Final Report
Sedimentation of binary mixtures:
Phase stacking and Nonequilibrium dynamics

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1 General Information

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2 Zusammenfassung / Summary

Zusammenfassung. Mittels der Theorie der Gleichgewichtssedimentationspfade und der lokalen Dichtefunktionalnäherung untersuchten wir die Auswirkungen der Schwerkraft auf binäre kolloidale Mischungen. Sedimentierte Systeme werden dabei durch Sedimentationspfade dargestellt, die die Abhängigkeit der nach Spezies aufgelösten chemischen Potentiale von der Höhe bestimmen. Durch Analyse der resultierenden Liniensegmente im Bulk-Phasendiagramm kann die vollständige Phänomenologie von Gleichgewichtsstapelungen unter Schwerkraft beschrieben werden. Der Ansatz sagt die Stapelsequenzen kolloidaler Mischungen aus Stäbchen und Plättchen voraus, wie sie in ikonischen Experimenten durch van der Kooij und Lekkerkerker beobachtet wurden. Dabei ergeben sich bis zu fünf gleichzeitige Phasenschichten aus dem bloßen Zusammenspiel von Schwerkraft und zweiphasiger Bulk-Koexistenz, ohne Partikelpolydispersität. Wir haben die Auswirkungen auf die Phasenstapelung bei Variation des Auftriebsmassenverhältnisses beider Komponenten untersucht und unsere Vorhersagen sind in Experimenten durch Variation der Höhe von Sedimentationssäulen überprüfbar. Ähnliche Sedimentationsstudien haben wir für Mischungen von Plättchen und Kugeln, massenpolydisperse Systeme und harte Sphärozylinder durchgeführt. Wir schlagen vor, dass mikroskopische Eigenschaften von Partikeln, wie die Auftriebsmasse, aus Messungen der Schichtdicken von Phasenstapeln abgeleitet werden können.

Wir haben durch Schwerkraft verursachte Nichtgleichgewichtsströmungen und Strukturbildungen mittels Powerfunktionaltheorie, adaptiver Brownscher Dynamik und funktionalem maschinellem Lernen untersucht. Powerfunktionaltheorie beschreibt das Nichtgleichgewichtsverhalten von Vielteilchensystemen auf der Grundlage von Einteilchendichte und -strom. Wir konnten damit verschiedene Typen von relevanten Nichtgleichgewichtskraftbeiträgen systematisch kategorisieren und entsprechende analytische Gradientennäherungen entwickeln. Neuronale Funktionale, die mittels Simulationsdaten sowohl im Gleichgewicht als auch im Nichtgleichgewicht trainiert wurden, liefern präzise Vorhersagen für die Strukturbildung und das Design von kollektiven Zuständen. Wir haben eine kraftbasierte Dichtefunktionaltheorie formuliert und gezeigt, dass neuronale Dichtefunktionale die besten Rosenfeldschen Dichtefunktionale in ihrer Vorhersagekraft übertreffen. Adaptive Brownsche Dynamik wurde als leistungsfähiges und hochstabiles numerisches Integrationsverfahren für die zeitliche Integration gekoppelter überdämpfter Bewegungsgleichungen entwickelt und auf ein Partikelgel mit konvektiver Sedimentationsströmung angewendet. Theorien wurden geschaffen für Fluktuationen einfacher und hyperobservabler Größen, für die zugehörigen Hyperkraft-Korrelationsfunktionen, sowie für die Eichinvarianz der statistischen Mechanik. Dabei liefert das Noether-Theorem exakte Summenregeln, die wir auf ideale und aktive Sedimentation angewendet haben.

