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FLUREN

**understanding the dynamics of complex FLuids to solve
frontier problems in Renewable ENergy technology**

A. STATE OF THE ART AND OBJECTIVES

A host of novel technologies for renewable energy production rely crucially on the physical and dynamical properties of complex fluids. Polymer melts and solutions, colloidal suspensions, emulsions, gels, to name but a few instances, elude the ordinary distinction between fluid and solid [1]. Unlike simple liquids, these consist of multiple phases and components arranged in some kind of internal structure. Understanding how such mesoscopic structural details determine the macroscopic bulk properties of the system is *per se* an open problem. The picture is obviously even more complicated when the dynamics is confined on a solid surface or inside complex geometries, as it occurs in processes of utmost relevance for two cutting-edge applications in renewable energy research (which are also the main research foci at the Helmholtz-Institute Erlangen-Nürnberg, HI-ERN): catalysis for energy storage and conversion and organic photovoltaics.

Assembling techniques for printable photovoltaics make an extensive use of suspensions of nanoparticles in organic solvents [2,3,4]. The bulk heterojunctions (BHJs) of organic photovoltaic (OPV) cells [5] consist of a blend of polymers and fullerene-based molecules which are deposited on a substrate as a solution, by a coating technique [6,7].

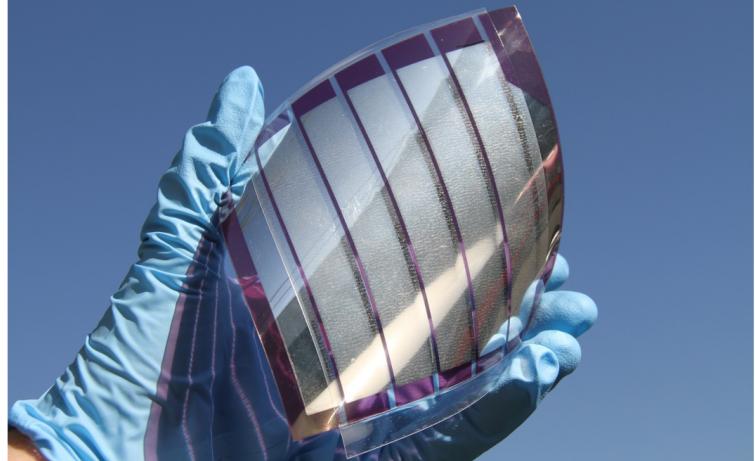


Figure 1. Flexible OPV device



Figure 2. Cross-sectional image of a BHJ [7]

An ideal BHJ should maximise the area of contact between donor and acceptor (to favour the particle-hole pair formation), maintaining continuity within each material (to optimise charge transport to the electrodes). The morphology of BHJs (figure 2) and of deposited nanoparticle layers is a determinant parameter for solar cell performance, which is extremely hard to predict and control. The deposition of material suspended or dissolved in a solvent, in fact, is an intricate process: upon casting the solution on the substrate, the layer further thins due to solvent evaporation, eventually becoming unstable and prone to rupture. The three-phase contact line starts to recede with a succession of pinning/depinning events (stick-slip motion) [8,9], leaving the deposited material on the substrate. As the solvent evaporates, the suspension becomes progressively more concentrated, and the nanoparticles closely packed; this changes the rheology of the material and therefore has a feedback on the contact line motion. Several complex non-equilibrium phenomena enter, then, the game and have to be understood: contact line motion,

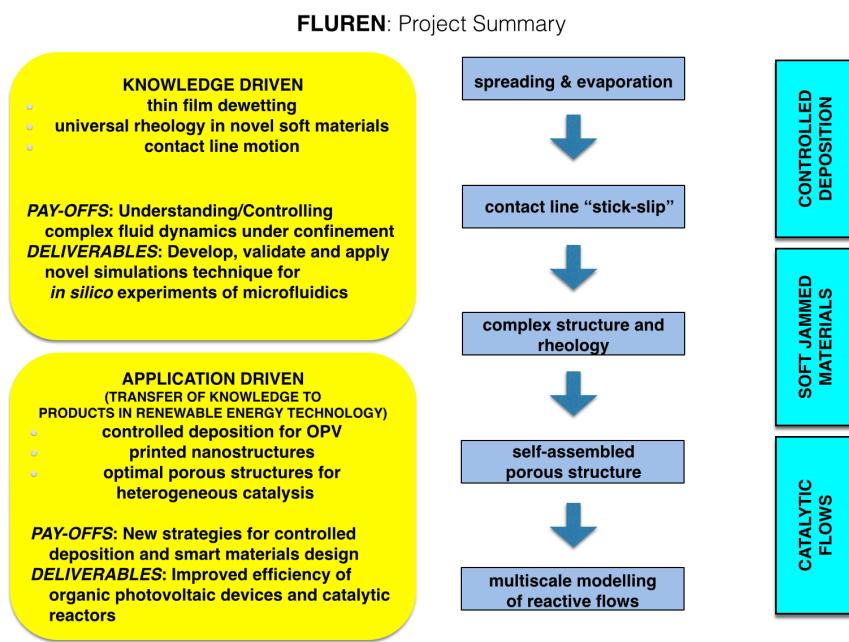
dewetting of thin liquid films, phase transitions, jamming of high-concentrated suspensions. Each of them depends on the microscopic details of the system, like the polymer/particle-wall and particle-particle interactions, the surface and particle wettability. The underlying physics is, thus, intrinsically multiscale, involving atomistic constituents, mesoscopic structures and hydrodynamical spatio-temporal evolution with complex rheology.

