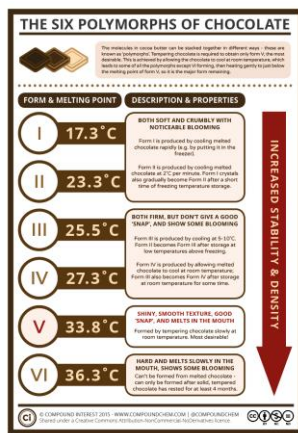


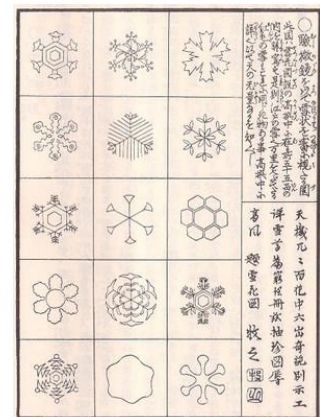
## “What states of matter are there?”

The Nobel Prize in Physics of 2016 was awarded to David Thouless, Michael Kosterlitz, and Duncan Haldane, for the discovery of topological phase transitions and topological phases of matter. The accompanying report of the Nobel Prize committee dedicated a special section to the question “What states of matter are there?” [1]

According to Nature, an overwhelming variety. Even a seemingly simple substance as water can appear in many different crystalline forms of ice, or descend in a wild mixture of perfectly regular snowflakes [2]. And then there are the six different crystalline forms of chocolate, of which one is particularly delicious [3] and difficult to obtain. Most real materials show a great variety of phases beyond the well-known division of solid, liquid or gas. Glasses, gels, polymers and liquid crystals each have their own unique properties, and there are many other complex manifestations of matter, in particular in organisms.



The six polymorphs of chocolate  
 (© Compound Interest)



Sekka Zusetsu,  
 by Doi Toshitsura (1832)

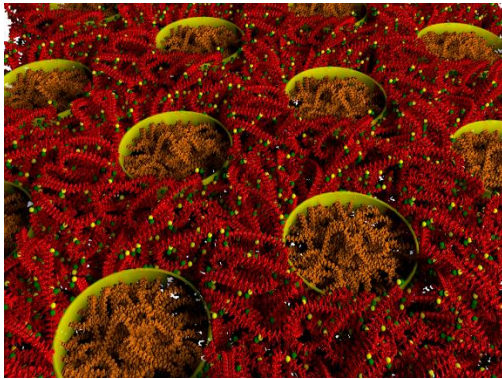
My research group develops theory to predict these phases, and to find the necessary conditions under which they form. Even more general, our goal is to characterize and understand the behavior of complex systems, and how this behavior is connected to its individual components. This includes phenomena such as pattern formation, spontaneous collective dynamics, sudden catastrophies, and the emergence of characteristic structures and time scales.

My group uses a variety of theoretical and computational methods invoking statistical mechanics, statistical thermodynamics, density functional theory, field theory, liquid state theory, Monte Carlo-type simulations, molecular dynamics, network theory, and other related methods. A few selected research topics are highlighted below, relating to polymers, pattern formation in ensembles of self-propelled particles, nanoparticles, and strongly interacting electrolyte solutions.

## Polymers

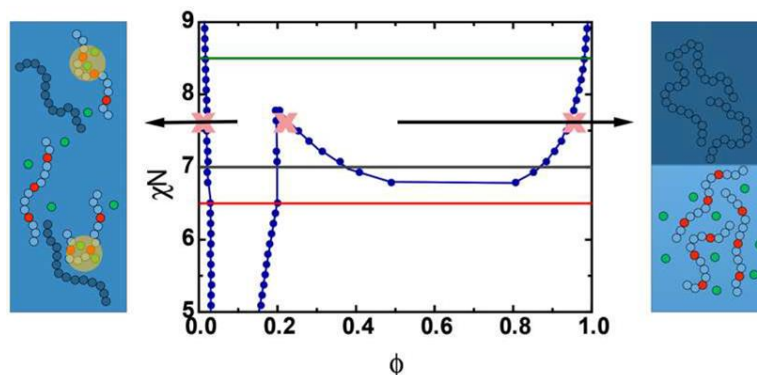
Polymers (plastics) are highly versatile materials that can combine different mechanical, electrical, and optical properties in a single material, and can be designed to form characteristic structures and symmetries at multiple length scales. The range of possibilities defies the imagination; organisms only need a handful of amino-acids to synthesize the millions of proteins that constitute the body and its functional properties. Progress in materials design would benefit greatly from predictive theory and computational methods, to support the experimental trial-and-error approach.

