From Spheres to Sheets: Colloidal Hydrodynamics, Thermodynamics, and Statistical Inference

by

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Abstract

This thesis involves the development of Bayesian methods for statistical inference of distributions, the construction of optimization and thermodynamic sampling algorithms, and the use of hydrodynamical simulations to better understand the physics of soft matter systems consisting of particles ranging in shape from spheres to sheets.

In the first part of this thesis, we introduce a Bayesian method that we call Maximum *A posteriori* Nanoparticle Tracking Analysis (MApNTA) for estimating the size distributions of nanoparticle samples from high-throughput single-particle tracking experiments. We show that this approach infers nanoparticle size distributions with high resolution by performing extensive Brownian dynamics simulations and experiments with mono- and polydisperse solutions of gold nanoparticles as well as single walled carbon nanotubes. We then extend the non-parametric Bayesian framework developed to infer the orientation probability distribution function (OPDF) of suspensions of rod-like particles from small-angle neutron scattering data with a method that we call Maximum *A Posteriori* Scattering Inference (MAPSI).

In the second part of this thesis, we create two high-performance algorithms — one for feasible optimization and the other for accelerated thermodynamic sampling — to aid in the simulation of large-scale physical models. Drawing on the Riemannian optimization and sequential quadratic programming literature, a practical algorithm that we call Locally Feasibly Projected Sequential Quadratic Programming (LFPSQP) is constructed to conduct feasible optimization on arbitrary implicitly defined constraint manifolds. Specifically, with n (potentially bound-constrained) variables and $m < n$ nonlinear constraints, each outer optimization loop iteration involves a single $O\left(nm^2\right)$-flop factorization, and computationally efficient retractions are constructed that involve $O(nm)$-flop inner loop iterations. The second algorithm developed, called Collective Mode Brownian Dynamics (CMBD), is a method based on Brownian dynamics simulations that uses a specially constructed mobility matrix that can reduce the computational time it takes to reach equilibrium and draw decorrelated thermodynamic samples. Importantly, the method is completely agnostic to particle configuration and the specifics of inter-particle forces and runs in $O(N)$ time on graphics processing units, where N is the

number of particles.

In the final part of this thesis, we study the behavior of flexible 2D materials. Using the LFPSQP algorithm for feasible optimization, the minimum-energy shapes of membranes with boundaries subject to fixed area and contour lengths (relevant to 2D biological objects like kinetoplasts) are found over a range of dimensionless areas and dimensionless spontaneous curvatures. Notably, as spontaneous curvature is increased, it is found that axisymmetry is broken. The constrained normal modes of the sheets are also computed and shed light on the behavior of fluctuations. Additionally, we perform numerical simulations of "tethered" semiflexible sheets with hydrodynamic interactions in shear flow. With athermal sheets, we find buckling instabilities of different mode numbers that vary with bending stiffness and can be understood with a quasi-static model of elasticity. For different initial orientations, chaotic tumbling trajectories are observed. With thermal sheets, we observe a dynamical transition from stochastic flipping to significant crumpling and continuous tumbling consistent with the onset of chaotic dynamics found for athermal sheets. The effects of different dynamical conformations on rheological properties such as viscosity and normal stress differences are also quantified.

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