Not surprisingly, a clear picture of how to control the pattern of the deposited layer lacks [10].

In heterogeneous catalysis, reactions occur within fluid phases confined inside porous structures [11,12]. The efficiency of a catalytic reactor depends critically on the physicochemical processes occurring, on molecular scales, at the interface between the solid catalyst and the fluid, but also on the hydrodynamics transport of heat and mass by the fluid flow.

The goal of this proposal is to unravel the basic mechanisms ruling the dynamics of complex fluids like suspensions, emulsions, polymeric liquid, deposited over surfaces and confined in micro- and nanostructures and of reactive fluid mixtures flowing in porous media. The matured knowledge will be applied to find new strategies to control the formation of optimal patterns in bulk heterojunctions and printed photovoltaic devices and to improve the efficiency of catalytic processes.

The route to these objectives, beyond its motivations, will naturally lead to explore challenging basic problems in fluid dynamics and soft matter physics, making the project of broader multidisciplinary impact.



The main ambitious questions that I intend to address in my project include:

- How to control the formation of an optimal bicontinuous structure in the bulk heterojunction of organic solar cells?
- How to design the assembly of a porous structure to improve the efficiency of a catalytic reactor?
- What is the role of particle-particle and particle-wall interactions in the contact line motion of a drying suspension?
- And what that of jamming and soft-glassy rheology which onset at high particle volume fraction?
- How do thermal fluctuations and non-Newtonian rheology compete in the dewetting of a thin film of polymeric liquid?

To solve these frontier problems, we will combine new theoretical and phenomenological models with state-of-the-art numerical simulations based on the lattice Boltzmann method (LBM, see box), coupled (when needed) with molecular dynamics (MD) schemes and continuum approaches. Fully resolved 3D simulations will account quantitatively for the dynamical processes at the solid-liquid-vapour contact line, describing explicitly suspended nanoparticles and dissolved macromolecules. Out of these micro-/meso-scopically resolved computations, we will derive effective boundary conditions for lubrication models which allow to probe larger length/time scales.

Although all topics are intimately connected to each other, the research activity, dealing with both fundamental and applied problems, will hinge on three main axes concerning:

- i) controlled deposition of functional materials (nanoparticles/polymers) on a substrate;
- ii) soft jammed materials for OPV;
- iii) catalytic flows.

The Lattice Boltzmann Method (LBM): a cursory look

The LBM solves numerically the Boltzmann kinetic equation with a suited collision operator. It describes the evolution of discrete probability densities, whose dynamics and interactions are confined to a regular lattice. Major strengths and advantages, as compared to other standard methods for computational fluid dynamics, are the capability of handling boundary conditions associated with highly irregular geometries and the efficiency to describe non ideal fluids with phase transitions/separation. On the other hand, unlike fully atomistic approaches (as, e.g., MD), the LBM allows to reach hydrodynamical scales with reasonable computational effort. This goes together with a dramatic reduction of the degrees of freedom associated with the (microscopic) velocity space, consequent computational boost and nearly ideal amenability to parallel computing (low communication/computation ratio). Besides the natural realm of macroscopic fluid dynamics, the LBM portfolio of applications keeps expanding across scales of motion, particularly towards micro- and nano-fluidics with active thermal dynamics.

A.1: Controlled deposition of nanoparticles and polymers

The deposition of light-absorbing nanoparticles (like chalcopyrite compounds) or of mixtures of photoactive polymers and organic molecules (as, e.g., poly(3-hexylthiophene and (6,6)-phenyl-C61 butyric acid methyl ester) on a substrate is at the core of modern technologies for photovoltaics. The functional material is first dissolved or dispersed in a solvent and then cast on the substrate in the liquid phase by spin coating. This technique consists in delivering the fluid on a rotating plate [13], so that the liquid layer thins by the concomitant action of radial spreading and solvent evaporation. If the solid surface is not perfectly wettable, below a critical value of thickness, the liquid film is not thermodynamically stable [8,14-19] and dewets, for the surface energy can be lowered by rupture of the film into droplets.

A bundle of mechanisms, then, contribute to the layer morphology: centrifugal spreading, moving contact lines, solvent evaporation, solute diffusion. The stick-slip motion of the contact line, for instance, is believed to cause modulation tangentially to it [20-22]. Moreover, as the drying progresses, the particle volume fraction increases leading to particle aggregation and jamming [23-26], which confers the material soft-glassy rheological features [27,28]. Under these conditions the spreading mechanics and the coating morphology are substantially affected by the particle shape, their aggregation and interactions with the wall and sensitive to rheological instabilities [29-31]. Overall, it is evident that a detailed microscopic understanding and a predictive model for the formation process represent a challenge and calls for an *ad hoc* methodological approach.

