# The European Centre of Excellence for Software, Training and Consultancy in Simulation and Modelling

Supporting HPC simulation in industry and academia

E-CAM Newsletter Issue 1, January 2016

Funded by the European Union

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# E-CAM Calendar of Events

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|---|---|---|
| | **JUNE 2016** | |
| **TBC** | State of the Art Workshop: Electronic Structure | Daresbury |
| **TBC** | ESDW: Trajectory Sampling | Vienna |
| | **JULY 2016** | |
| **TBC** | ESDW: Quantum Mechanics and Electronic Structure | Paris |
| | **AUGUST 2016** | |
| **29 Aug -2 Sept** | State of the Art Workshop: Reaction Coordinates from Molecular Trajectories | Leiden |
| | **SEPTEMBER 2016** | |
| **7-9 Sept** | Scoping Workshop: Industry Partnerships | Mainz |
| | **October 2016** | |
| **TBC** | ESDW: Wannier Functions | London |
| | **November 2016** | |
| **7-9 Nov** | 2nd General Assembly | Paris |


*Editors: Kate Collins & Dónal Mac Kernan Main Contributors: Luke Dury; Damien English Minister for Skills, Research and Innovation. Includes edited excerpts from recent topical publications by members of the E-CAM consortium and their collaborators.*

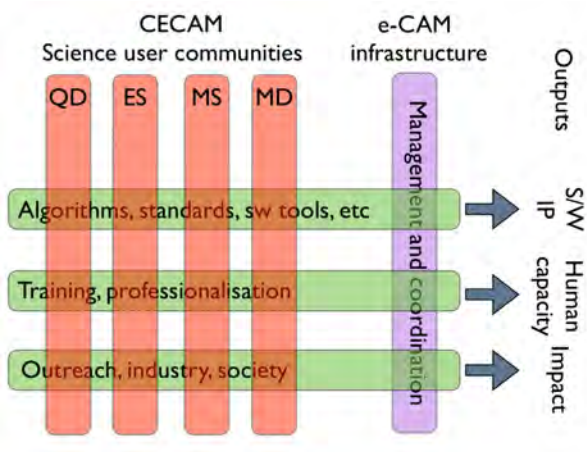
# 1 E-CAM in a nutshell

Luke Drury E-CAM Chair, University College Dublin & Dublin Institute for Advanced Studies, email: ld@cp.dias.ie


The E-CAM centre of excellence is based around the experience and scientific community of the extended CECAM family, established over more than four decades, as well as the computational and hardware expertise of the European partnership PRACE. Since its founding in 1969 CECAM has been at the forefront of promoting computational simulation as a powerful research tool for understanding and predicting the properties of materials, including biological systems, both at European and international level. E-CAM in partnership with PRACE and the other centres of excellence will now build on and broaden this by adding a strong infrastructural element as part of the European Union's ambitions for HPC under Horizon 2020.

At the scientific level E-CAM has chosen to prioritise four broad areas of science that are central to the interests of CECAM. These vertical scientific pillars are electronic structure calculations, classical molecular dynamics, quantum dynamics, and meso-scale and multi-scale modelling; in addition to covering most of the scientific interests of the extended CECAM community these areas were chosen because they are also of considerable interest to industrial researchers. At the institutional level E-CAM takes advantage of the distributed nodal structure of CECAM and brings together 18 institutions with a good geographic distribution across Europe including three PRACE centres. It already has twelve industrial partners and aims to significantly increase this number over the life of the project as part of its road map to long-term sustainability.

E-CAM complements the scientific focus of CECAM by emphasising three transversal activities that cut across the various scientific fields represented in CECAM and provide essential supports for the work of CECAM and PRACE (and are thus infrastructural in character). These are, first, the provision of an expert consultancy service to industry and the involvement of industrial scientists and partners in the activities of E-CAM. Cutting edge techniques and methods used in academic computational science currently take too long to transfer to industry, and conversely, interesting and significant problems and techniques thrown up by industrial research are not efficiently communicated back to the world of academic research. E-CAM will address this by building communication channels between these two worlds at both personal and at institutional level. This is a key defining characteristic of E-CAM; it is firmly industry-facing (including both SMEs and multi-nationals) and is determined to break down, or at least lower, the barriers between academic and industrial research in its areas of science. Just as the distinction between basic and applied research is at root a false dichotomy, so too is that between industrial and academic research; ultimately what matters is good and interesting science wherever it is done and excellence can be found outside the pale of academia.




The second transversal activity of E-CAM focuses on the need for new and improved algorithms and code modules. There is growing recognition that Moore's law is beginning to break down and that we can no longer expect newer and faster processors to improve the performance of our old legacy codes. Recent advances in computational power depend on either massive parallelism, or specialist hardware accelerators, or both; this means that the old legacy codes need to be rewritten to exploit these possibilities and in many cases that totally new algorithms have to be implemented. E-CAM will do this in collaboration with the other centres of excellence and the European partnership for supercomputing PRACE. In many ways it is not just a question of new software, but of finding new and more efficient ways to produce robust and well documented software that is easily ported and adapted for new challenges. At present people developing new codes waste too much time on routine aspects replicating what has been done before. Frameworks, tools and standards need to be developed to allow better use of the creativity of programmers and the extraordinary success of many free-software projects in using distributed networks of volunteer programmers needs to be replicated in the sphere of scientific software. This also throws up the difficult question important for the long-term health of the field of how the work done by scientific programmers should be adequately recognised and rewarded by career progression; we have all seen good students careers blighted by writing code and not scientific papers.

The same applies to the question of gender stereotyping and implicit biases. That said, the primary output of this activity will be the online E-CAM repository of tested and robust code modules, snippets, wrappers and tests that support modern simulation science across a range of platforms. These will be developed in association with PRACE and other FET projects to enable efficient exploitation of the current and next generation of European supercomputer facilities.

The third transversal activity is associated with the broad issue of training, mentoring and continuing professional development of the European pool of human capital available in support of computational simulation. This is crucial. The health of computational science depends on a steady influx of new people into the field and on a continuing effort to maintain the skills of its established practitioners. E-CAM recognizes this and will devote significant effort to training and up-skilling workshops. An important aspect of these workshops is that they will address a broad audience of both academic and industrial scientists and they will combine more traditional training with practical hands-on training. In particular extensive use will be made of "extended software development workshops" which will have a two-fold purpose. On the one hand they will be the primary means of generating the software modules that ultimately constitute the E-CAM repository. On the other they will have an explicit training dimension in that participants will gain direct experience of using modern software engineering techniques and open-source development tools to generate community code.

These three actions should not be seen as disjointed activities. As we have seen the extended software development workshops address both the training and the algorithmic innovation transversal themes. Equally the software repository, and especially the expertise to use it, will be the key to the success of the industrial consultancy action. And ultimately it all depends on having a good pool of human capital to draw on. Nor will E-CAM operate in a vacuum. Just as the three E-CAM actions enhance and complement each other, so too E-CAM will exploit synergies and overlaps with other centres of excellence and HPC initiatives.