Summary. Based on equilibrium sedimentation path theory and the local density functional approximation, we investigated the effects of gravity on several relevant types of binary colloidal mixtures. Settled systems are represented by so-called sedimentation paths, which determine the variation of the species-resolved chemical potentials with altitude. Analysing the resulting line segments in the plane of chemical potentials of the bulk phase diagram allows one to rationalize the full equilibrium stacking phenomenology for a given system under gravity. The approach predicts theoretically the stacking sequences of colloidal rod-plate mixtures that were observed in iconic experiments by van der Kooij and Lekkerkerker. Thereby the occurrence of up to five simultaneous phase layers emerges naturally from the mere interplay of gravity and two-phase bulk coexistence, without invoking particle polydispersity. We studied the effects on equilibrium phase stacking upon varying the buoyant mass ratio of both components and our predictions are testable in experiments by systematic variation of the height of sedimentation columns. We have carried out similar sedimentation studies for: plate-spheres mixtures, mass-polydisperse systems, and hard spherocylinders. We suggest that microscopic particle properties, such as the buoyant mass, can be inferred from macroscopic measurements of layer thicknesses in phase stacking sequences.

We addressed gravity-induced nonequilibrium flow and structure formation on the basis of power functional theory, adaptive Brownian dynamics computer simulations, and functional machine learning. Power functional theory allows one to rationalize and to model the nonequilibrium behaviour of many-body systems based on the one-body density and velocity field. We have used the approach to categorize systematically the different types of relevant nonequilibrium force contributions and have developed corresponding analytical gradient approximations. Neural functionals, as trained on the basis of both equilibrium and nonequilibrium computer simulation data, were shown to yield accurate predictions for structure formation and design of nonequilibrium flow. We have formulated force-based density functional theory and have demonstrated that neural density functionals outperform the best available hard sphere fundamental measure functionals. We have developed adaptive Brownian dynamics as a performant and highly stable numerical integration scheme for the temporal integration of overdamped many-body Langevin equations of motion, as demonstrated for a particle gel subject to convective sedimentation flow. We have put forward general frameworks for fluctuations of general hyperobservables, for their associated hyperforce correlation functions, and for the gauge invariance of statistical mechanics, where Noether's theorem yields exact sum rules that constrain correlations, as exemplified for ideal and for active sedimentation.

3 Progress Report

Part I: Sedimentation-diffusion-equilibrium in colloidal mixtures (de las Heras)

Overview. Experiments in colloidal systems are suited ideally to investigate collective bulk phenomena such as phase transitions. Colloidal sedimentation experiments require only relatively simple setups and they allow one to observe directly, e.g., the thermodynamically stable