The main goals are, then: i) to identify the mechanisms driving contact line instabilities and inhomogeneous drying which cause unwanted non-uniformities in the deposited layer; ii) to develop predictive models to prevent such non-uniformities and methods for the active control over otherwise spontaneous processes.

To achieve this, a sequence of fundamental tasks need to be undertaken.

A.1-I First, we will carry out LBM numerical studies of the spin coating of suspensions, that account, dynamically, for the solvent evaporation and that explicitly resolve suspended rigid and soft nanoparticles. Typically, in the first part of the spin coating process, the film thickness (of the order of 500 μm or more) and the speed of the advancing front are such that the Reynolds number is finite and, therefore, inertia plays a role. Therefore, the lubrication approximation fails and a full description of Navier-Stokes hydrodynamics, that we provide in our simulations, is needed.

We will perform a systematic study of the morphology of the deposited layer at varying the particle-particle and particle-wall interactions, the wettability and, thanks to the versatility of LBM in handling complex boundary conditions, the surface topography (modelled in terms of geometrical posts or grooves). We will, then, extend the investigation to magnetic and thermophoretic particles, thus exploring further ways to optimise the layer structure formation. Magnetic particles are a feature already available in the simulation package that I have at disposal. Thermophoresis will be

implemented, according to the general theory of colloidal phoresis [32], through an effective slip velocity at the solid particle surface, proportional to the local tangential gradient of the temperature field [33-35]. The aim is to control particle deposition by means of a modulated heating of the substrate, in order to hinder layer non-uniformities.

A.1-II In the case of polymers, the deposition may be affected also by internal dynamical degrees of freedom. Polymer under flow, for instance, being stretched by velocity gradients, migrate across curved streamlines [36] driven by configurational entropic forces; consequently, the longer the chain the stronger the tendency to migrate. In an evaporating droplet this drift mechanism must be expected to alter the deposition pattern, as compared to the usual “coffee-stain” effect [37]. Although the shear-induced drift for chain macromolecules has been recognised for a long time [38,39], it has been somewhat overlooked in this context. To probe the role of configurational dynamics in the deposition dynamics of polymers, we will perform hybrid simulations, coupling a fluctuating LBM scheme with a Molecular Dynamics (MD) solver for chains of point-like monomers. The clarification of this mechanism would open new ways to actively control the deposition of polymeric material, e.g., by modulated heating of the substrate.

My plan is to use the numerics as a *surgery* for these complex systems, adding or removing selectively the different mechanisms (e.g. switching on/off the evaporation), something obviously unfeasible in an actual experiment, in order to disentangle the various possible causes of the observed phenomena.

A.1-III Building upon previous works [17,19,40-44], we will develop a long-wave model where, the spreading and (de)wetting dynamics are described by a set of coupled partial differential equations for the film thickness and vertically averaged variables (solute concentration, temperature). Substrate-layer interactions (yielding the disjoining pressure) and boundary conditions (contact angles) for such equations will be distilled phenomenologically out of the microscopically resolved LBM computations. In the case of polymer solutions, the main novelty of our model consists in introducing the non-Newtonian properties of the fluid explicitly via the coupling with the vertically averaged equation of viscoelastic constitutive models [45]. This represents a major improvement in the context of lubrication models. Viscoelastic effects, in fact, have been proven to influence the dewetting of thin polymer films [46], however they have been mostly disregarded in the modelling, or taken into account only in the linear regime [47].

These investigations will boost the state-of-the-art in the field. In recent years, a huge effort has been spent in developing lubrication models for dewetting and for thin films of solutions/suspensions [17,19,40-44]; nonetheless, certain important aspects remain unexplored or unsolved. Long-wave models are derived from the equations of viscous hydrodynamics; although these remain a valid tool also at the nano-scales of very thin films, the continuum assumption must be expected to fail to capture quantitatively certain features, as the characteristic widths are further decreased. These arguments have motivated the development of stochastic lubrication equations [48-50], derived from the fluctuating Navier-Stokes equation [51]. Stability analysis and numerical integration of such equations in 1D have shown that, indeed, thermal noise affects the growth of the dewetting instability and the spectrum of capillary waves, but also the late stage droplet distribution and coarsening dynamics [48,52,53]. An interesting question that arises, then, concerns the role of thermal fluctuations on the dewetting of thin films of viscoelastic fluids [46,47,54].

A.1-IV We will extend the stochastic lubrication equation [48] to the case of fluids with non-Newtonian constitutive relations for the stress tensor (e.g. a power-law fluid) [55,56]; we will perform stability analysis of the equation (in 1D) and numerical simulations (in 1D and 2D) to assess the combined impact of thermal fluctuations and viscoelasticity on the morphology of a dewetting thin film. The results will be validated against LBM simulations with thermal fluctuations.