# 2 E-CAM Kick-off Meeting

The kick-off meeting and first General Assembly was held in the historic meeting room of the Royal Irish Academy. In welcoming participants Luke Drury gave a short account of the history of the Academy from its foundation in 1785 and mentioned in particular its most distinguished scientific member, Sir William Rowan Hamilton. He then called on Christoph Dellago, President of the CECAM council to say a few words on its behalf, noting that he was seated in the chair once used by Hamilton when presiding over meetings of the Academy. Christoph Dellago replied by welcoming the establishment of E-CAM as an important development for CECAM. This was followed by a series of talks and open discussions including: the implementation of E-CAM by Dominic Tildesley Director of CECAM; consultancy moderated by Mike Payne, University of Cambridge; algorithm and software development moderated by Godehard Sutmann, Forschungszentrum Jülich; and mentoring and training moderated by Michael Lysaght, ICHEC. A pause from disussions was taken to receive an address by Minister Damien English.

## 2.1 Speech by Minister Damien English

*Minister for Skills, Research and Innovation Damien English T.D. speaking on the launch of E-CAM*

**Introduction**

Good afternoon to you all, I am very pleased to have the opportunity to speak to you today on the occasion of the E-CAM kick-off and first meeting of the General Assembly. I would like to thank Prof. Padraig Dunne, Head of the School of Physics in UCD and his colleagues for inviting me here today and to the Royal Irish Academy for hosting this event. I would also like to take the opportunity to welcome the E-CAM consortia members that have travelled from across Europe to be here for this inaugural meeting and to congratulate all involved in this successful Horizon 2020 project.

*E-CAM Administrator Kate Collins and E-CAM consortium members and friends after the address by Minister English.*

**Horizon 2020**

As some of you know Ireland performed well in FP7, the programme which preceded Horizon 2020. We had set ourselves a target of €600 Million and Irish researchers in academia and industry were awarded €625 Million in funding in FP7, significantly exceeding our target. Horizon 2020 is a core part of the Europe 2020 strategy, designed to deliver on priorities set out in the Innovation Union and the European Research Area. It is responding to the economic crisis to invest in future jobs and growth, addressing people's concerns about their livelihoods, safety and environment and strengthening the EU's global position in research, innovation and technology. Horizon 2020 focuses on 3 key areas – excellent science, industrial leadership and societal challenges. This approach sees a focus on innovation across the entire continuum of research from basic science moving to applied science into commercialisation via competitive industries in the interest of addressing the great societal challenges of our time. Most especially, in these times of economic challenge and austerity, the conversion of scientific effort into real and sustainable jobs for citizens is a key priority. Ireland aims to win €1.25 Billion over the lifetime of Horizon 2020. This is a doubling of the target we had under FP7. While ambitious, I feel this is an achievable target given the growing strength of our national research system which has now, in so many spheres, achieved a world class standard. E-CAM is an excellent example of success to date. We now have full year data for 2014 and we can see some very encouraging results. Irish researchers and companies have secured funding in excess of €127 million. We have surpassed our target for 2014 by 27%. Stiff competition has always existed for funding under EU framework programmes. In Horizon 2020 it is particularly intense. Our success to date is therefore a real testament to the quality of the proposals coming from Ireland. Successful participation in Horizon 2020 is valuable at any level. But where the leading role is taken on by Ireland as is the case with E-CAM, greater rewards are achieved, on all dimensions.


*President of the CECAM council Christoph Dellago with Minister Damien English*

**E-CAM Project Success**

I would like to congratulate the E-CAM consortium on its success in securing 4,8M€ of the 140M€ recently allocated by the European Union to support high performance computing applications, and in particular of course the Irish organisations involved. It is a source of pride to me that Ireland has been trusted by you to lead this consortium and I would like to congratulate all those involved, in particular Dr Dónal MacKernan, Director of the Irish node of CECAM, Professor J-C Desplat, Director of the Irish Centre for High-End Computing, and Professor Luke Drury of the Dublin Institute for Advanced Studies. As I have mentioned the government has set a very ambitious target for Irish participation in Horizon 2020 and I am delighted to see this excellent project as a great example of Irish and European success.

*Deputy Director of CECAM Sara Bonella, Carlo Piereloni (University of Rome ) and Carsten Harmann (Free University of Berlin)*

This next generation supercomputing technologies and applications are very important as tens of thousands of researchers across Europe already use the power of massively parallel supercomputers to solve scientific problems that cannot be answered in the laboratory. Super Computing is increasingly a key tool of researchers in all fields, from genomics and ecology to medicine, engineering and education. It, and more generally large scale distributed computing, is now central to much of modern commerce and social interaction. This will only increase with the development of the "Internet of things", involving vast numbers of interacting sensors combined with GPS technology to build new capabilities. But there are obstacles to the realisation of this opportunity.

*Director of IDRIS (the Super Computer and PRACE Centre) of the French CNRS Denis Girou with Minister Damien English*

Many researchers in academia and industry still do not have easy access, or the skills needed to exploit Super Computers or for that matter Cloud Computing. Moreover, the ability to extract meaning from vast amounts of data, whether for scientific purposes or for commerce and societal needs, remains a challenge.

Software plays a crucial role in theefficiency of super computers, the science to be simulated on them, and the accessibility of such machines to a vastly larger potential community of users. Thus investment in algorithm and software development is essential and integral to any large-scale computation program. It is also true that computer scientists and mathematicians are only beginning to understand how to optimally use the types of highly parallel designs that computer architects are exploring.

*Godehard Suttman from the German National Super Computer & PRACE Centre at Forschuncentrum Jülich with Minister Damien English*

E-CAM I am told will create, develop and sustain a European infrastructure for computational science applied to simulation and modelling of materials and of biological processes of industrial and societal interest through three complementary instruments:

1. through the development, and dissemination of software targeted at end-user needs;
2. through advanced training of current and future academic and industrial researchers to exploit this software and associated underpinning software standards; and,
3. through multidisciplinary, applied consultancy to support industrial end-users (both large multinationals and SMEs) in their use of simulation and modelling.

*Daniel Borgis from the Maison de Simulation with Minister Damien English*

It will do this directly through 18 institutions across Europe including four national super computer centres, and industrial associates (including multi-nationals and SME's) through some 30 postdoctoral researchers, programmers and their laboratories through an initial award of nearly 5 million euro. The project will also involve the CECAM community of thousands of scientists and engineers and young researchers, and the wider community of researchers in the many tens of thousands across Europe and further afield.

*Michael Lysaght from ICHEC the Irish National Super Computer & PRACE Centre with Minister Damien English*

**New Science and Innovation strategy**

In Ireland we are currently developing our new Strategy for Science, Technology Innovation as we move into a new phase of economic growth and societal development. It is now time for us to advance fresh strategic ideas that will distinguish Ireland globally through its ability to make research work to maximum effect for the country.