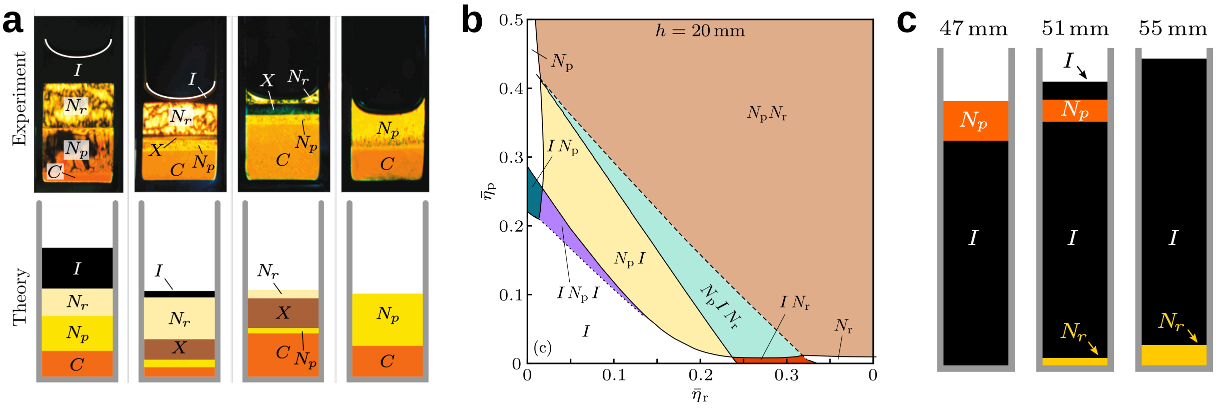

Figure 1: **Sedimentation of binary plate-rod mixtures**. (a) Experimental samples by van der Kooij and Lekkerkerker and corresponding theoretical predictions of stacking sequences in a plate-rod mixtures using sedimentation path theory. The bulk phases are isotropic (I), nematic rich in rods (N_r), nematic rich in plates (N_p), plate-rich columnar phase (C), and rod-rich smectic-phase (X). (b) Stacking diagram in the plane of packing fraction of rods, η_r, and packing fraction of plates, η_p. Each color represents a different stacking sequence, labeled from bottom to top. The sample height is fixed to 20 mm, and the ratio between buoyant masses is set at $m_r/m_p = 0.5$. (c) Predicted evolution of the stacking sequence by changing the sample height and keeping the value of the overall packing fractions constant. Adapted from Ref. [1].

phases of a given colloidal suspension. In typical colloidal systems, gravity has a profound influence and it can generate new and counterintuitive phenomena, as we have addressed here. The effects of gravity on binary colloidal mixtures are particularly interesting as, in general, each species is affected differently by gravity.

Gravity-induced phase phenomena in plate-rod colloidal mixtures. In Ref. [1] we re-considered the arguably best-known experiments in the field, those by van der Kooij and Lekkerkerker [Phys. Rev. Lett. **84**, 781 (2000)] for colloidal plate-rod mixtures. Naturally their systems were equilibrated under the influence of gravity in the lab. By changing the overall colloidal packing fraction, composition, and sample height, several distinct stacking sequences appeared, including a stack of five different bulk phases. We used an extended Onsager density functional theory to obtain the bulk phase diagram of a corresponding theoretical model. Sedimentation path theory then allows one to incorporate the effect of gravity. We demonstrate that the experimental occurrence of multiple simultaneous layers is due to gravity and does not directly translate to corresponding multi-phase bulk coexistence. Our theoretical predictions for stacking sequences are in excellent agreement with the experimental observations, see Fig. 1a. We also addressed in Ref. [1] the inverse problem of obtaining (approximate) results for the bulk phase diagram directly from sedimentation experiments. We investigated the effects of changing the buoyant mass ratio and the sample height (an example is shown in Fig. 1b). Several of our predictions are testable in experiment, including striking changes in the stacking sequence by varying the height of the sample (see Fig. 1c) or the buoyant mass ratio.

Phase behavior of a binary mixture of patchy colloids. The possibilities to synthesize colloidal particles with controlled shapes and tailored interparticle interactions have proliferated over recent years. A popular theoretical model for complex colloids are patchy particles which can form reversible bonds via interaction sites (patches) that are located on the particle surface. In Ref. [2] we show theoretically how to control the phase behavior and sedimentation-diffusion-equilibrium of a colloidal linker–particle system modeled as a patchy colloidal mixture with size variability. Specifically, we consider two species with respectively two and three patches and differing particle sizes. Only interspecies bonds are allowed to form. The particle size ratio can be used to control the phase behavior of the mixture, to tune the extent of phase separation, and to control the stacking sequences displayed under gravity. The bulk phase diagrams exhibit two distinct topologies, depending on size ratio, and complex coexistence phenomena such as upper and lower critical points, miscibility gaps, and azeotropic points. Gravity generates complex stacking sequences with up to six layers.

Sedimentation of colloidal plate-sphere mixtures. While experiments in colloidal systems are typically subject to gravity, in theoretical studies one often ignores its effects when focusing on bulk properties of a given system. In Ref. [3] we attempt to close the gap between sedimentation experiments and theoretical studies of bulk behaviour, addressing here plate-sphere colloidal mixtures, while the method is applicable to general binary mixtures. We studied the effect of gravity on the mixture using density functional theory to describe the bulk. Sedimentation path theory allowed us to incorporate the effect of gravity. Our theoretical results are in good agreement with previous experimental findings. We also make new predictions that can be tested experimentally and we present a method to infer microscopic particle characteristics, such as the buoyant masses of the particles, from macroscopic experimental information, such as measured layer thicknesses in phase stacking sequences.

