THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

A Tale of Scales: Dynamics of Complex Materials

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Department of Physics CHALMERS UNIVERSITY OF TECHNOLOGY Göteborg, Sweden 2025 A Tale of Scales: Dynamics of Complex Materials ESMÉE BERGER

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Cover: A tale of scales, including a plasmonically active nanodisk, surfactant-surface phases, and nuclear quantum effects of water molecules. Different probes provide information about structure and dynamics.

Chalmers digitaltryck Göteborg, Sweden 2025

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Abstract

Complex materials, such as amorphous solids, liquid-solid mixtures, or aggregates of organic molecules, offer vast possibilities for scientific and technological advancement. In recent years, the capabilities of computationally understanding and predicting material properties have experienced rapid progress, but these are in many cases still limited to ordered crystalline solids. Complex materials exhibit relevant structure and dynamics on a wide range of spatio-temporal scales, so for investigating them a multi-scale modeling approach is necessary. In this context, efficient methods for sampling and computation of observables are crucial. Additionally, understanding of complex materials can benefit from close comparisons between computational predictions and experimental observations.

This thesis contains contributions to the study of dynamics of complex materials at different length and time scales and is based on three papers. The first paper revolves around atomic-scale investigations and accompanies a software package developed for computing correlation functions from molecular dynamics trajectories, which have a strong tie to experimental observables. The second paper studies nuclear quantum effects on thermal properties through large-scale simulations. The third paper is a case study of applying a multi-scale modeling approach to investigate surfactant-surface phase behavior, which dictates the functionality in many applications. This behavior is challenging to model due to the combination of inorganic surfaces, liquid solvent, and supramolecular assemblies of organic molecules. Thus, a multi-scale modeling approach is required, which spans the atomic and continuum level. In this case, comparison to experiment is enabled via the computation of the optical response.

Keywords: multi-scale dynamics, computational modeling, molecular dynamics, correlation functions, nuclear quantum effects, optical response

LIST OF APPENDED PAPERS

This thesis is based on work presented in the following papers:

- I Dynasor 2: From Simulation to Experiment Through Correlation Functions Esmée Berger, Erik Fransson, Fredrik Eriksson, Eric Lindgren, Göran Wahnström, Thomas Holm Rod, and Paul Erhart Submitted for publication, preprint at arXiv:2503.21957
- Highly efficient path-integral molecular dynamics simulations with GPUMD using neuroevolution potentials: Case studies on thermal properties of materials
 Penghua Ying, Wenjiang Zhou, Lucas Svensson, Esmée Berger, Erik Fransson,
 Fredrik Eriksson, Ke Xu, Ting Liang, Jianbin Xu, Bai Song, Shunda Chen,
 Paul Erhart, and Zheyong Fan
 The Journal of Chemical Physics 162, 064109 (2025)
- III In-situ Plasmonic Sensing of Surfactant Structures Esmée Berger, Narjes Khosravian, Ferry A. A. Nugroho, Joakim Löfgren, Christoph Langhammer, and Paul Erhart In manuscript

PUBLICATIONS NOT INCLUDED IN THIS THESIS

The following publications are outside the scope of this thesis:

Predicting neutron experiments from first principles: A workflow powered by machine learning

Eric Lindgren, Adam Jackson, Erik Fransson, **Esmée Berger**, Svemir Rudić, Goran Škoro, Rastislav Turanyi, Sanghamitra Mukhopadhyay, and Paul Erhart *Submitted for publication, preprint at arXiv:2504.19352* The author's contribution to the papers included in the thesis:

- I The author has been a main developer of the DYNASOR package during its extension to version 2.X. The author performed the Ni₃Al calculations, co-wrote the perovskite example sections (III.B and III.C), and wrote the remainder of the paper.
- II The author contributed with the example of PIMD applied to a liquid system; carried out the liquid water simulations, analyzed and visualized the results, and wrote all parts related to liquid water in the paper.
- III The author performed the simulations, analyzed the results, and wrote the manuscript.