*E-CAM a moment of reverie and multiple discussions*

In Ireland, we are proud of our achievements to date. In the past decade and a half we have made significant progress in our national innovation system which started from a very low base by international comparisons. We have successfully built up research capacity and now we have a significant reputation for research excellence along with an increasing base of RD active enterprises. Nonetheless, we now need to build on this progress made in developing Ireland's research and innovation system. As economic recovery takes hold this is not the time to stand still. Scientific and technological progress advance at rapid rates, and we are competing in an ever-growing competitive global environment. Supporting effective research that produces outputs of maximum impact for Ireland's economy and society is our goal but we now have an opportunity. The new Strategy will seek to articulate a broader and longer term vision for Ireland's Research and Innovation system and identify its defining characteristics. It will also set out strategic goals and targets, based on a robust evidence base, our own vision and an examination of international trends and good practice. We plan to bring it to fruition this year, and work is well underway to this end.

*E-Cam Chair Luke Drury, Giovanni Ciccotti from the University of Rome, UCD and the Free University of Berlin with Minister Damien English*

Today's meeting and the E-CAM project embody many of the strategic priorities we will be setting out in our new Strategy including: Increased collaboration between academia and industry; and between academic and research performing institutions; International collaboration, to maximise return on investment and to optimise success under EU Framework programmes; and Facilitating the translation of knowledge and the transfer of technology into jobs E-CAM with its focus on the development of expert computational science skills, support for cutting-edge research, and consultancy services to innovative industries is perfectly aligned with my portfolio and clearly has the potential to be of significant importance in the national, European and global stage.

*Minister Damien English with E-CAM Chair Luke Drury, and E-CAM technical manager and Director of CECAM Dominic Tildesley*

It remains for me to congratulate Dr Dónal MacKernan, Professor J-C Desplat, and Professor Luke Drury and the other consortia members for winning support for this very worthwhile project from Horizon 2020 and to wish you all every success in in bringing this vision to a reality. *Go n'éirí an bóthair libh* – which for those of you who not know Irish literally means "May the road rise with you", loosely translated as "May you rise to the challenge".

*E-CAM Ignacio Pagonabarraga from the University of Barcelona, Peter Bolhuis from the University of Amsterdam, and Burkhard Dünweg from the Max Planck Soceity Polymer Research Centre in Mainz.*

## 2.2 Actions and General Assembly

The first E-CAM General Assembly (GA) took place on 20th October 2015 at the Royal Irish Academy in Dublin, Ireland. All 18 membrs of the consortium had voting representatives present and therefore the meeting was quorate. The GA, by a unanimous vote, approved the appointment of the Executive Board (EB) consisting of Luke

Drury, Dominic Tildesley, project administrator (Kate Collins), and the software manager (Alan O'Cais) with an industrial cooption. The EB is responsible for appointing the three management support teams specified in the consortium agreement: software group, human capital group, and industry group. The GA also had a long discussion over the issue of software licensing where it was concluded that, pending further analysis and discussion, the GPL, LGPL, and FreeBSD licences could be used. This was approved by 17 votes with UCD abstaining. Under AOB the technical manager asked, and got approval by unanimous vote, that the GA agree that travel expenses of representatives attending the GA be chargeable to the project. The next meeting of the GA will take place 7-9 November 2015 and will be hosted by the *Maison de la Simulation*.


*E-CAM engrossed in conversation, only Carlo Pierleoni (University of Rome) is looking at the photographer.*

# 3 E-CAM Management Appointments

Two key full-time management positions of the E-CAM CoE are the project Administrator (based in NUID UCD), and the software manager (based at Forschuncentrum Jülich) have been filled. The E-CAM project Administrator, Dr. Kate Collins leads the administrative management activities of E-CAM and sits on the Executive Board reporting to the E-CAM chair; participates in the General Assembly, the Human Capital Group and the Industry Group. She is responsible for reporting to the European Commission on administrative issues. She is also responsible for coordination and dissemination activities as described in several of the E-CAM work packages. The Software Manager, Dr. Alan O'Cais leads the software development in the project, supporting the technical manager with specialist knowledge of software development. Alan sits on the Executive Board reporting to the E-CAM chair with an additional line to the Technical manager. He is responsible for setting up and participating in the Software Management Group. Short biographies of each post-holder follow.

## 3.1 E-CAM Administrator

Kate Collins is an accomplished project manager, researcher, administrator and trainer. She has worked across the public, private and not for profit sectors over the past 10 years. She has previously worked in roles such as managing editor of the Journal of Agricultural Education and Extension at Wageningen University in the Netherlands and operations manager for Worklink Partners Ltd, a not for profit company that she helped to setup in Ireland. She joined UCD in 2012, and until recently acted as PhD Training Coordinator for the PhD Simulation Science at UCD. Kate has also lectured in Scientific Writing both in the Netherlands and in Ireland. Kate holds a PhD from the Dublin Institute of Technology (DIT) in the area of workplace learning, a MSc Marketing also from DIT, and a BA from University College Dublin.

*Mikko Alava from University of Aalto Finland, enjoying a provocation of Mike Payne from the University of Cambridge*

## 3.2 E-CAM Software Manager

Dr. Alan O'Cais has been active in the field of computational research and high performance computing since receiving his bachelors degree in Theoretical Physics from Trinity College Dublin in 2001. He received a Masters Degree in High Performance Computing in 2002 and a PhD in Lattice Quantum Chromodynamics in 2005. He has held research positions at Trinity College and the University of Adelaide. In 2008 he joined the Cyprus Institute as Scientific Coordinator of the Computation-based Science and Technology Research Centre (CaSToRC) and has worked at the Jülich Supercomputing Centre since 2010 within the Application Support division. Until 2015, he was primarily focussed within the LinkSCEEM-2 project helping to develop a Virtual Research Community in Computational Science in the Eastern Mediterranean region. He has been an invited speaker for "Performance Analysis and Optimisation" lectures with PRACE Advanced Training Courses on multiple occasions and currently manages the user software and application environment on the multi-PFlop JURECA hybrid cluster system at JSC.

# 4 E-CAM Science View

Dónal Mac Kernan

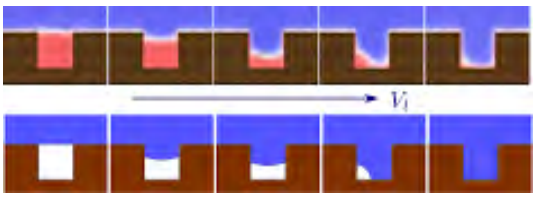
E-CAM Scientist at University College Dublin, email: Donal.MacKernan@ucd.ie

E-CAM laboratories have interests across its 4 principle scientific platform areas of molecular simulation, electronic structure, quantum dynamics and meso-scale/multi-scale simulation. In this first issue, as an indication of the capabilities of E-CAM partners just before its launch we have chosen to report only on published work in 2015-2014 in molecular simulation and meso-scale/multi-scale simulation, with a strong emphasis on results which have a reasonable direct bearing on potential industry applications, or are so general in scope that they need to be highlighted. Below is an overview, followed by longer summaries of each work. In the next issue, the focus will instead by on electronic structure, quantum dynamics, and algorithms/coding methods.