The level of complexity poses great challenges to theoretical modeling. Each polymer is in itself a complex object consisting of many segments, and capable of assuming various forms, depending on the environment. An ensemble of trillions of polymers therefore seems impossible to describe, and resembles in many aspects a gigantic can of worms. Field theory of polymers is a powerful



method to reduce the complexity to that of a single polymer, suspended in a 'field' that mimics the effect of all the other polymers. By a special coupling between the behavior of the single polymer and the field, one can calculate a 'self-consistent' solution to the problem that was demonstrated to be useful for neutral polymers[4]. Recently we developed a hybrid method, invoking liquid state theory, to include the effects of charge and strong coupling. However there are still formidable outstanding

questions with regards to the behavior of semi-dilute solutions, heterogeneous copolymers, and polymers out of equilibrium. We approach these complex systems from multiple directions, using theoretical and computational tools.



Phase diagram of a binary mixture of charged and neutral polymers

## Self-propelled particles, dissipative structures, and oscillatory states

Ludwig Boltzmann developed a theory that connected the thermodynamic laws of gases to the chaotic microscopic mechanics of tiny gas-particles. Ensembles of bacteria, fish and bird flocks behave similar to gas molecules in the sense that they form complex structures and group behavior based on relatively simple neighbor interactions. There are many examples of ‘active particles’ that have the ability to propel themselves by dissipation of energy and interact with other particles according to a non-random protocol. The emergence of structure in ensembles of such particles is a challenging problem and beyond the very assumption of Ludwig Boltzmann of ‘molecular chaos’ which was required to understand ‘passive matter’.

Ensembles of self-propelled squares show a very specific collision dynamics that is dependent on the direction of self-propulsion [5]. We found that particles that swim in the direction perpendicular towards their side (TS particles) quickly reach a steady state with a characteristic cluster distribution and Gaussian fluctuations. In sharp contrast, particles that swim in the direction towards one of their corners (TC particles) form large transient clusters and show periodic oscillations between a state of large dense clusters and mobile small clusters. TC particles are also more mobile within a cluster than TS particles. Both particle types seem to be miscible in a 50-50 ratio, but also form small micro-domains within transient clusters. TS particles also mix well with passive particles and impart their dynamic properties onto the passive ensemble, in contrast to TC particles.

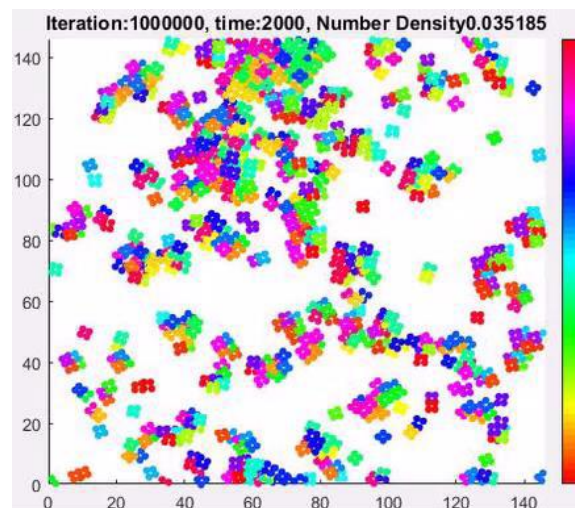
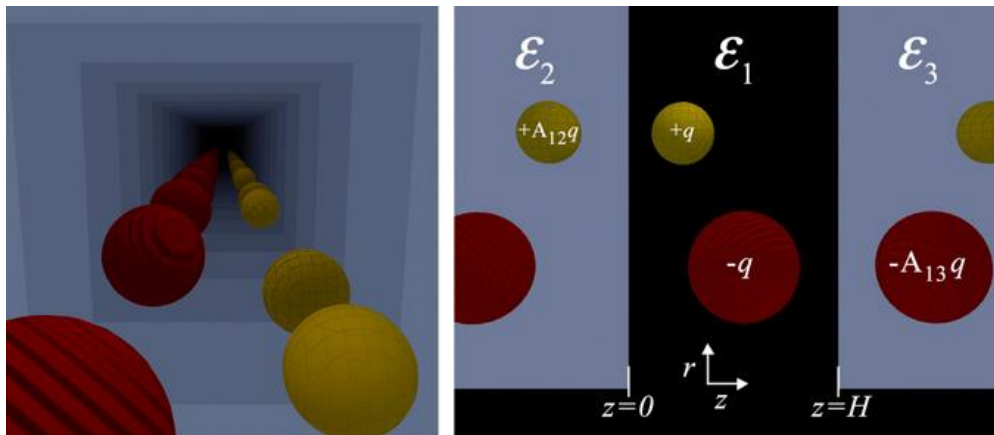


Figure 1 Snapshot of an ensemble of TC particles.  
 The colors represent their direction of motion.