A.2: Structure and rheology of soft jammed materials

Particle aggregation is ubiquitous in micro- and nanoscopic systems. One instance of such mechanism occurs when colloids are suspended in a binary fluid non-ideal mixture: the particles tend to be sequestered at the fluid-fluid interfaces, a process favoured thermodynamically by the

lowering of the surface energy. Depending on the particle-fluid affinity and on the molar composition of the mixture, different arrangements take place [57], giving rise to capillary suspensions [58], Pickering emulsions [59] and bijels [60-61]. In the latter case, the arrested coarsening of an emulsion by jamming of colloidal particles absorbed at the interface yields two interpenetrating bicontinuous liquid domains, separated by a multiply connected solid-like layer. This peculiar structure makes bijels suitable candidates for numerous technological applications, as, for instance, microreactors [60,62], or precursors of porous materials [63], to be used as catalyst carriers. Surface modified nanoparticles have been employed to stabilise bicontinuous interpenetrating structures in polymer blends [64,65]. This suggests a new strategy to engineer BHJs for OPV with controlled morphology: the use of nanoparticles with properly treated surfaces to achieve optimal bicontinuous patterns. This possibility is appealing but poses, from a theoretical point of view, important problems that need to be clarified; some of them are motivated by the applications, others are mainly knowledge-driven and relate to the rheological properties of these materials.

The key questions are: i) how can one obtain a certain structure of the polymeric bijel, for given particle geometry (size and shape), particle/fluid interactions and fluid properties? ii) How does the rheology of the material depend on the characteristics of the structure (porosity, tortuosity)? iii) Can one capture theoretically the rheological properties of bijels within the framework of soft-glassy models?

A.2-I We will set up LBM simulations of mixture of two immiscible fluid with suspended resolved particles; the non-Newtonian properties typical of a polymeric liquid will be accounted for via the coupling with continuum

equations of viscoelastic constitutive models, as mentioned in A.1-III (further details on the method are discussed in section B.). This comes along with the issue of the implementation of the proper boundary condition for the polymer stresses on the particle surface. The latter will be inferred phenomenologically from the outcome LBM-MD simulations, of the type described in A.1-II, with a single resolved particle, for a given particle/polymer microscopic interaction.

To the best of my knowledge, such hybrid LBM/continuum approach to binary polymer liquids coupled with resolved solid particles is totally new. A related model has been proposed for colloids in liquid crystals, though for a single fluid [66].

We will characterise the kinetics of formation of the bijel and the morphology of the jammed structure for different particle/polymer interactions and for three combinations of fluids, where: both are Newtonian, only one is Newtonian, both are viscoelastic. In the latter case, different degrees of polymer elasticity will be explored. In particular it is interesting to ask whether the emergence of the bicontinuous structure and its porosity are affected by the viscoelasticity the two liquid phases. This aspect is important, since viscoelasticity depends on polymer concentration in the solution; hence, one can control it by regulating the amount of solvent (e.g., via the ambient temperature) in the spin-cast layer, i.e. when the blend starts to demix.

A.2-II We will look for a quantitative matching between the structure and rheology, namely between yield stress and elastic modulus and porosity/tortuosity. To this aim, we will perform rheometric numerical tests on polymeric bijels, probing both the elastic and viscous regimes. Different loads will be applied: Couette flow, time-oscillating strain and Kolmogorov flow, to assess whether the global rheology can be captured by a general viscoelastic Herschel-Bulkley-like [1,67] relation; the study will then be extended to the case of confined geometries: under these conditions, it is known

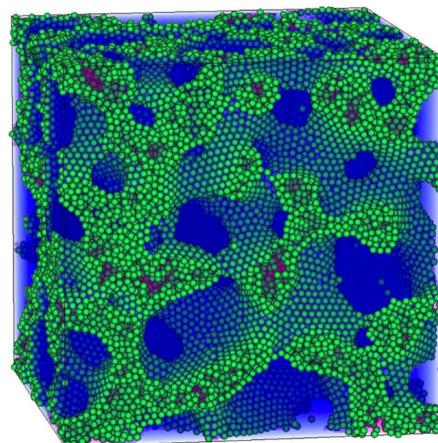


Figura 3. Snapshot from a LBM simulation showing the formation of a bijel

for many soft materials [68-71] that deviations arise from global rheological constitutive equations, owing to non-local correlations over length scales comparable with those of the confinement. For bijels, squeezing one (or more) spatial dimension (e.g. between two parallel walls) would change the particle structure, also in dependence of the particle-wall interaction. The objective is to detect signatures of confinement-induced breakdown of global rheological relations and to check to which extent the behaviour under confinement is universal; this means that the flow profiles can be captured with universal analytic expressions, upon rescaling the variables by quantities containing the specificities of the wall interaction (in analogy to models for soft-glassy rheology [72,73]).