Sedimentation path theory for mass-polydisperse colloidal systems. Disentangling the effects of the gravitational field from bulk phenomena is a particularly complex issue in polydisperse colloidal suspensions. In general the polydispersity in, e.g., the size distribution of the particles, determines both the coupling to the gravitational field as well as the bulk properties of a system. To make progress, we introduced in Ref. [4] a mass-polydisperse model in which the particles have identical properties except for their buoyant masses which follow a prescribed, yet arbitrary, distribution function. The polydispersity in mass has no effect on the bulk, which simplifies the treatment. Nevertheless, we argue that this setup is useful to highlight the effects of polydispersity in sedimentation. It is not inconceivable that such size-monodisperse, yet mass-polydisperse particles could be synthesized experimentally using, e.g., core-shell methods. We develop a general theory for such systems and use it to investigate sedimentation of mass-polydisperse colloidal hard spheres. We find strong effects, in particular near density matching, when the mass density of the (implicit) solvent and that of the particles are comparable in magnitude.

Sample height and particle elongation in colloidal rod sedimentation. Hard spherocylinders are a key model for properties of elongated colloidal particles. The bulk phase behaviour, as well as wetting and interfacial phenomena of the model are well studied and it serves as a reference to construct more complex interparticle interaction potentials. However, the sedimentation-diffusion-equilibrium of a system of hard spherocylinders has received little attention in the literature. In Ref. [5] we apply a mass-polydisperse sedimentation path theory to hard spherocylinders and in particular vary the length-to-width aspect ratio. We investigate the dependence of the stacking sequences on the height of the vessel at constant packing fraction.

In mass-polydisperse systems it is possible to find stacking sequences with up to seven layers and, in contrast to monodisperse systems, new layers can appear in the middle of the sample.

Part II: Nonequilibrium dynamics of sedimentation in colloidal systems (Schmidt)

Power functional theory for nonequilibrium. The complexity of the nonequilibrium phenomena that many-body systems display originates ultimately from the coupling via the interparticle interactions. Power functional theory provides a formally exact and microscopically sharp description on the basis of a formally exact one-body variational principle. Classical density functional theory is recovered in the equilibrium limit. While power functional theory operates on the level of time-dependent one-body correlation functions, two- and higher-body correlation functions are accessible both via the dynamical test-particle limit and the nonequilibrium Ornstein-Zernike route. Ref. [6] gives a detailed pedagogical introduction to the theory and describes applications to a range of dynamical problems, such as the decay of the van Hove function in liquids, flow in nonequilibrium steady states, motility-induced phase separation of active Brownian particles, both steady and transient shear phenomena, and lane formation in binary colloidal mixtures, as is relevant for sedimentation under gravity. In Ref. [7] we provide a classification scheme for the different types of force contributions that occur in flowing Brownian many-body systems. The interparticle one-body force field is thereby split systematically into contributions that are either relevant for the spatial structure formation or for the flow. Both contributions can be accessed in computer simulations. Gradient power functional approximations describe the different types of spatially inhomogeneous force fields quantitatively.

Limitations of dynamical density functional theory. We have put forward how to overcome the deficiencies of dynamical density functional theory in Ref. [8]. Instead of the adiabatic sequence of equilibrium states that this approach provides to mimic the true nonequilibrium time evolution, we posit that power functional theory is the only present nonequilibrium contender to shed similar insight into the behaviour of inhomogeneous systems as density functional theory provides in equilibrium. As a representative case, we considered the three-dimensional Lennard-Jones fluid under stationary uniaxial compressional flow as a model for spatially modulated steady-state sedimentation. Using machine-learning allowed us to capture the kinematic dependence of the interparticle force field on the density and current. The neural functional is trained with adaptive Brownian dynamics simulation data (see next paragraph) and we demonstrated that the theory can be used successfully for complex tasks, such as predicting and designing steady states. The significant potential of using machine-learned functionals promises to overcome both the conceptual constraints of dynamical density functional theory, as well as the limited availability of its analytical functional approximations.

