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Modern simulation approaches in soft matter science: From fundamental understanding to industrial applications

Festschrift on the occasion of Kurt Kremer's 60th birthday

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Abstract. This special topics issue offers a broad perspective on recent theoretical and computational soft matter science, providing state of the art advances in many of its sub-fields. As is befitting for a discipline as diverse as soft matter, the papers collected here span a considerable range of subjects and questions, but they also illustrate numerous connections into both fundamental science and technological/industrial applications, which have accompanied the field since its earliest days. This issue is dedicated to Kurt Kremer, on the occasion of his 60th birthday, honouring his role in establishing this exciting field and consolidating its standing in the frame of current science and technology.

Soft matter science has been the center of attention during the last decades, either for technological advancements (e.g. the development of light but resistant new materials) or for scientific discoveries of unexpected phenomena (e.g. conducting polymers, honoured by the 2000 Nobel Prize). Biophysics, a closely related and partly overlapping discipline, has grown considerably in the last decades, and this has facilitated many important breakthroughs, ranging from fundamental biology to biomedical applications, some of which have immediate relevance to us, such as drug delivery.

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A key role in this expansion has always been played by theory, especially in synergy with computer simulations that cover a wide spectrum of resolutions. From the earliest days of computational science, simulation has served as a fundamental link between soft matter theory and experiment, and as a key tool to find the properties of a given theoretical model, typically without the need to employ uncontrolled approximations. In the context of soft matter, models aiming at chemical specificity have always coexisted with those focusing instead on decisive aspects of the physics, while deliberately neglecting most details. Scientists understood—and made it a guiding principle in their approach to any new problem—that the choice of modeling resolution depends on the question one wishes to answer. This has enabled deep insights across all scales, while it also implied that many advances in disciplines ranging from quantum chemistry to continuum mechanics happened side by side, and essentially independent of each other.

And yet, nature is undivided. Models at different resolution merely capture different aspects of the same reality. In domains where models overlap in scope, consistency demands connections that hint at deeper physical truths. Especially at the coarse level of resolution, this insight led scientists to pursue how tiers connect, how emergence happens, and how information gets compressed into a small number of effective parameters. This pursuit shared both motivation and many techniques with the discovery of renormalization. For instance, it was noticed that approximate mapping schemes between different models at different resolution, which are typically forced upon practitioners by the need to avoid unfeasible computational complexity, lead to difficult-to-control renormalization errors, known in the field of coarse-graining as transferability and representability issues.

Efforts to clarify these connections have not only led to fundamental insights into the nature of reality, but are increasingly contributing to technological advances. An example is rational materials design, where we begin to understand how molecular details result in large-scale material properties, and how, conversely, a desired material property might be created through cleverly chosen chemistry. In this spirit, the aim of the present collection of papers is to offer an overview and reference for the development of theoretical/computational methods and their application to systems of experimental and technological relevance.

This issue comprises 32 papers, which can be roughly divided into two major categories: advancing the foundations of the field by developing new theory, methods, or models; and contributing to new scientific discoveries by applying the broad set of tools available in computational soft matter science to a specific system of interest. Let us provide a brief overview of what the reader will find in this special topics issue.

The theoretical part of this issue is opened by a set of papers that inquire into methodological aspects of coarse-graining, especially the development of reliable force fields. Rosenberger et al. draw our attention to the fact that several iterative inverse coarse-graining strategies, while reproducing structure very well, often fail to capture thermodynamic variables, and they demonstrate how the addition of thermodynamic constraints (such as pressure or Kirkwood-Buff-Integrals) can remedy such a situation [1]. Kalligiannaki et al. focus on the parametrization of molecular systems at equilibrium (using a spectrum of different methods, ranging from structure based over force matching to relative entropy minimization) [2], while Rudzinski and Bereau explore how a simultaneous parametrization against both static and kinetic information can improve the robustness of coarse-grained force fields [3]. Elfgen et al. construct force fields for salt solutions containing magnesium chloride and calcium chloride, using both a static (density) and a dynamic (shear viscosity) observable to tune the interactions, and they discuss what level of error one would need to tolerate in order to obtain a transferable force field [4]. Doi also explores the problem of coarse-graining

in a dynamic context, but starting with Onsager's principle in its variational formulation as the basis of a general framework, which can be applied directly in practical computations [5]. Zhang et al. develop a hybrid particle/density-functional representation for polymers adsorbed to solid substrates (considering the specific example of poly (methyl methacrylate) adsorbed on silica) and examine the range over which reliable results can be obtained for several standard observables characterizing this geometry [6]. Scherer and Andrienko compare systematic coarse-graining strategies for the special case of soluble conjugated polymers, where different projections of the many-body potential of mean force onto the coarse-grained force field result in very different coarse-grained potentials [7]. In contrast, Dalgicdir et al. explore how to investigate environment-induced helix-coil transitions in a coarse-grained peptide model, a problem where large-scale effects triggered by changes in the surroundings constrain the choice of coarse-grained interactions [8].