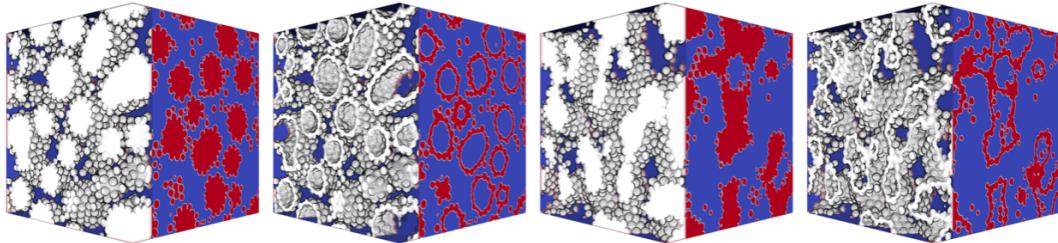


Figura 4. Images from LBM simulations of a self assembled porous structure from nanoparticle suspensions (S. Frijters and J. Harting, preprint)

A.3: Fluid dynamics of catalytic processes

The performance of a catalytic reactor is the result of the interference of many complex physical and chemical phenomena taking place on different scales. At the microscale, reactants diffuse, adsorb at the solid catalyst surface, react and the desorb and diffuse again towards the bulk. On the other extreme, the hydrodynamic transport of heat and mass plays also a crucial role; mass transfer limits the access of fresh reactants at the catalyst surface and temperature changes the local reaction rate. These two aspects of the process, moreover, influence each other: an exothermic reaction (like certain oxidations), for instance, heats up the fluid and generates convective flow transporting heat and mass, which, in turn, affects the reaction rate. The fluid dynamics of the problem is complicated by the geometry, i.e. the reactive fluid flows through the porous structure of the reactor.

Having to cope, simultaneously, with the physicochemical characteristics of the catalyst and the reaction (availability of active sites, binding efficiency, reaction rate, reaction energetics) and with the macroscopic heat and mass transport, modelling heterogeneous catalysis is challenging and, therefore, relied mainly on phenomenological models based on average quantities and effective parameters. However, no general consensus exists about them. Numerical simulations can represent, instead, an invaluable tool

for a precise understanding of the relevance of physical processes (heat and mass transfer) for given chemical characteristics of the catalyst and to identify optimal conditions to control the catalytic performance, in terms of maximisation of the yield and minimisation of the by-products.

As witnessed by the extensive literature, LBM is particularly fledged to simulate fluid flow in complex geometrical landscapes like porous media [74,75] and it has been employed successfully to model reactive flows in simpler geometries [76]. To attack the highlighted fundamental problems, I plan to advance the current state-of-the-art setting a novel numerical framework for the simulation of catalytic flows. The realisation of this objective needs the achievement of the following tasks.

A.3-I We will develop a thermal multicomponent LBM scheme to simulate reactive fluid flows through porous media. The reactivity will be embedded in the LBM via diffusive boundary conditions at the walls, mimicking chemical processes occurring at a catalytic surface [77]. The chemistry of the reaction will be resolved by means of *ab initio* MD studies out of which the

reaction rate coefficients and their dependence on the temperature are computed and then fed into the LBM.

A.3-II The implementation will be first validated in simple setups like a straight channel flow with pure reactant entering at the inlet and undergoing a first order reaction at the wall (and benchmarked against analytical results [78]), to be able to gauge reaction rates with the LBM units. In a second stage, I intend to perform large-scale direct numerical simulations in more complex geometries and, eventually, porous media. For the latter, various templates will be tested, e.g. different arrangements of solid spheres or self-assembled structures of nanoparticles (see A.3).

A.3-III We will investigate systematically different flow regimes, changing the inlet condition, the thermal boundary condition at the solid surfaces, the porosity and tortuosity of the medium. Through these resolved computations we will be able to control which are the relevant variables and how they determine the heat and mass fluxes (non-dimensionally expressed as the Nusselt and Sherwood numbers) and the reactor efficiency.

B. METHODS

This multidisciplinary project has the ambition to probe phenomena and mechanisms which are hard (next to impossible in certain cases) to access experimentally and prohibitive to simulate with fully atomistic approaches. The *in silico laboratory*, based on new theoretical models and an innovative numerical platform, that I propose to develop offers, in this respect, a unique framework.

B.1: Numerics

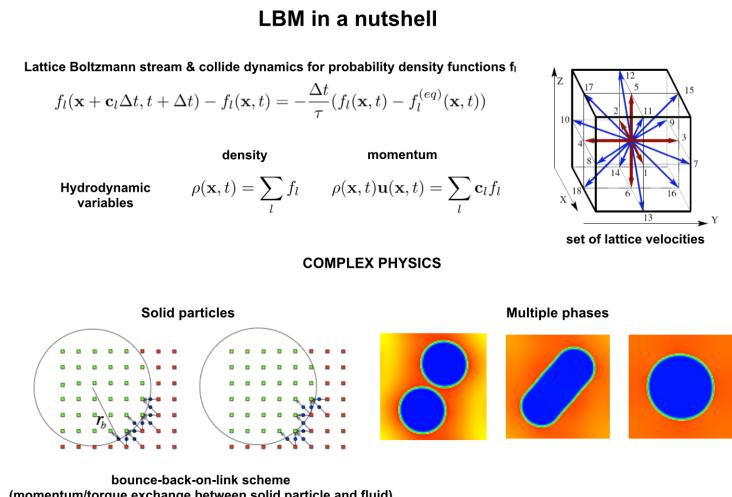
The methodology stems from mesoscopic approaches, grounded in kinetic theory. The central quantity, here, is the one particle probability density function, evolving according to the Boltzmann equation. The LBM solves a discrete version of such equation with a properly chosen collision operator [79]. There are many advantages in using LBM to study flowing complex fluids in simple and complex geometries:

- i) the method naturally describes a diffuse interface physics between species and/or phases [80-82];
- ii) it allows for simple and precise rules to incorporate non-trivial fluid-solid interactions [83-88];
- iii) it is fully local in space, making upscale and parallelisation effective;
- iv) at difference from atomistic approaches, like MD, it has access to hydrodynamic scales. The LBM-based numerical platform that will be employed features a number of multiphysics modules to simulate multiphase and multicomponent fluids, suspensions of finite size solid and soft particles, and fluctuating hydrodynamics [57,89-91].

During the development of the project,

this existing and well validated tool-kit will be integrated with i) the dynamics of the temperature field [92]; ii) the coupling with the MD solver for polymer molecule dynamics; iii) the coupling with the evolution of the polymer conformation tensor; iii) thermal fluctuations for multicomponent systems [93,94]. After the implementation of the temperature dynamics has been accomplished and tested, we will implement the numerical model for the evaporation, one of the main features of the proposed methodology. This will be done introducing the dependence of the parameter which control the lattice interaction [80], hence the phase separation, on the dynamical temperature. A similar procedure will be implemented to model thermocapillarity.

In the LBM-MD scheme, polymers will be modelled as linear chains of point-like monomers (various possible choices for the bond potential will be implemented), following the scheme of [95].



In order to allow for the description of polymer dynamics at a coarser level, so to get access to hydrodynamic scales and to introduce in a more straightforward way non-Newtonian rheology effects in continuum models, we will develop a hybrid approach where the LBM is coupled to continuum equations (solved with finite difference schemes) for the conformation tensor field of the polymer (i.e. the ensemble average of the tensor product of its end-to-end distance vector) [96]; these equations come from constitutive viscoelastic models, like the upper convected Maxwell model or the Oldroyd-B model [45].

The implementation of the thermal fluctuating LBM scheme for multicomponent systems will be need to describe more accurately phenomena at nanometric scales (e.g. very thin films) where the continuity assumption loses validity.

For the sake of studying catalytic flows in porous media, the implementation of a thermal LBM will be developed, with proper diffusive wall boundary conditions [77], to simulate reactions within multicomponent fluids catalysed at solid surfaces. These simulations will be integrated with *ab initio* MD studies of the chemical reactions to extract realistic reactions rates, calculated with a Density Functional Theory approach.

B.2: Theory

From the theoretical point of view, the proposed research activity will make use and extend analytical tools coming from thin film lubrication theory [8,9,10,17,19]. By lubrication approximation one means a perturbative (long wavelength) expansion of the equations of viscous hydrodynamics. One of the objective is to develop lubrication equations for fluctuating viscoelastic hydrodynamics: these will be derived, in analogy with [46,47] and [53,54], from the Landau-Lifshitz equations of fluctuating hydrodynamics [49] (in the zero Reynolds number limit), with a non-Newtonian constitutive relation for the stress tensor.

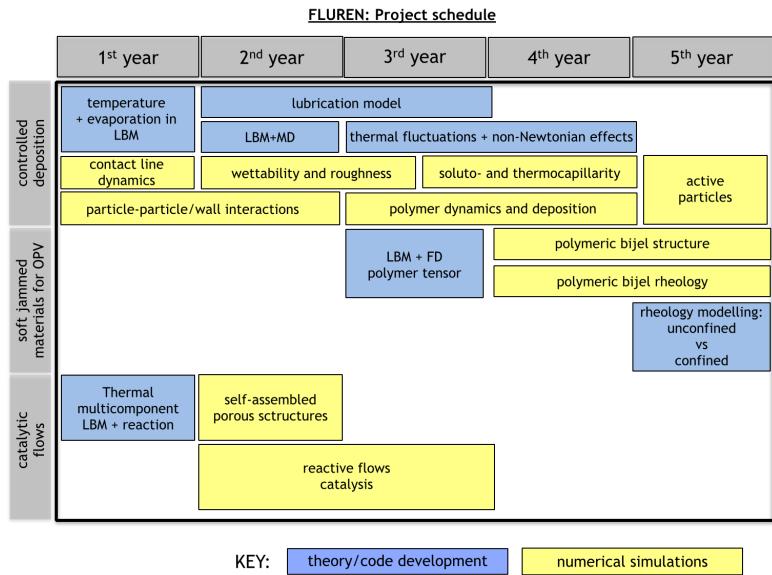
In the context of long-wave theories for solution/suspensions, we will introduce non-Newtonian behaviours explicitly, coupling the equation for the vertically averaged velocity with one for the vertically averaged conformation tensor field.

C. PROJECT MANAGEMENT AND TIME-SCHEDULE

The time-schedule will be discussed with reference to the three thematic axes in which the project is structured and the corresponding tasks, as indexed in section A.