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List of Abbreviations

ACF autocorrelation function. 12, 28, 29, 35, 40

DFT density-functional theory. 1, 25, 40

FDTD finite-difference time-domain. 2, 32, 33, 37, 39, 40

LSPR localized surface plasmon resonance. 17, 19, 39

MD molecular dynamics. 1, 2, 11, 21–23, 26, 28–31, 33, 36, 37, 39–41

MLIP machine-learned interatomic potential. 25-28, 36, 41

NEP neuroevolution potential. 25-28, 31, 36

NP nanoparticle. 5, 8, 16-19, 32, 39-41

NQE nuclear quantum effect. 2, 3, 14, 15, 21, 26, 30, 31, 36, 39

PES potential energy surface. 2, 10, 41

PIMD path-integral molecular dynamics. 2, 21, 30, 31, 36, 39

RDF radial distribution function. 12, 14, 15, 31, 36, 39

vdW van der Waals. 24, 25

Introduction

It was the hardest of dynamics, it was the softest of dynamics...

Anonymous, 2025

Understanding the link between the macroscopic properties of a material and its structure and dynamics at small length scales permeates materials physics. Indeed, a major goal of computational materials physics has historically been—and still is—to investigate this link by systematically improving methods such as density-functional theory (DFT) for studying the electronic level [1–5] and molecular dynamics (MD) for gaining insight into the atomic level [6–10]. With the increase of computer power and everimproving algorithms, the predictive possibilities of computational materials physics have rapidly progressed, approaching the semi- or even fully quantitative level [11–13]. This has led to the ability of designing new materials *in silico*, albeit largely limited to ordered crystalline materials [14]. Amorphous, mixed solid-liquid, or other complex materials still prove challenging, not only for interpretation but particularly for prediction, largely due to the wide range of time and length scales involved in governing their macroscopic behavior. Such materials are, however, prevalent in many systems and processes of fundamental and technological relevance, which means that there is great interest in extending the interpretative and predictive possibilities in this direction.

The span of length and time scales involved requires a combination of computational techniques to investigate the behavior of such complex materials. At the atomic scale, the electronic degrees of freedom are generally coarse-grained and the nuclei are often treated as classical particles. In practice, the common method of choice at this scale is the aforementioned MD approach. To analyze the microscopic structure and dynamics and relate them to macroscopic properties, physically relevant observables must be obtained from the simulations. Many such observables can be expressed in the form

of correlation functions, which turns the problem of obtaining observables into one of sampling. For complex systems, however, sampling the potential energy surface (PES) is challenging due to the high likelihood of getting stuck in one of the many local minima. This means that long simulation times and efficient techniques for calculating the correlation functions are needed. Additionally, it can be beneficial to connect to experiment. This is not only helpful for validating simulations, but can also serve to aid the interpretation or even prediction of experimental results. In fact, many of the computable correlation functions are also observable in experiment. One example is the dynamic structure factor, which is the material response recorded when probing dynamics with, e.g., neutron or electron probes.

Treating the nuclei as classical particles is not always a suitable modeling approach. When the material contains light atoms or when low temperatures are of interest, nuclear quantum effects (NQEs) alter the material response [15–18]. In this situation, classical MD no longer suffices, and other methods such as path-integral molecular dynamics (PIMD) are needed. Methods accounting for NQEs are in general more computationally expensive, which can put limitations on the time and length scales accessible in simulations. For complex materials this poses a hurdle, which necessitates efficient implementations to reach the relevant scales.

Another type of material response is that to visible light or other electromagnetic radiation, which is described by the dielectric function [19]. Depending on the frequency of the radiation, different constituents of the material react to the electromagnetic field, with resonances when the frequency matches material-specific oscillations at, e.g., the electronic or ionic scales. Taking all degrees of freedom into account, both for the matter and the light, quickly becomes intractable, but luckily the continuum level often suffices when studying material response to electromagnetic fields. At this level, Maxwell's equations can be solved to obtain the absorption and scattering of light, which is achieved computationally through, e.g., the finite-difference time-domain (FDTD) method. There are also plenty of opportunities for experimental connections here because light scattering, absorption, and extinction are common measurement outputs.

When computationally investigating a complex material with interesting structure and dynamics on multiple spatio-temporal scales, there are thus many considerations: Which length and time scales are of interest? Which techniques do we combine into a multi-scale modeling approach to study the particular system? How do we sample efficiently enough to reach the relevant scales?

In this context, surfactant surface-phases pose a suitable platform for exploration. Not only do these phases and the transitions between them exhibit dynamics on multiple length and time scales, but surfactants are also interesting in their own right as they govern the behavior of many systems, with applications ranging from improving the stability of perovskite solar cells [20] to promoting nucleation and growth of clathrate hydrate [21]. Self-assembling at a liquid-solid interface, surfactants reside on the threshold between hard and soft matter. They decrease the surface tension, which fundamentally alters the structure and dynamics of the system, opening up to a wealth of possibilities for tuning the functionality if their phase behavior is understood.