Nucleation, including crystallization has been a central topic of interest in simulation, with applications such as purification and processing in industries as disparate as advanced materials, pharmaceuticals and food. At times many have been perplexed by the apparent discrepancies in estimates of reaction rate constants between experimentalists and simulation. In a beautiful and profound molecular simulation study of a comparatively simple model, Jungblut at al have shown how changes in the structure of small crystalline seeds in undecooled melts can lead to widely different rate constants - and indeed counter-intuitive results, see 4.1 for a summary.

Continuing the theme of using simple models to investigate profound problems, Goujon et al examine, and resolve the discrepancy between experiment and simulation of liquid argon in the presence of interfaces, by demonstrating that the addition of three body interactions responsible for polarization is critically required, in addition to proper treatment of Van der Waals long range coupling. The importance of this result goes far beyond simply the case of argon. That a comparatively simple to compute correction could resolve such a serious discrepancy is particularly useful see 4.2 for a summary.

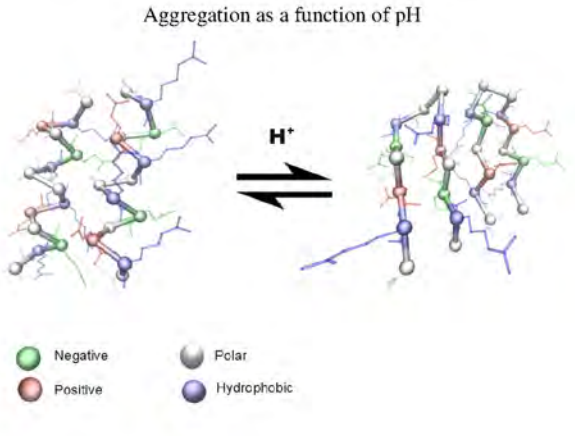
The possibility of designing anti-fouling surfaces that self-clean and minimise drag under flow conditions has a variety of industrial applications. Hydrophobic materials can be turned into superhydrophobic ones if their surfaces are decorated with micro- or nano- corrugations, and gives rise to a phenomenon, known as “lotus effect” from the properties and structure of lotus leaves. What is the effect of the shape of the surface corrugation and its size on the mechanism of stability of such superhydrophobic states is elucidated in 4.3 using molecular dynamics and rare-event based methods.




*Exploring loss of superhyrophobicity: comparison of continuum and molecular simulation predictions*

Biological and soft matter systems are characterized by the existence of processes with many different length and time scales. computationally treating very large systems with full molecular detail is not possible, and one needs to deal with simplified, or coarse-grained versions of the system. However, in any coarse-grained model some atomic/molecular detail is lost, which can be problematic if crucial mechanisms occurring at an atomistic or molecular level are missing. In some cases, the need for atomistic detail is confined in small regions of space, and there is hope that a hybrid scheme coupling an atomistic with coarse-grained descriptions may be a successful approach. A variety of methods have been developed over the years, many of which despite their success had practical and conceptual difficulties, including for instance, lack of energy conservation. In the publication highlighted in 4.4 the authors derive a rigorous hybrid coarse grained atomistic method termed Hamiltonian Adaptive Resolution Scheme (H-AdResS) which can be used for all of the standard ensembles of statistical mechanics.

Continuing with the coarse graining theme, a series of papers have been recently published that seek either to model very large systems, or perhaps even more ambitiously, design through simulation new systems, that can be subsequently built in the laboratory through appropriate experimental techniques. In 4.5 coarse graining is used to investigate the mechanisms involved when nanoparticles (NP) pass through cellular membranes - which is of great interest not only to nano-toxicology but also more widely, for instance in the context of complex fluids interacting with inorganic surfaces. In a similar vein, how coarse graining methods can be extended to allow simulation of constant pH conditions is highlighted 4.6 where is is used to investigate aggregation of peptides.




For many practical applications in electronics, photo-

voltaics, and biomimetic material synthesis, ordered mono- and bilayers are often needed. An approach based on coarse graining providing a novel and simple way to tune via external parameters the ordering of heterogeneously charged colloids into quasi two-dimensional structures is outlined in 4.7. Such tuning can be implemented through subtle variations of the relative charge of the system components, emerging via pH modification, and give rise to reversible changes either from extended aggregates to a monomeric phase or from triangular to square domains.

Tribology, literally, the study of rubbing, has been studied at a formal level at least as far back as Leonardo Da Vinci in work on friction. Controlling tribology interactions, including friction, wear, and adhesion, is a topic of considerable industrial importance. From antiquity if not before, lubricants have been used to reduce the detrimental effects of friction and wear. In the publication summarized in 4.8, the authors, through a model employing molecular dynamics, have focused on the properties of nematic liquid crystals (LCs) as a particularly interesting lubricant. LC systems can be characterized by the presence or absence of positional and/or orientational order of the elongated molecules, which is controllable by tuning the temperature or applying external electric or magnetic fields.

Self organization in nature exhibited, for example, in the flocking of birds, bacteria colonies tissue repair, and colloids, has fascinated many. Breakthroughs in particle synthesis have enabled the fabrication of artificial colloidal micro-swimmers that show a high potential for application, in, for instance, bio-sensing and drug delivery. In the publication summarized in 4.9 the authors show that active matter can serve as a medium to generate unexpectedly large effective interactions between large immersed objects to direct their motion and assembly, and find surprising results.

Exploring the properties of very large biological systems including explicit water is immensely difficult and indeed a major limitation on the size of system that can be simulated. Classical density functional theory is one approach to try to resolve this difficulty, but until now has had considerable problems of its own, particularly regarding accuracy. In the publication outlined in 4.10 not only are corrections to classical functional theory are derived, they are used to find that the hydration free-energies computed for a dataset of 500 organic compounds are of similar quality as those obtained from molecular dynamics free-energy perturbation simulations, with a reduced computational cost of two to three orders of magnitude.

Beauty is said to be in the eyes of the beholder, and when it comes to the notion of what can be abstracted to be a particle - this beauty can be found at many scales. In the provocative publication summarized in 4.11, the authors explore the phenomena of clogging, with examples ranging from the common experience that the pouring of salt from a salt-cellar frequently requires shaking so as to break the clogging arches, to flow interruptions in industrial conduits and silos, and at smaller scales, to provoke embolization of blood vessels in order to shrink a tumour, or at the nano-scale when electrons on the liquid helium surface pass through nano-constrictions. Despite the extraordinary range of scales, the authors show that clogging in several disparate systems is amenable to a unified treatment, including a model colloidal suspension. simulated using the Lattice Boltzmann method.

