fluctuations cause molecules to hop from one stable state to the other, but long molecules become kinetically trapped in deep local minima in the non-equilibrium free energy. This leads to strong memory effects and slow dynamics.

Constitutive models derived using moment-closure approximations for coarse-grained dumbbell models of polymer molecules incorporating a conformation-dependent friction coefficient, incorrectly predict two steady-states close to the transition, whereas in the exact model, hysteretic effects vanish beyond a characteristic ergodic time-scale, leading to unique steady-state properties. We show that a maximum-entropy closure approximation avoids this problem. The approximate steady-state probability distribution is bimodal in the coil-stretch hysteresis regime, and compares well with the true distribution. Implications to other thermally fluctuating systems with multiple mechanical steady states is discussed.
Nonequilibrium depletion force in a temperature gradient

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We found a novel nonequilibrium phenomenon of colloids in polymer solution. The nonequilibrium distribution of colloids in a polymer solution under a temperature gradient is studied experimentally. A slight increase of local temperature by a focused laser drives the colloids towards the hot region, resulting in the trapping of the colloids irrespective of their own thermophoretic properties. An amplification of the trapped colloid density with the polymer concentration is measured, and is quantitatively explained by hydrodynamic theory. The origin of the attraction is a migration of colloids driven by a nonuniform polymer distribution sustained by the polymer \(\Delta T\) thermophoresis. These results show how to control the thermophoretic properties of colloids and provide a new micromanipulation.
Spatio-temporal variation of granular temperature in the pattern formation of vibrating granular material

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Trajectories of particles in vertically vibrating granular systems under atmospheric pressure were measured by a high-speed video camera. Kinetic energy, or effective temperature, of each particle was visualized in color scales, which clearly reveals the onset and characteristic behavior of the vibration-induced pattern formation in either planar patterns in a thin flat layer (e.g., squares and stripes) or vertical patterns in a layer between narrowly spaced vertical walls (e.g., undulations and ripples). In the former, we found

(i) a peculiar orientational distribution of velocity of the constituent particles relative to the planar cellular structures, which depends on the material properties like particle size $d$, density $\rho$, and friction coefficient $\mu$, besides external forcing (frequency $f$ and amplitude $a$).

On the other hand, in the latter, we found

(ii) the propagation of density waves along the bending waves of a thin granular layer in an elastic phase (i.e., undulation mode), which is generated by the horizontal dilatation of the material at the impingement on the container wall, and which depends on the microscopic properties like $d$, $\rho$, $\mu$ and the number of particles $N$ in the layer, whereas we found

(iii) the development of locally "melted" region to and from fluid-like surface waves (i.e., ripples) in a thicker granular layer, whose wavelength depends on the mobilized part of the layer thickness and the wave propagation speed.

These solid-fluid transitions and the spatio-temporal variations are well described by the granular temperature that is calculated from the velocity measurement of the particles.
Disordered spherical bead packs are anisotropic

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Investigating how tightly objects pack space is a long standing problem, with relevance for many disciplines ranging from discrete mathematics and the theory of glasses to the shipping industry. Here we report on the fundamental yet so far overlooked geometric property that disordered mono-disperse spherical bead packs have significant local structural anisotropy manifest in the shape of the free space associated with each bead (i.e. its Voronoi cell). Jammed disordered packings from several types of experiments and simulations reveal very similar values of the cell anisotropy, showing a linear decrease with packing fraction. This behaviour is universally observed, independent of the preparation method. Strong deviations from this trend are observed for unjammed configurations and for partially-crystalline packings above 64%. These findings suggest an inherent geometrical reason why, in disordered packings, anisotropic shapes can fill space more efficiently than spheres and have implications for packing effects in non-spherical liquid crystals, granular aggregates, foams and structural glasses.
An accurate, simple and robust microscopic model for the prediction of fluid slip

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In this presentation we provide a derivation to predict the slip velocity for a fluid flowing in the near vicinity of walls. In particular we present results for a system of an atomic fluid confined by atomistic walls at the nano-scale. Our derivation is based upon forming equilibrium time correlation functions of relevant measurable fluid properties. These correlation functions are formed for increasingly fine-grained slabs of fluid adjacent to the walls. By computing the various correlation functions we are able to extract the slab friction coefficient adjacent to the wall for a limiting slab width, and hence the slip velocity for the fluid, to very high accuracy. We present numerical results from non-equilibrium molecular dynamics (NEMD) simulations to verify our theoretical predictions. We further demonstrate the model’s high accuracy and robustness by presenting excellent agreement between predicted and NEMD slip lengths for several flow geometries and fluid-wall interaction potentials that mimic hydrophobic and hydrophilic behaviour. Our method allows for predictions of slip and flow profiles for highly confined fluids at a fraction of the time it would take for brute force NEMD simulations.
A systematic study of the influence of torsional flexibility on the self-diffusivity of a series of linear alkanes.