Adaptive Brownian Dynamics. A performant adaptive Brownian Dynamics simulation method is presented in Ref. [9]. Different from the Euler-Maruyama scheme of standard Brownian Dynamics, here an embedded Heun-Euler integrator is used for adaptive adjustment of the time step to integrate the over-damped coupled Langevin equations of motion. Local error estimates enable one to control precisely the optimal timestep size. Thereby rejection sampling with memory is used to implement the Brownian bridge theorem for the correct treatment of rejected trial steps. For Lennard-Jones fluids in bulk and in confinement, we have shown that the method is superior in both performance and stability to conventional Brownian dynamics. We expect this novel computational approach to be useful in long-time simulations of complex systems and in nonequilibrium, in particular when concurrent slow and fast processes occur. We have used the method for investigating film formation where a downward moving interface compresses particles towards the lower wall of the system, reminiscent of dense sediment formation in the late stages of sedimentation. Also stratification phenomena in binary mixtures were shown to possess rich spatial structure. In Ref. [10] we used adaptive Brownian dynamics to investigate the steady state flow of a colloidal gel under an inhomogeneous external shear force. The sinusoidal spatial variation of the shear field is a toy model for a mesoscopic convection roll, as is relevant for colloidal sedimentation with upward streams coexisting with downward streams. The gel is stabilized by the Stillinger-Weber potential where the three-body term is tuned for network formation. The inhomogeneous shear induces remarkable local density modulations. Depending on the shear strength, particles accumulate either in quiescent regions or near maximum net flow, which we deduce to be characteristic nonequilibrium responses of the gel. The internal force field features rich interplay between significant viscous and structural superadiabatic forces. The magnitude and nature of the observed nonequilibrium phenomena are in stark contrast to the corresponding behavior of simple fluids. A simple analytical power functional reproduces accurately the viscous force profile and hence allows one to rationalize the complex emergent dynamical behavior of the gel.

Fluctuation profiles for inhomogeneous fluids. To characterize spatial structure formation, we have shown how three one-body fluctuation profiles, namely the local compressibility by Evans and co-workers, the local thermal susceptibility, and the reduced density, emerge naturally in a statistical mechanical many-body description of classical many-body systems [11, 12]. Several different and equivalent routes to each fluctuation profile facilitate the access to numerical results for inhomogeneous equilibrium systems. Hard wall contact theorems and novel types of inhomogeneous one-body fluctuation Ornstein-Zernike equations are derived. The practical accessibility of all three fluctuation profiles is exemplified by grand canonical Monte Carlo simulations for: hard spheres, Gaussian core particles, and Lennard-Jones fluids in confinement, as is relevant for sedimentation near container walls.

Force-density functional theory. A theoretical density functional framework, based explicitly on the two-body density, is given in Ref. [13]. The method requires numerical solution of the inhomogeneous two-body Ornstein-Zernike equation and it provides an alternative to standard density functional theory for the study of inhomogeneous systems. In Ref. [14] we compare inhomogeneous density profiles for hard sphere fluids from force-based and standard density functional theory with simulation data. Test situations include the equilibrium hard sphere fluid adsorbed against a planar hard wall and the dynamical relaxation of hard spheres in a switched harmonic potential. The comparison to grand canonical Monte Carlo simulation profiles shows that the force-density functional alone does not improve upon results obtained with the standard Rosenfeld functional. Similar behavior holds for the relaxation dynamics, where we use our event-driven Brownian dynamics data as benchmark. Based on an appropriate linear combination of standard and force-based results, we investigate a simple hybrid scheme which rectifies these deficiencies in both the equilibrium and the dynamical case. We explicitly demonstrate that although the hybrid method is based on the original Rosenfeld fundamental measure functional, its performance is comparable to that of the advanced White Bear theory.