(A.1) The activity of the Young Investigators Group (YIG) will begin with the implementation of temperature dynamics and phase transition in the LBM. In parallel we will start to perform fully resolved simulations of spin-coating (yet without the evaporation), investigating the effects of different inter-particle and particle-wall interactions on the contact line dynamics. This activity will be extended to the first two years of the project (A.1-I).

MILESTONE M1 (end of year 1): temperature and evaporation dynamics successfully implemented in the LBM code and validated.



During the second year we will start to work at the long-wave model and to study it numerically (A. 1-III). In parallel we will develop the hybrid LBM-MD code for polymer dynamics (A.1-II). Productive runs of spin-coating and deposition will continue during years 2 and 3: extra complexities and parameters will be explored, namely the substrate wettability, the geometrical roughness and the

evaporation (A.1-I). While carrying out the simulations, we will start to approach the phenomenological derivation of effective boundary conditions for the lubrication model (A.1-III).

MILESTONE M2 (end of year 2): hybrid scheme LBM-MD implemented and ready for production.

With the third year, productive runs on polymer dynamics inside evaporating droplets with the LBM-MD code will start and will go on until the end of the fourth year (A.1-II). At the same time, we will also start to elaborate the derivation of the stochastic non-Newtonian lubrication equation (A.1-IV) and we will implement the thermal fluctuations in the multicomponent LBM.

MILESTONE M3 (end of year 3): derivation of effective boundary conditions for the lubrication model.

Meanwhile, we will carry on numerical studies of the long-wave model, focusing in particular on the effects of temperature and solute concentration dependent capillary forces (A.1-III). Such studies will continue during the fourth year, in parallel with stability analysis and numerical studies of the coupled thermal and non-Newtonian effects in the lubrication equation (A.1-IV). During the last year we will focus on the active control of layer formation using magnetically and thermally activated nanoparticles. We will allow the resolved particles in LBM to perform thermophoresis, i.e. the movement of particles in temperature gradients. This will be realised adding an effective slip velocity proportional to the local tangential gradient of temperature [32,33], in the bounce-back-on-link scheme [83], that is the boundary condition for the fluid at the particle surface.

(A.2) In the third year we will develop the LBM-FD solver for the polymer conformation tensor (A.2-I). With this new feature in the 3D-LBM tool, we will start, from the beginning of the fourth year, to analyse systematically the morphology of the particle networks formed in bijels with polymeric liquid phases. This imply a non-trivial problems: the implementation of a proper boundary condition for the polymer conformation tensor dynamics at the moving particles surfaces.

MILESTONE M4 (mid-year 4): Implementation of the dynamics for the polymer conformation tensor, together with the moving boundary conditions.

With this machinery set up, during the years 4 and 5, we will explore numerically the parameter space spanned by the degree of viscoelasticity of the polymeric liquid, particle shape, wettability and volume fraction and characterise the morphology of the jammed structure of the bijel (A.2-I) and then the structure-rheology relation (A.2-II).

(A.3) The studies on catalytic flows will start from the first year of the project, which will be dedicated to the code development for the thermal multicomponent LBM with reactive boundary conditions (A.3-I) and to its validation in simple setups (A.3-II).

MILESTONE M5 (end of first year): Development and validation of the thermal multicomponent LBM with reactive boundary condition.

In the years 2 and 3, then, production will take place: various inlet conditions, boundary conditions for temperature and morphology of the porous medium will be investigated (A.3-III).

D. BUDGET JUSTIFICATION

D.1: Personnel

The project will cover full-time my research activity, whence the expenses for my salary for five years. In addition, the realisation of the planned tasks calls for hiring two PhD students, each for four years. One of them will be hired starting from the first year and until the end of the fourth, while the other will be hired starting from the second year until the end of the project. A PostDoc researcher, from the existing staff, will be also paid on the granted funds for the whole duration of the project.

PhD 1: focusing on 3D LBM simulations of controlled deposition and continuum model

- **Year 1:** Extending existing simulation code towards consistent treatment of temperature and evaporation. Starting systematic investigation of the impact of microscopic particle-particle and particle-substrate interaction on contact line dynamics (A.1-I).
- **Year 2:** Continuing resolved 3D simulations, addressing the effect of substrate wettability, roughness, evaporation (A.1-I). Starting the development of the lubrication model (A.1-III).
- **Year 3:** Studying the effects of soluto- and thermocapillarity on deposition by receding contact lines in the framework of the continuum model (A.1-III). Derivation of the lubrication equation with thermal fluctuations and non-Newtonianity (A.1-IV).
- **Year 4:** Analysis of the stochastic non-Newtonian lubrication equation (A.1-IV). Ultimating studies of the continuum model (A.1-III). Writing PhD thesis.

PhD 2: focusing on LBM with polymers and soft materials

- **Year 2:** Development and validation of the LBM-MD code for resolved polymer simulations (A.1-II).
- **Year 3:** Carrying out productive runs with the LBM-MD code (A.1-II). Development of the hybrid LBM-FD code for the simulation of the polymer conformation tensor (A.2-I).
- **Year 4:** Continuing simulations of polymer deposition with LBM-MD (A.1-II). Performing simulations of emulsions of polymeric liquids with suspended particles. Studying the structure of bijels (A.2-I).
- **Year 5:** Ultimating studies on bijels. Writing PhD thesis.