## 4.1 On the reaction coordinate for seeded crystallisation

Jungblut, Swetlana, and Christoph Dellago*. Molecular Physics, **113** (2015) 2735-2741.
* E-CAM Scientist at University of Vienna, email: christoph.dellago@univie.ac.at

The crystallisation of under-cooled liquids is a widely studied topic with many technological implications. Classical nucleation theory posits that a small crystalline nucleus forms within an under-cooled liquid. Due to the creation of a crystal–liquid interface surrounding the nucleus, this process is free-energetically uphill in its initial stages. Driven by thermal fluctuations, the crystalline nucleus may nevertheless grow until it reaches a critical size after which further growth is thermodynamically favourable eventually leading to the crystallisation of the entire system. While the basic perspective provided by the classical nucleation theory is essentially correct, its details are still subject of current discussions.

By introducing small seeds with various structures into the under-cooled liquid, one can modify the crystallisation mechanism by favouring the nucleation of particular arrangements and inhibiting the formation of others. Several computer simulation studies agree that the structure of the crystalline clusters formed in the course of the transition is not uniform and reorganises as the reaction proceeds. In LJ crystallisation, the body-centred cubic (bcc) structure is formed first and subsequently transforms into the face-centred cubic (fcc) structure, such that the crystalline clusters have, on average, an fcc-structured core and a bcc-structured surface. While fcc is the thermodynamically stable phase in bulk LJ crystals and the bcc phase is only metastable, the initial formation of bcc crystals is favoured kinetically by a lower free energy barrier.

In earlier studies, the same authors showed that the effect of the seed is related to its structure in the sense that the commensurability with the bulk equilibrium structure is one of the factors which influence the crystallisation rate.

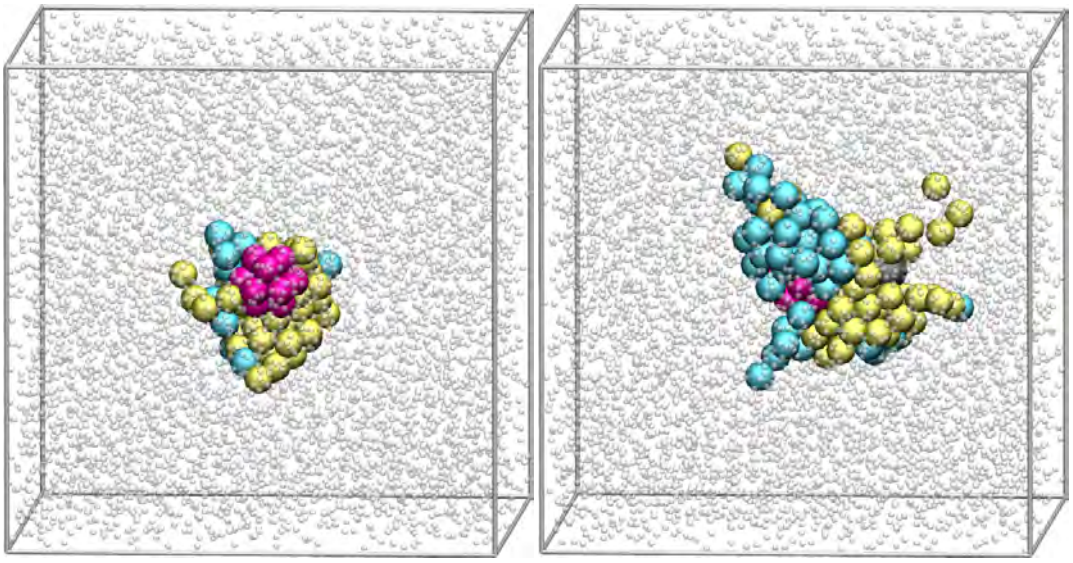


Figure 1: *Examples of seeds having body-centred cubic and face-centred cubic structure respectively.*

In particular, they found that the seeds with a regular fcc structure produced the largest increase of the reaction rate. This tendency was expected, but the increase of the reaction rate by several orders of magnitude was rather surprising considering the size of the seeds.

In the publication higlighted here, the authors study seeded crystallisation at a slightly larger under-cooling and found that, in this case, the largest increase of the crystallisation rate is obtained with bcc rather than fcc seeds. Their result, as they explain, is counter-intuitive, because in the bulk the bcc structure is only metastable. As in the case of homogeneous crystallisation, the analysis of recurrence times has revealed that the size of the largest crystalline nucleus evolves in a non-Markovian way, pointing to the necessity to include additional collective variables such as structure and shape into the description of the nucleation mechanism.

## 4.2 The gas-liquid surface tension of argon: A reconciliation between experiment and simulation

Florent Goujon, Patrice Malfreyt, and Dominic J. Tildesley*, J. Chem. Phys. **140** (2014), 244710
∗ E-CAM Technical Manager and CECAM HQ director at EPFL, email: dominic.tildesley@epfl.ch

The success of molecular simulations in the quantitative prediction of thermodynamic properties of bulk liquid and inter-facial systems has been achieved with the use of relatively simple effective potentials which model the van der Waals and electrostatic interactions. In most cases, the simulations use two-body Lennard-Jones site-site potentials and partial charges. These pair potentials have been shown to be successful in reproducing the temperature dependence of the surface tension of various organic liquids,water,and acid gases. Although, the surface tension, $\gamma$ of the simple Lennard Jones liquid was the first to be studied,the agreement between the simulated surface tension and the experimental results for liquid argon is poor (with typical deviations greater than 20 %.

In the above article, the authors explain that the discrepancy with experiment cannot be attributed to methodological problems such as finite size-effects, long range corrections, and the intrinsic accuracy of different routes to estimating $\gamma$. A hint to the origin of the discrepancy can be gleaned from the fact that Argon has a large atomic polarizability, which is such that a the triple induced-dipole potential is likely to make a significant contribution to the surface tension. The authors, to the best of their knowledge, are the first to perform simulations including three-body potentials on argon involving an explicit interface, which allows an accurate calculation of the surface tension. In a very detailed study taking great care to incorporate long range interactions they investigated the performance of various two body potentials, combined with the triple-dipole Axilrod-Teller potential, and succeeded in reproducing the experimental values of the surface tension of Argon within about 3 %.

### 4.3 Mechanism of the Cassie-Wenzel transition via the atomistic and continuum string methods

Alberto Giacomello, Simone Meloni, Marcus Müller and Carlo Massimo Casciola* J. Chem. Phys. **142** (2015): 104701. ∗ E-CAM Scientist at University of Rome La Sapienza, email: carlomassimo.casciola@uniroma1.it

The possibility of designing anti-fouling surfaces that self-clean and minimise drag under flow conditions has a variety of industrial applications. In fact, hydrophobic materials can be turned into superhydrophobic ones if their surfaces are decorated with micro- or nano- corrugations, and gives rise to a phenomenon, known as the "lotus effect" from the properties and structure of lotus leaves, which results in liquid droplets forming with high contact angles that can reach almost complete de-wetting values. Superhydrophobicity is related to the trapping of gaseous pockets (air and/or vapour) inside surface roughness, which the authors refer to as as the Cassie state. However, superhydrophobicity breaks down as soon as the surface roughness becomes wet in the so-called Wenzel state. In earlier work, the authors established that the Cassie state consists of two metastable states associated with two distinct contact angles, as well as exploring the nature of the free energy barrier associated with the Cassie-Wenzel transition. One of the objectives of the present highlighted publication was to elucidate the effect of the shape of the surface corrugation and its size on the mechanism of the Cassie-Wenzel transition, and on the related free-energy barrier.