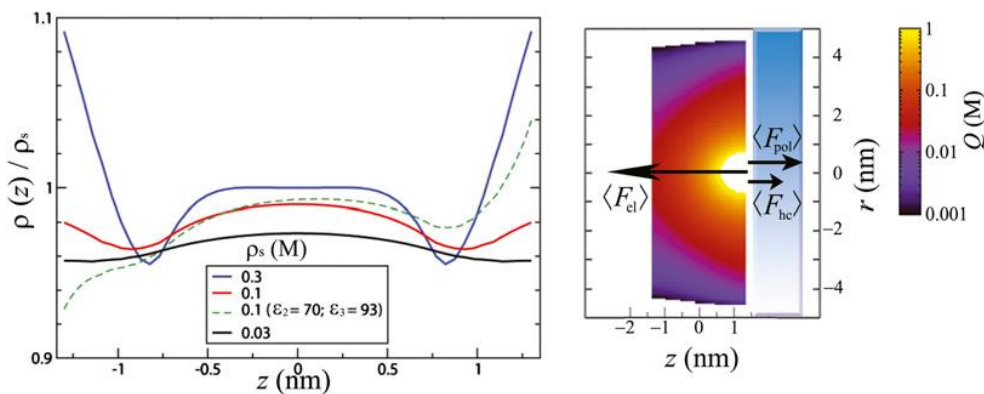
These radical differences in behavior are purely based on the direction of self-propulsion and can therefore not be understood from the well-known ensemble theory of statistical thermodynamics. We find inspiration in approaching the clustering dynamics as a reaction network, where the clusters are considered reaction products, and the collisions and break ups as reactions. The topology of this reaction network suggests the possibility of long reaction chains that loop back to their starting point, within a characteristic time. The dynamics of reaction networks can underpin the complex ensemble behavior of self-propelled particles, but is also a meaningful approach to other complex phenomena such as gene expression and other biological, social and economic networks.

## Charge at the Interface

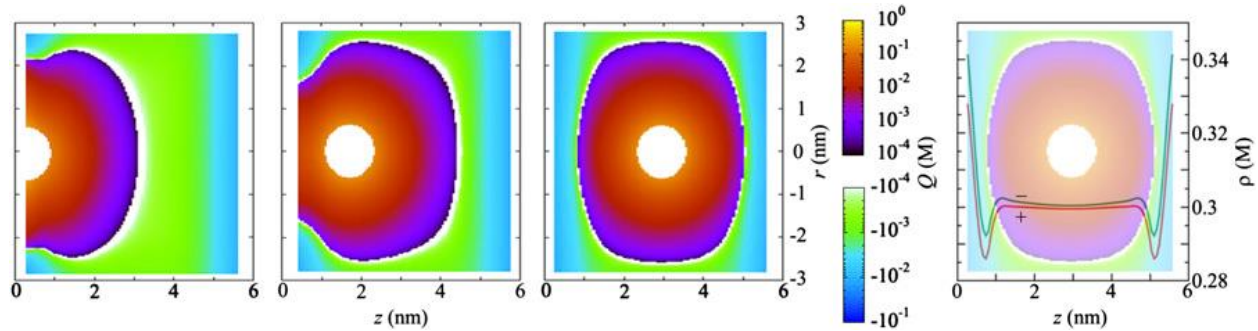
“The behavior of ions in liquids confined between macromolecules determines the outcome of many nanoscale assembly processes in synthetic and biological materials such as colloidal dispersions, emulsions, hydrogels, DNA, cell membranes, and proteins. Theoretically, the macromolecule-liquid boundary is often modeled as a dielectric interface and an important quantity of interest is the ionic structure in a liquid confined between two such interfaces. The knowledge gleaned from the study of ionic structure in such models can be useful in several industrial applications, such as in the design of double-layer supercapacitors for energy storage and in the extraction of metal ions from wastewater.” [excerpt from: Yufei Jing, Vikram Jadhao, Jos W. Zwanikken, and Monica Olvera de la Cruz. "Ionic structure in liquids confined by dielectric interfaces." The Journal of chemical physics 143, no. 19 (2015): 194508.]



The 'method of images' applied to mobile ions in a slab geometry [7]



Average density of ions between two neutral walls (left) and mean forces acting on an ion near a dielectric boundary (right) [7]



Average charge density around an ion between two charged walls, surrounded by a sea of other ions [7]

[1] Scientific Background on the Nobel Prize in Physics 2016 *topological phase transitions and topological phases of matter* compiled by the Class for Physics of the Royal Swedish Academy of Sciences

[2] Sekka Zusetsu, Doi Toshitsura (1832)

Kajikawa, Masahiro. "Structure and falling motion of early snowflakes." *Annals of Glaciology* 6 (1985): 269-271.

[3] Schenk, H., and R. Peschar. "Understanding the structure of chocolate." *Radiation physics and chemistry* 71, no. 3-4 (2004): 829-835.

[4] Edwards, S.F., 1965. "The statistical mechanics of polymers with excluded volume". *Proceedings of the Physical Society*, 85(4), p.613.

[5] Robert Martin and Jos W. Zwanikken

[6] Yufei Jing, Vikram Jadhao, Jos W. Zwanikken, and Monica Olvera de la Cruz. "Ionic structure in liquids confined by dielectric interfaces." *The Journal of chemical physics* 143, no. 19 (2015): 194508.]

[7] Jos W. Zwanikken, and Monica Olvera de la Cruz. "Tunable soft structure in charged fluids confined by dielectric interfaces." *Proceedings of the National Academy of Sciences* 110, no. 14 (2013): 5301-5308.