Neural functional theory. While the development of accurate analytical equilibrium density functionals for general soft matter systems remains a major theoretical challenge, in Ref. [15] we introduced a universal machine learning scheme for training a neural network with Monte Carlo simulation data to represent the density functional relationship via one-body direct correlations. For hard sphere fluids the neural functional exceeds in accuracy all current analytic approaches, including the White Bear functional, and it provides immediate access to the full structure of homogeneous and heterogeneous fluid states. Predictions of density profiles have near-simulation precision at negligible computational cost even in challenging multiscale problems, such as sedimentation between hard walls on length scales that far exceed the training simulation box sizes. The method reproduces both the highly correlated fluid structure near each wall as well as the large-scale slow density gradient along a sedimentation column. We have given an introductory account [16] of this neural functional approach, aimed at a general audience interested in the statistical mechanical description of many-body systems via machine learning. We present a pedagogical application to the prototypical hard rod system in one spatial dimension, where Percus' exact solution for the free energy functional provides an unambiguous reference. Sedimentation-diffusion equilibrium is considered between two widely spaced hard walls. A corresponding standalone numerical tutorial demonstrates the neural functional concepts, together with the underlying fundamentals of Monte Carlo simulations, classical density functional theory, machine learning, differential programming, and automatic differentiation; see https://github.com/sfalmo/NeuralDFT-Tutorial for online access. Free access to simulation code and training data, as well as to the trained neural functionals is provided via Zenodo and GitHub, as referenced in the respective publications [15, 16].

Noether's theorem in statistical mechanics. Standard application of Noether's calculus of invariant variations yields exact identities from functional symmetries, such as conservation laws that follow from invariances of an action integral. In Ref. [17] we rather considered the free energy density functional and the power functional under translational and rotational shifting symmetry operations. The resulting global identities express vanishing of total internal and total external forces and torques. Functional differentiation then leads to hierarchies of local sum rules that interrelate density correlators as well as static and time direct correlation functions. The theory sheds new light on the spatio-temporal coupling of correlations in complex systems. As applications we consider active Brownian particles, where in active sedimentation, the center-of-mass motion is constrained by an exact internal Noether sum rule, see Figure 5 of Ref. [17] for an illustration. We have given an introductory account [18] of the Noetherian approach to statistical mechanics, aimed at a general physics audience, which lays out that Noether's reasoning applies to thermal systems, where fluctuations are paramount and one aims at a statistical mechanical description. Working with functional dependencies allows one to use functional differentiation to obtain exact identities that express properties of both macroscopic average forces and molecularly resolved correlations in many-body systems, both in and out-of-equilibrium, and for active Brownian particles. To exemplify the theory in a pedagogical way, we have applied it to ideal sedimentation; see Figure 3 in Ref. [18].

Generality of Noether's concepts. We explored the fertility of the Noetherian approach in number of subsequent investigations. In Ref. [19] we demonstrate that fluctuations are constrained by the inherent symmetries of particle-based classical many-body systems. Noether invariance at second order leads to exact sum rules that interrelate the global force variance with the mean potential energy curvature. Noether invariance implies an exact balance between these distinct mechanisms. The sum rules provide a practical guide for assessing and constructing theories, for ensuring self-consistency in simulation work, and for providing a systematic pathway to the theoretical quantification of fluctuations. In Ref. [20] we addressed the consequences of invariance properties of the free energy of spatially inhomogeneous quantum many-body systems. A quantum canonical operator transformation is equivalent to a unitary transformation on the underlying Hilbert space. The resulting invariance of the free energy allows one to apply Noether's theorem for invariant variations to derive the locally resolved equilibrium one-body force balance. Returning to classical systems in Ref. [21], we showed that the structure of liquids carries deep imprints of the inherent thermal invariance. While at first the local force balance follows, three distinct two-body correlation functions emerge at second order, namely the standard two-body density, the localized force-force correlation function, and the localized force gradient. An exact Noether sum rule interrelates these correlators. Simulations of Lennard-Jones, Yukawa, soft-sphere dipolar, Stockmayer, Gay-Berne and Weeks-Chandler-Andersen liquids, of monatomic water and of the above colloidal gel former demonstrate the fundamental role in the characterization of spatial structure. In particular, while the pair distribution function has the generic long-range decay that one expects of network-forming systems, both the curvature and the force-force correlator are much more specific indicators. In particular the striking shape of the transversal tensor component indicates network connectivity, which provides a mechanism for the remarkable dynamical behaviour of the gel under convection [10].