### 4.4 Statistical mechanics of Hamiltonian adaptive resolution simulations

P. Espagnol , R. Delgado-Buscalioni , R. Everaers* , R. Potestio , D. Donadio, and K. Kremer. J. Chem. Physics **142** (2015): 064115. ∗ E-CAM Scientist at ENS Lyon, email: ralf.everaers@ens-lyon.fr

Biological and soft matter systems are characterized by the existence of processes with many different length and time scales. These processes are usually coupled, making their theoretical, experimental, and computer simulation description a daunting task. The functioning of a protein, for example, involves chemical processes at active sites as well as the overall dynamics of the protein and its environment. Crack propagation is another example in which the atomic processes occurring at the crack tip affect crucially the overall elastic behaviour of the sample, and vice-versa. Treating such large systems computationally with full molecular detail is not possible, and one needs to deal with simplified, or coarse-grained versions of the system. By definition, in any coarse-grained model some atomic/molecular detail is lost. In some fortunate cases, the need for atomistic detail is confined in small regions of space as in the examples above, and there is hope that a hybrid scheme coupling all atom (AA) with coarse-grained (CG) descriptions may be a successful approach.

A particular difficulty arises in liquid systems. When a molecule crosses the interface between the AA and CG regions, its interaction with other molecules changes accordingly. The idea of interpolating AA and CG interactions through a hybrid region is not new. However, the force-based Adaptive Resolution Scheme (AdResS) and the potential based adaptive Multi-scale Molecular Dynamics (MMD) suffered various methodological difficulties associated with the conservation of energy. In the present highlighted publication, the authors have resolved many of these vexations through what they have termed a Hamiltonian Adaptive Resolution Scheme (H-AdResS), that they derived on a statistical mechanics basis, and which includes a switching field that allows for a swift interpolation between the truly microscopic Hamiltonian and a CG version of it. Several exact results concerning the local equations of state for the pressure and temperature allow for the formulation of the free energy compensation term in an iterative way. They also showed that under a local equilibrium approximation, valid when the hybrid region is wide, the iterative procedure can be simplified leading to an approximate but very efficient way for the calculation of the free energy compensation term in the Hamiltonian. They have analysed the effect of the width of the transition layer where molecules gradually change their resolution. A significant outcome is that the H-AdResS total free energy compensation is independent on the layer, even for widths of the same order of the molecular diameter. Another very important observation is that the H-AdResS total free energy correction is equal, within error bars, to the free energy difference between both fluids (atomistic and coarse-grained) evaluated from Kirkwood thermodynamic integration. Although more research is required in this direction, this would allow H-AdResS to be used as a flexible tool for estimation of free energy differences in different scenarios.

### 4.5 Coarse-grained model of adsorption of blood plasma proteins onto nano-particles

Hender Lopez and Vladimir Lobaskin*, J. Chem. Phys. **143** (2015): 243138
* E-CAM Scientist at University College Dublin, email: vladimir.lobaskin@ucd.ie

When uncoated nano-particles (NP) enter a living organism, they are first exposed to biological fluids, which results in a formation of stable or transient NP-biomolecule complexes. For large NPs, the biomolecular coating is referred to as the (protein) corona. The composition and structure of the corona determines the biological reactivity and toxicity of the NPs as well as the NP systemic transport including NP uptake into cells. An additional interest in such interactions is driven by applications of NPs in food, cosmetics, and medicine.

There is still much controversy about the physical picture of protein adsorption on NPs including: disagreement on whether the adsorption is reversible; whether proteins change conformation and preserve their functionality when complexed with certain particle types: whether the corona survives the NP uptake into the cell, etc. While full atomistic simulations of protein on surfaces have already proved useful to advance the understanding of molecular interactions, they are limited to systems composed of one or a few proteins at most, and give information well below the time scales relevant for the formation of the protein corona. This restriction can in principle be overcome using coarse-grained (CG) models. Some CG models to study the kinetics of the protein corona formation have already been proposed,but most lack the level of molecular detail required to study reliably adsorption kinetics.

Lopez and Lobaskin in the above publication report on a a CG model they have developed that allows calculation of adsorption energies of arbitrary globular proteins onto hydrophobic NPs of arbitrary size. Protein molecules are represented by one bead per amino-acid and the nano-particle by a homogeneous sphere that interacts with the amino-acids via a central force that depends on the nano-particle size, while water is treated implicitly. The methodology is used to predict the adsorption energies for six common human blood plasma proteins on hydrophobic charged or neutral nano-particles of different sizes as well as the preferred orientation of the molecules upon adsorption. Their approach allows proteins to be ranked by their binding affinity to the nano-particle, which can be used for predicting the composition of the NP-protein corona. The predicted ranking is in good agreement with known experimental data for protein adsorption on surfaces

### 4.6 Influence of pH and sequence in peptide aggregation via molecular simulation.

Marta Enciso, Christof Schütte, and Luigi Delle Site*, J. Chem. Phys **143** (2015): 243130.
* E-CAM Scientist at the Free University of Berlin, email luigi.dellesite@fu-berlin.de

Protein aggregation is a ubiquitous event that may happen to any known protein. Aggregation propensities, however, depend on the particularities of protein sequence and structure, as well as on external factors like pH, concentration, ionic strength, to cite a few. Among the latter, pH is of key importance because of its clinical relevance (it has even been suggested as a diagnosis method) and its impact in drug production and synthesis. From a computational point of view, media acidity is also a challenge, as a proper description of the system pH implies instantaneous changes in the protonation states of the involved species. Several simulation strategies have been developed over the last 2 decades. The most relevant drawback of constant-pH atomistic simulations for aggregation studies is their computational cost, which usually makes these models impractical for aggregation purposes. Coarse-grained pH-dependent methods, in contrast, are still competitive and, if a discrete protonation approach is used, do not even have a large impact on computational efficiency. Enciso et al have recently proposed a constant-pH simulation algorithm in combination with a simple but accurate coarse-grained force field wherein each amino acid of a peptide is described as a bead centre, placed at the $\alpha$-carbon position, and such that each molecule is embedded in an environment described via an implicit solvent approximation. The system pH is modelled through discrete protonation states, which are allowed to fluctuate during the simulation according to a Monte Carlo scheme, where in each “pH move,” a protonable site is randomly selected and its protonation state is accepted or rejected according to the detailed balance condition, which depends on the “sensitivity” of the specific amino acid towards protonation and on the particular pH value. Overall, this approach allows for an order of magnitude increase in the systems’ size compared with molecular simulation, as well as the exploration of several pH conditions and sequence alternatives within the same study.