The next set of papers is dedicated to hybrid and adaptive methods — approaches that aim to capture different resolutions within the same simulation, an approach that promises not only enhanced computational efficiency, but also elegant solutions to a certain class of domain bridging problems. Everaers starts off by investigating the very fundamental question of translational invariance in concurrent multiscale simulations of liquids, when different molecular resolutions are simultaneously employed in different regions of space [9]. Heidari et al. propose an accurate general scheme for treating long-range electrostatic interactions in Hamiltonian adaptive resolution simulations [10]. Qi et al. show how adaptive resolution ideas can be used to derive elegant coupling schemes between the worlds of particle and continuum polymer models [11]. Guo et al. pursue the same goal and propose a multiscale scheme that bridges between the worlds of Molecular Dynamics and Navier-Stokes, for treating electroosmotic flow through micro- and nano-channels [12]. Similarly, Zorkot et al. look at the effects of electrostatic and hydrodynamic interactions on the electric current through nanopores, finding that, contrary to expectation, the exponent of the current's power spectral density is not affected by the neutral solvent—at least in the frequency range studied [13]. And Zavadlav et al. demonstrate that adaptive methods can be pushed to the extreme by coupling an atomistic model of DNA with a coarse-grained (MARTINI-level) representation of a salt solution [14].

When running any type of simulations, proper sampling of the important region of phase space (or trajectory space, when studying dynamics) is a major concern. Borrero and Dellago show how to use metadynamics in order to improve trajectory sampling when studying the transition path of a reaction [15]. Perego et al. take a fresh look at the problem of calculating the chemical potential in dense liquids, using metadynamics [16].

Slotted between the "theory" and "application" side, this issue contains a number of papers that look at specific model systems in order to gain insight on numerous quite fundamental questions. That these two modes of inquiry have always blended into each other is in fact one of the characteristic hallmarks of soft matter science.

Ferrario et al. take a new look at thermal diffusion in a binary Lennard-Jones liquid beyond the stationary state, i.e. the evolution of the density and temperature fields following the onset of a thermal gradient, and they demonstrate that a suitable non-equilibrium Molecular Dynamics technique can access thermal diffusion characteristics of such a system, even transient ones [17]. Ustach and Faller investigate the diffusion of model proteins through cylindrical pores, accounting for both hydrodynamics (using Lattice-Boltzmann techniques) as well as nontrivial particle shape (by constructing spheres and ellipsoids in a "raspberry fashion" from simple coarse grained spheres) [18]. Binder et al. revisit the notion of persistence length, whose traditional definition as the decay length of the bond angle autocorrelation

function only holds for Gaussian phantom chains, a limit far away from objects such as bottle brush polymers [19]. Tito and Frenkel investigate an interesting switching behavior in the binding of two different species of multivalent particles—one with a few strong ligands, the other with many weak ones—to a surface covered by receptors: changing the receptor concentration can switch which particle type predominately binds [20]. Stevens and Saleh investigate the scaling regime in the force-distance curves of stretched polyelectrolytes subject to screened Coulomb interactions, paying particular extension to a logarithmic scaling regime and its connection to excluded volume interactions [21]. Bordin et al. probe a different electrostatic phenomenon, the effect of static polarizability effects on counterion distributions near charged dielectric surfaces (within the framework of a Drude model), which they find to be relevant for ions with high excess polarizability near surfaces with high surface charge [22]. Salerno et al. study how the degree of coarse graining effects the dynamics of polymer melts, showing that after suitable rescaling, consistent results can be obtained; they reach effective times beyond half a millisecond, permitting a quantitative comparison of observables such as stress relaxation function, plateau modulus, and shear viscosity with experiment [23]. And Humpert et al. investigate the orientational dynamics of single particles in nematic liquid crystals, providing the first simulation evidence of long-time tails characteristic of coupling to director fluctuations [24].

Finally, this issue concludes with a number of papers that illustrate how theoretical and computational tools can deepen our understanding of specific model systems. Pelizza et al. conduct a density functional study of a particular ferroelectric polymer—poly(vinylidene difluoride) or PVDF—and show that the inclusion of van der Waals interactions is crucial in order to predict the correct lattice structures, polarisation, and energetics of PVDF polymorphs, which matter in applications such as flexible electronic devices [25]. Bagheri et al. use QM/MM simulations and many-body Greens function theory to explore what effects the solvent has on optical excitations of the conjugated polymer poly-*para*-phenylene ethynylene—finding that the electronic environment contributes negligibly compared to the conformational dynamics of the polymer [26]. Krishnamani et al. crack open a systematically coarse grained model of cowpea chlorotic mottle virus by uniaxial compression, showing that beyond quantitatively reproducing the force-compression curve, they can infer the relative stabilities of different interfaces and from there deduce a plausible assembly order of the full capsid [27]. Jang and Abrams study a pair of epoxy-based thermoset polymers—diglycidyl ether of bisphenol-A (DGEBA) and poly(oxypropylene) diamine (POP-DA)—and show that a correct prediction of the cross-linked compound's Young modulus might fail if the coarse-grained potentials contain regions of incorrectly extrapolated functional form, but that this can be fixed without sacrificing the already correct prediction of densities [28]. Tang et al. explicitly model two technologically important types of multi-block-copolymer self-assembly, namely solvent casting and spray coating, showing how the different processing conditions affect material properties in numerous ways and—due to very slow dynamics—for extremely long times [29]. Pacalin et al. investigate how the chirality of peptides in polyelectrolyte complexes can be used to direct the phase behavior of these systems [30]. DeNicola et al. study a different type of composite—a mixture of long-chained polymers and nanoparticles—and pay particular attention to how a suitable combination of modeling choices can overcome severe modeling challenges arising from slow relaxation times [31]. And finally, Ibrahim and Liverpool investigate how walls affect the dynamics of swimmers which are propelled by asymmetric catalytic physico-chemical properties over their surface, developing phase diagrams that categorize various characteristic swimming behaviors [32].

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