Hyperforce sum rules and gauge invariance. In Ref. [22] we have addressed the Noetherian implications for general observables and order parameters. We demonstrated that thermal averages of general classical phase space functions are associated with exact hyperforce sum rules that follow from translational Noether invariance. Both global and locally resolved identities hold and they relate the mean gradient of a phase-space function to its negative mean product with the total force. Similar to Hirschfelder's hypervirial theorem, the hyperforce sum rules apply to arbitrary observables in equilibrium. Exact hierarchies of higher-order sum rules follow iteratively. As applications we investigated via simulations the emerging one-body force fluctuation profiles in confined liquids and near substrates, as is relevant for sedimentation near container walls. The local correlators quantify spatially inhomogeneous self-organization and their measurement allows one to develop stringent convergence tests and enhanced sampling schemes in complex systems. In Ref. [23] we transcended conventional views of statistical mechanics by identifying the shifting operation on classical phase space as a gauge transformation for microstates. The infinitesimal generators of the continuous gauge group form a noncommutative Lie algebra, which induces exact sum rules when thermally averaged. Gauge invariance with respect to finite shifting is demonstrated via Monte Carlo simulation in the transformed phase space which generates identical equilibrium averages. These results open up avenues for systematic construction of exact identities and of sampling algorithms to address relevant soft matter behaviour, including sedimentation and beyond.

4 Published project results

4.1 Publications with scientific quality assurance

[1] T. Eckert, M. Schmidt, and D. de las Heras, Gravity-induced phase phenomena in plate-rod colloidal mixtures, Commun. Phys. **4**, 202 (2021).

[2] R. Braz Teixeira, D. de las Heras, J. M. Tavares, and M. M. Telo da Gama, Phase behavior of a binary mixture of patchy colloids: Effect of particle size and gravity, J. Chem. Phys. **155**, 044903 (2021).

[3] T. Eckert, M. Schmidt, and D. de las Heras, Sedimentation of colloidal plate-sphere mixtures and inference of particle characteristics from stacking sequences, Phys. Rev. Res. **4**, 013189 (2022).

[4] T. Eckert, M. Schmidt, and D. de las Heras, Sedimentation path theory for mass-polydisperse colloidal systems, J. Chem. Phys. **157**, 234901 (2022).

[5] T. Eckert, M. Schmidt, and D. de las Heras, Effect of sample height and particle elongation in the sedimentation of colloidal rods, Soft Matter **19**, 2214 (2023).

[6] M. Schmidt, Power functional theory for many-body dynamics, Rev. Mod. Phys. **94**, 015007 (2022).

[7] D. de las Heras and M. Schmidt, Flow and structure in nonequilibrium Brownian many-body systems, Phys. Rev. Lett. **125**, 018001 (2020).

[8] D. de las Heras, T. Zimmermann, F. Sammüller, S. Hermann, and M. Schmidt, Perspective: How to overcome dynamical density functional theory, J. Phys.: Condens. Matter **35**, 271501 (2023); (Invited Perspective).

[9] F. Sammüller and M. Schmidt, Adaptive Brownian dynamics, J. Chem. Phys. **155**, 134107 (2021); (Selected as Featured, Coverpage).

[10] F. Sammüller, D. de las Heras, and M. Schmidt, Inhomogeneous steady shear dynamics of a three-body colloidal gel former, J. Chem. Phys. **158**, 054908 (2023); (Special Topic on Colloidal Gels).

[11] T. Eckert, N. C. X. Stuhlmüller, F. Sammüller, and M. Schmidt, Fluctuation profiles in inhomogeneous fluids, Phys. Rev. Lett. **125**, 268004 (2020).