The present highlighted publication exploits this methodology to explore the effect of pH and peptide sequence on aggregation in a systematic way, and used realistic systems sizes, i.e., larger than the critical nucleus size. This critical size is a function of the peptide sequence and its length and it is usually set (by both experimental and computational means) to between four and ten polypeptide chains. The authors used twenty-four peptides per simulation box in replica exchange Monte Carlo and kinetic Monte Carlo pH-dependent simulations; which is, apparently, the first time that such a large scale approach has been used to take into account the effect of pH in the aggregation process. They

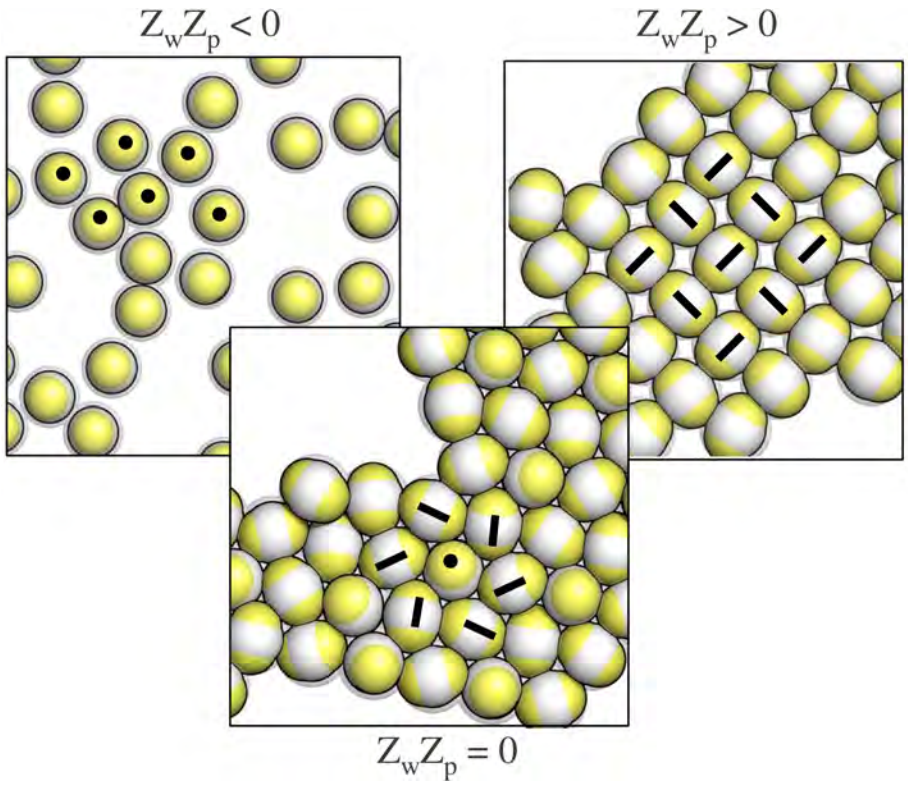
took the de novo sequence KTVIIE as a starting point, designed by de la Paz and co-workers as intrinsically amyloidogenic, and then enlarged simulation study to include other peptide sequences.

### 4.7 Tunable assembly of heterogeneously charged colloids

Bianchi, Emanuela, Christos N. Likos, and Gerhard Kahl*. Nano Letters **14** (2014): 3412-3418.
∗ E-CAM Scientist at University of Vienna, email: gerhard.kahl@tuwien.ac.at

Colloids, that is systems comprising one substance consisting of insoluble particles suspended in another consisting typically of a fluid, have long been exploited in applications as diverse as food, medicine, rubber production, and increasingly of late, advanced materials. For the latter, the colloidal particles, typically of micron scale but can be indeed far smaller, can have a variety of interesting electronic and optical internal properties. And, via suitable synthesis processes, the interactions between colloidal particles can be easily manipulated to give rise of structurally ordered materials at length scales ranging from nano- to micrometers, through self-assembly, with remarkable properties. Such manipulations can be made at the processing level, allowing the creating of materials with very well defined structural properties.

For many practical applications in electronics, photovoltaics, and biomimetic material synthesis, ordered mono- and bilayers are often needed. In this highlighted publication the authors present a novel and simple way to tune via external parameters the ordering of heterogeneously charged colloids into quasi two-dimensional structures. Upon subtle variations of the relative charge of the system components, emerging via pH modification, reversible changes either from extended aggregates to a monomeric phase or from triangular to square domains are observed. The authors have discovered a novel and until now unexplored route to steer in a reliable and reversible manner the self-assembly of colloidal particles possessing heterogeneously charged surfaces, so-called inverse patchy colloids (IPCs), consisting of two charged, broad polar caps and an oppositely charged equatorial region.




*Typical self-assembly scenarios of IPCs (with patch charge $Z_p$) confined between two parallel, charged walls (with wall charge $Z_c$) for representative values of $Z_p$ and $Z_c$. The patches of the IPCs are marked in yellow, while the body of the particles is grey.*

Depending on the charge balance between the different surface regions, IPCs can be overall either neutral or charged. In their coarse grained simulation, an aqueous solution of IPCs is confined between two horizontal, parallel planes either under tight or loose confinement conditions. Experimental systems that feature in-homogeneously charged surfaces are diverse: they include, for example, PbS-Au4 nano-structures and PbS-Au4 nanocubes, synthesized spotted vesicles, viral capsids, and virus-like nano-particles. In the latter case, the overall particle charge can be controlled via pH modifications, allowing for a tuning of both their propensity to act as assembly sites for viral capsids and their

functionality as building blocks for two-dimensional self-assembly into ordered structures. Using the pH, the salinity, and the wall charge as external control parameters, the authors find that one self-assembly scenario can be transformed into another in a reversible fashion.

### 4.8 Friction control with nematic lubricants via external fields

W Chen, S Kulju,AS Foster,MJ Alava*,L Laurson Physical Review E**91** (2015): 012504.
∗ E-CAM Scientist at the University of Aalto, mikko.alava@aalto.fi

Tribology, literally, the study of rubbing, or more precisely, the rubbing of surfaces was studied as far back as Leonardo Da Vinci in work on friction. Controlling tribological interactions, including friction, wear, and adhesion, is a topic of considerable importance. In the absence of proper control of such effects in micro- and nano-scale mechanical devices, their lifetimes and reliability are greatly reduced, which has motivated an extensive search for strategies to control friction, ranging from electric field control of polyelectrolytes coatings or ionic liquids to applying vibrating normal forces to tuning of van der Waals forces and using magnetic nano-fluids. From the earliest times, lubricants have frequently been used to reduce the detrimental effects of friction and wear. The authors of this highlighted article have focused on the properties of nematic liquid crystals (LCs) as a particularly interesting lubricant as it has recently been shown to give rise to low friction coefficients and wear rates. LC systems can be characterized by the presence or absence of positional and/or orientational order of the elongated molecules, which is controllable, for instance, by tuning the temperature or applying external electric or magnetic fields.