PostDoc: focusing on simulations of catalytic flows and rheology

- **Year 1:** Development of the thermal LBM code with reactive boundary condition (A.3-I) and validation in simple setups (A.3-II).
- **Year 2:** Design of porous structures from templates of self-assembled nanoparticles (A.3-II). Simulations of reactive flows in catalytic porous media (A.3-III).
- **Year 3:** Simulations of reactive flows in catalytic porous media.
- **Year 4:** Numerical studies of the rheology of bijels and soft jammed materials (A.2-II).
- **Year 5:** Modelling the rheology of bijels (A.2-II). Simulations of thermally and magnetically activated particles (A.1-I).

D.2: Investments

The realisation of the planned research relies on the massive use of high resolution numerical simulations, so the required computational resources are huge. Therefore, I will employ the assigned investment costs to buy memory extensions and new processors for our local cluster at HI-ERN, in Nuremberg.

D.3: Utilisation costs

The utilisation costs will be devoted mainly to cover expenses of the YIG staff to attend workshops, conferences, but also to consolidate international scientific collaborations and open new ones. Here it is meant also to invite prominent scientist from abroad to co-work on the topics of FLUREN. I also plan to spend part of this money for the organisation of a kick-off meeting, during the first year, to *advertise* FLUREN to the scientific community.

E. RELEVANCE OF THE PROJECT FOR HOST INSTITUTION

The goals of the project, outlined in section A, promise to shed light on a set of frontier problems of utmost relevance for the research programme carried out at HI-ERN; in particular, topic-wise, FLUREN represents the theoretical-numerical support to the experimental activities focusing on catalysis and on the development of materials and nanoparticles for printable photovoltaics. Moreover, the host of scientific themes proposed fits well with those of the research unit Modelling of Thin Films; at the same time, my YIG would strengthen, in terms of staff units and variety of research topics, the theory sector of the Institute.

My expertise in statistical mechanics, theoretical and computational fluid dynamics and soft matter physics would be beneficial also for the Faculties of Physics, Chemical and Biological Engineering and Computer Science at the Friedrich-Alexander University of Erlangen-Nuremberg (FAU), where

I may deliver lessons in courses associated to the Chairs of Statistical Physics, Condensed Matter Physics, Fluid Mechanics, Multiscale Simulation, Applied Thermodynamics and System Simulation.

F. COOPERATION

The possibility of realising FLUREN at HI-ERN, on the other hand, represents also a unique advantage for its successful outcome. Here, the project will benefit from synergies with the groups led by Prof. Jens Harting (concerning the computational techniques) and by Prof. Peter Wasserscheid and Prof. Karl Mayrhofer (for the experimental benchmark and validation of the catalysis modelling).

At the Jülich Research Centre (FZJ), scientific interactions are foreseen with the activity carried out at the Institute for Energy and Climate Research, in particular that on photovoltaics at IEK-5. Being part of FZJ will also allow me to access computational facilities at the Jülich Supercomputing Center, necessary for the feasibility of a research heavily based on computations.

Moreover, the Erlangen-Nuremberg area represents an excellence in the fields of Energy Technology, Soft Matter and Fluid Dynamics, with worldwide renowned scientists working at FAU and at the Energy Campus Nuremberg.

At the FAU, I envisage various collaborations with researchers from the Departments of Physics and Chemical and Biological Engineering.

Prof. Klaus Mecke, in the Department of Physics, is one of the pioneers of the introduction of thermal fluctuations in the theory of lubrication; exchanges of ideas with him would definitely favour the rapid and successful outcome of the planned studies on stochastic non-Newtonian lubrication equations.

In the same Department, Prof. Ana-Sunčana Smith is interested in numerical studies of catalysis; a synergic cooperation with her on this topic would certainly be advantageous for the realisation of the tasks outlined in section A.3, thanks to the combination of two complementary expertise (mine of LBM and hers on quantum MD methods).

In the Department of Chemical and Biological Engineering, I plan to involve Prof. Robin Klupp Taylor and his lab in the activities of FLUREN as the experimental support; Prof. Klupp Taylor, who is also associated with the HI-ERN, focuses on nanostructures particles, with an interest for applications to printable photovoltaics.

Finally, regular interactions with the laboratories of Prof. C. Brabec and Prof W. Peukert are foreseen for the experimental implementation of the techniques of active control on solution processing in organic photovoltaics, elaborated with our theoretical work.

At international level, I plan to strengthen ongoing collaborations with Prof. Mauro Sbragaglia and Prof. Roberto Benzi from the Statistical Mechanics and Complex Fluids group at the University of Rome "Tor Vergata", with Prof. Sauro Succi at the Institute for Applied Computing in Rome, with Prof. Ignacio Pagonabarraga, leading the Soft Condensed Matter group at the University of Barcelona, and with the group of Prof. Federico Toschi at the Eindhoven University of Technology. All of them are active and with outstanding records of research in microfluidic and soft matter topics closely related to the objectives of this proposal.

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