[12] T. Eckert, N. C. X. Stuhlmüller, F. Sammüller, and M. Schmidt, Local measures of fluctuations in inhomogeneous liquids: Statistical mechanics and illustrative applications, J. Phys.: Condens. Matter **35**, 425102 (2023).

[13] S. M. Tschopp, F. Sammüller, S. Hermann, M. Schmidt, and J. M. Brader, Force density functional theory in- and out-of-equilibrium, Phys. Rev. E **106**, 014115 (2022).

[14] F. Sammüller, S. Hermann, and M. Schmidt, Comparative study of force-based classical density functional theory, Phys. Rev. E **107**, 034109 (2023).

[15] F. Sammüller, S. Hermann, D. de las Heras, and M. Schmidt, Neural functional theory for inhomogeneous fluids: Fundamentals and applications, Proc. Natl. Acad. Sci. **120**, e2312484120 (2023).

[16] F. Sammüller, S. Hermann, and M. Schmidt, Why neural functionals suit statistical mechanics, J. Phys.: Condens. Matter **36**, 243002 (2024); (Invited Topical Review).

[17] S. Hermann and M. Schmidt, Noether's theorem in statistical mechanics, Commun. Phys. **4**, 176 (2021).

[18] S. Hermann and M. Schmidt, Why Noether's theorem applies to statistical mechanics, J. Phys.: Condens. Matter **34**, 213001 (2022); (Invited Topical Review).

[19] S. Hermann and M. Schmidt, Variance of fluctuations from Noether invariance, Commun. Phys. **5**, 276 (2022).

[20] S. Hermann and M. Schmidt, Force balance in thermal quantum many-body systems from Noether's theorem, J. Phys. A: Math. Theor. **55**, 464003 (2022); (Special Issue: Claritons and the Asymptotics of ideas: the Physics of Michael Berry).

[21] F. Sammüller, S. Hermann, D. de las Heras, and M. Schmidt, Noether-constrained correlations in equilibrium liquids, Phys. Rev. Lett. **130**, 268203 (2023).

[22] S. Robitschko, F. Sammüller, M. Schmidt, and S. Hermann, Hyperforce balance from thermal Noether invariance of any observable, Commun. Phys. **7**, 103 (2024).

[23] J. Müller, S. Hermann, F. Sammüller, and M. Schmidt, Gauge invariance of equilibrium statistical mechanics, Phys. Rev. Lett. **133**, 217101 (2024); (Editors' Suggestion, Featured in Physics **17**, 163 (2024)–Viewpoint by B. Rotenberg).

References [1–3, 8, 12, 15–20, 22, 23] are available in Open Access form, with Ref. [23] being accessible via the pdf-link in the Viewpoint. The DOI number is given as a link in each reference above. All 23 publications are available as preprints on arXiv.

4.2 Other publications

The results of the project have been disseminated in several seminars, workshops, and at international conferences.

The research has been publicised by the following three Bayreuth University press releases.

BAYREUTH PHYSICISTS DEVELOP POWERFUL ALTERNATIVE TO THE DYNAMIC DENSITY FUNCTIONAL THEORY, University of Bayreuth, Press release No. 077/2023 – 7 June 2023.

BREAKTHROUGH FOR DESCRIBING SOFT MATTER THROUGH AI AT THE UNIVERSITY OF BAYREUTH, University of Bayreuth, Press Release No. 171/2023 – 13 December 2023.

DEEPER UNDERSTANDING OF THE PHYSICS OF COMPLEX LIQUIDS, University of Bayreuth, Press Release No. 128/2024 – 19 November 2024.

Entry-level access to the concepts of machine-learning density functional relationships on the basis of many-body simulation data and using automatic differentiation is provided by:

F. Sammüller, Neural functional theory for inhomogeneous fluids – Tutorial; for online access see the URL: https://github.com/sfalmo/NeuralDFT-Tutorial

4.3 Patents (applied for and granted)

N/A