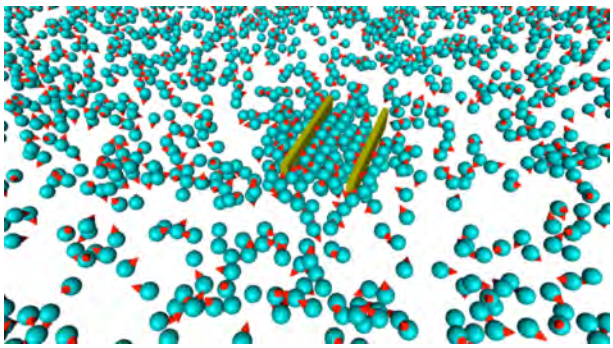
To elucidate the fundamental mechanisms via which order and orientation of a nematic lubricant affect its frictional properties, the authors have performed extensive molecular dynamics simulations of a rigid bead-necklace model of elongated molecules, confined by two rigid, parallel plates in relative sliding motion. The equilibrium system displays fluid like isotropic and layered in-plane nematic phases depending on temperature and the confining pressure. Sliding slowly the top surface gives rise to a preferred in-plane molecular orientation along the sliding direction and leads to a small perturbation of the equilibrium phase diagram. The two phases are found to be correlated with the frictional properties of the lubricant, with higher friction coefficients observed in the fluid like isotropic phase. Their detailed study of the effect of applied fields reveals that the related tunability of friction is intimately connected to the phase behaviour of the lubricant: the largest relative increase in friction is obtained when in-plane fields perpendicular to the sliding direction are applied with the system close to the nematic-isotropic transition boundary; and, the largest relative friction reduction occurs in the isotropic phase with applied fields along the sliding direction.

### 4.9 Tunable long range forces mediated by self-propelled colloidal hard spheres.

Ni, Ran, Martien A. Cohen Stuart, and Peter G. Bolhuis*. Physical review letters**114** (2015): 018302. ∗ E-CAM Scientist at University of Amsterdam, email: p.g.bolhuis@uva.nl

Self organization in nature exhibited, for example, in the flocking of birds, bacteria colonies tissue repair, and colloids, has fascinated many, and indeed been also the subject of a number of CECAM workshops. Developments in particle synthesis have enabled the fabrication of artificial colloidal micro-swimmers wit applications such as biosensing and drug delivery. A number of different active colloidal systems have been realized in experiments, such as colloids with magnetic beads acting as artificial flagella, catalytic Janus particles, laser-heated metal-capped particles, light-activated catalytic colloidal surfers, and platinum-loaded stomatocytes. In contrast to passive colloids undergoing Brownian motion due to random thermal fluctuations of the solvent, active self-propelled colloids experience an additional force due to internal energy conversion.

In this highlighted work, the authors address the question whether active matter can serve as a medium to generate large effective interactions between large immersed objects to direct their motion and assembly. In their model study, they explore the effective interaction between two parallel hard walls immersed in suspensions of self-propelled colloidal hard spheres, and find that that when the density of particles is relatively high, a dynamic crystalline bridge forms between the two walls, which induces a strongly oscillating repulsive dynamic wetting force, with a range depending on the size of the dynamic clusters. With decreasing density of particles, this dynamic crystalline bridge becomes smaller, and the effective force between the two walls develops a long attractive tail. remarkably, in the limit of zero density, the effective interaction turns into a long range dynamic depletion force, with a range depending on the persistence length of the mean free path of the particles, which can be tuned by varying the self-propulsion on the particle.



*Snapshot two parallel hard walls immersed in a of suspension of self-propelled colloidal hard spheres*

Their results suggest a novel way to tune the interaction between large objects by immersing them in suspensions of small self-propelled colloids. The sign of interaction can be tuned from long range repulsive to long range attractive by changing the density of particles, and the range of interaction can be controlled by varying the magnitude of self-propulsion of the particles.

## 4.10 Fast computation of solvation free energies with molecular density functional theory: Thermodynamic-ensemble partial molar volume corrections

Volodymyr P. Sergiievskyi, Guillaume Jeanmairet, Maximilien Levesque, and Daniel Borgis* The Journal of Physical Chemistry Letters **5** (2014): 1935-1942.
∗ E-CAM Scientist ENS Paris & CNRS, email: daniel.borgis@ens.fr

Solvation Free Energy (SFE) is one of the main physical quantities of interest in solution chemistry. Many important characteristics, such as dissociation constants, partition coefficients, which are necessary for describing most of the processes in physical chemistry and biochemistry are expressed through the SFE. Unfortunately, the determination of SFE is often problematic. Experimentally, it can require very significant time and resources, especially if SFE is calculated for low soluble and low volatile substances, and underlies the importance of estimating SFE computationally. Molecular Density Functional Theory (MDFT) offers an efficient implicit solvent method to estimate molecule solvation free-energies while retaining a molecular representation of the solvent. Even within a second order approximation for the free-energy functional, the so-called homogeneous reference fluid approximation, the authors find that the hydration free-energies computed for a dataset of 500 organic compounds are of similar quality as those obtained from molecular dynamics free-energy perturbation simulations, with a reduced computational cost of two to three orders of magnitude. The high quality results entailed the introduction of a proper partial volume corrections to account for a value of the pressure on the solute that is pertinent to experiments. In addition, the author established that this correction can be extended to 3D-RISM calculations, giving a sound theoretical justification to empirical partial molar volume corrections that have been proposed recently.

## 4.11 Clogging transition of many-particle systems flowing through bottlenecks

Iker Zuriguel Daniel Ricardo Parisi ,Raúl Cruz Hidalgo, Celia Lozano,Alvaro Janda,Paula Alejandra Gago, Juan Pablo Peralta, Luis Miguel Ferrer,Luis Ariel Pugnaloni, Eric Clḿent, Diego Maza, Ignacio Pagonabarraga*, Angel Garcimartín, Scientific reports**4** (2014).
∗ E-CAM Scientist at University of Barcelona, email: ipagonabarraga@ub.edu

In this provocative article the authors ask if it be taken for granted that an enclosure filled with particles could be emptied through a small opening in a finite time, with examples ranging from the mudane everyday experience that the pouring of salt from a salt-cellar frequently requires shaking so as to to break the clogging arches, to flow interruptions in industrial conduits and silos, and at smaller scales, to provoke embolization of blood vessels in order to shrink a tumour, or at the nano-scale when electrons on the liquid helium surface pass through nano-constrictions. And at its most dramatic, in human stampedes frequently leading to a clog in narrow passages.

Despite the extraordinary range of scales, the authors show that clogging in several disparate systems is amenable to a unified treatment, including that it can be analysed through a model colloidal suspension, simulated using the Lattice Boltzmann method. Previous studies in colloids have focused on the mechanisms leading to the development of permanent clogs. Instead, the approach taken by the authors above is conceptually different, and focuses on the the

statistical analysis of the flow intermittencies, without the necessity of observing permanent clogs. In particular, they find that time lapse distributions display power-law tails while the burst size distributions remain exponential, that is the approach to complete obstruction in colloidal suspensions obeys the same universal scenario that is observed in the human models and granular materials, demonstrating that the transition to clogging is not very sensitive to the microscopic details of the system.