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Chain flexibility is known to have an impact on the transport properties of non-simple fluids. Measuring the extent of this coupling between torsional flexibility and the simplest transport property, self-diffusion, in isolation of all other contributing factors is beyond the reach of current experimental methods. However, the task is perfectly suited to a computational statistical mechanical approach.

A computational scheme has been devised by which the contributions to chain mobility arising solely from torsional motion can be determined unambiguously. The method, known as Frozen Distribution Sampling (FDS), ensures that comparisons are made between fluids in corresponding thermodynamic states. Using FDS in conjunction with equilibrium Molecular Dynamics, the extent of this coupling has been determined for a series of straight chain alkanes ranging from 4 to 40 carbon atoms in length. For the shorter chain alkanes, the coupling appears to be weak. In the 40 carbon chain, however, the coupling is strong – removal of all torsional degrees of freedom leads to a significant reduction in self-diffusivity.
Flexible polymer chains under shear flow

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The presence of low amounts of polymer in a Newtonian solvent can change the properties of the solution, in particular change it to a Non-Newtonian fluid. These solvents have been studied for many years and in the last decade also the dynamics of a single polymer has been explored theoretically and experimentally.

We present results for the structure and dynamics of a single flexible polymer under shear flow, studied by Brownian dynamics simulation of the bead-spring model. The role of different kind of interactions, bond spring, exclude volume and hydrodynamic interactions have been considered. The results show that a coupling between the polymer modes in the three directions of space is needed for recover the experimental scaling laws. The key interaction required for achieve this coupling is a finite compressibility along the chain. Such coupling can be maintained over a wide range of shear rate, from Weisemberg number 1 to 1000.

We present an analysis of the single chain dynamics, in particular the existence of two characteristic times which depends on the shear rate. One time is associated with a tumbling processes in the flow-gradient plane and the other's associated with the diffusion of the chain in the gradient-vorticity plane.
A thermodynamic route through the glass transition to solid phase/size separated states of colloids

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We study at equilibrium, by means of microcanonical Monte Carlo simulations, a polydisperse soft-spheres model for colloids with a polydispersity as high as 24%. Although solidification occurs, neither an homogeneous crystal nor an homogeneous amorphous state are thermodynamically stable.

By introducing suitable order parameters to measure the degree of crystallinity and inhomogeneity, a finite size scaling analysis reveals that in the thermodynamic limit: a) the fluid-solid transition is rather a crystal-amorphous phase-separation, b) such phase-separation is preceded by the dynamic glass transition, and c) a size-separation also occurs, where small and big particles arrange themselves in the two phases according to a complex pattern not predicted by any existing fractionation scenario.
The effect of interfaces on the self-assembly of nanorods

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This work describes recent progress in understanding how to direct the self-assembly of nanorods, using the tools of continuum energetics, statistical mechanics and computer simulation at multiple scales.

Synthesizing nanometer-scale objects with controlled optical and electronic properties is now a relatively straightforward task, however organizing such objects into extended structures that could revolutionize technology remains a challenge, especially for anisotropic particles.

Nanorods behave like liquid crystals in solution and can form ordered structures with the rods oriented parallel or perpendicular with respect to a substrate upon drying, assemblies that could potentially be used to print nanostructured solar cells.

For ligand-passivated nanorods, we analyse rod-rod and rod-interface interactions using Hamaker-Lifshitz theory, surface energies, and constraint MD simulations with explicit ligands and solvent. We show that the ligands can undergo a phase transition, and that the choice of substrate and solvent is often more important than the nature of the crystalline core.

We derive coarse-grained potentials for the rod-rod and rod-substrate vdW interactions, the rod-substrate depletion-attraction interaction, and the rod-solvent-air interface interaction. Using MC simulations we characterize the effect of these interactions on the phase behavior and mechanism of self-assembly of the rods.

We show that the rod-rod interaction determines whether multilayer or single-layer lamellar crystals nucleate and grow in solution. Further, we find that a subtle balance between the rod-rod and rod-interface interactions determines whether nucleation occurs in solution, on the substrate, or at the air-solvent interface, and whether it occurs with the rods oriented parallel or perpendicular to the interface.