1.1 Fundamental Questions and Thesis Overview

Having set the stage, we can capture the topic of this thesis in the following fundamental questions:

- How can insight be gained into multi-scale dynamics of complex materials? In particular, how can simulation and experiment be connected?
- How can these approaches be applied to study a complex system, such as one involving surfactant surface-phases?

The thesis is based on three attached papers, where I and II are related to the first question, as the focus of these is methodological, each targeting the study of materials at different scales. In particular the former of the two treats the topic of connecting simulation and experiment. Paper III relates to the second question, as it is about studying the behavior of surfactant surface-phases using a multi-scale approach, although the topic of connection to experiment is also at its core.

To tackle these fundamental questions throughout the thesis, we first turn to a chapter outlining the relevance of studying multi-scale dynamics in general and the interest in surfactant surface-phases in particular (Chapter 2). Next, we turn to the theory of material response (Chapter 3). Taking the atomic level as a starting point for understanding connections between macroscopic functionality and microscopic structure and dynamics, we encounter a number of ways for gaining insight into the mechanisms at these scales (Sect. 3.2). Atomistic insight is, however, not enough to capture the full picture, missing NQEs that are particularly relevant when working with lighter atoms. As such, NQEs are treated next (Sect. 3.3). Furthermore, light is often employed as a probe for studying material properties, which makes it relevant to also consider the theory of optical response of materials (Sect. 3.4). Equipped with knowledge about the relevant theory of material response, we devote the subsequent chapter (Chapter 4) to discuss the computational methods suitable for studying such response at each of the aforementioned scales. Thereafter, the three papers around which this thesis is built are summarized (Chapter 5), followed by a concluding chapter (Chapter 6).

2

Multi-Scale Dynamics

The chemical elements as the fundamental building blocks of materials are ordered in the periodic table and the vast range of material properties that we encounter stem from the endless possibilities for combining these into larger structures. It is not only the structural arrangement of the atoms that determines material properties, but also how they move around, i.e., their dynamics. The atoms, however, include even tinier building blocks such as neutrons, protons, and electrons. Turning an atom into an ion by removing an electron fundamentally alters the way it interacts with its surroundings, affecting both structure and dynamics. The electrons determine how atoms interact with each other through bonded and non-bonded forces, e.g., electrostatically in the case of ions. Atoms that bind together can, in turn, form molecules, which can subsequently order into supramolecular structures, or nanoparticles (NPs), with completely different properties or emergent behavior that is not present in the individual constituents. Here, in just a few sentences, we have already touched upon fundamentally different scales that affect material properties and depending on what we wish to know about a material, the dynamics must be studied at one, or a combination, of these scales.

If there were endless computational resources, the many-body Schrödinger equation for interacting electrons and atomic nuclei could simply be solved no matter the complexity of the system, to in principle obtain everything there is to know about it. As this is very far from reality, a balance must be struck between computational cost and the interpretative and predictive possibilities. For ordered crystalline materials, a small unit cell can be used to represent the entire system, which allows for studying it quantum mechanically. But even then, if the aim is to investigate a rare event or, e.g., how the material interacts with light or other probes, a quantum mechanical treatment might be too costly.

This is especially true for soft matter systems and many different approaches have been devised to circumvent the issue. One example is coarse-graining, where certain degrees of freedom are treated in detail at shorter length and time scales, while others, which are too costly or not relevant for the investigation at hand, are treated at larger spatio-temporal scales. Another approach is to use computational methods specialized for each scale, but combine them such that the outcome from one is used as input to another, together providing an overall picture of the dynamics of a system. This is called a multi-scale approach.

There are many examples of systems where multi-scale dynamics are relevant. In proteins, for instance, binding at active sites and macroscopic folding occur at very different length and time scales. There is not a single computational approach that can capture all of these processes, and many multi-scale modeling techniques have been used to investigate protein behavior [22–25]. Another example is glasses, where the individual disordered atoms vibrate and diffuse on comparatively short length and time scales, but where macroscopic processes such as relaxation lead to glassy dynamics and aging. The extremely long time scales on which glassy dynamics occurs means that multi-scale approaches are necessary [26–28]. A third example is surfactants and their ordering into supramolecular phases on surfaces.

2.1 Surfactant Surface-Phases

Aqueous surfactant-surface systems exhibit structure and dynamics relevant for their macroscopic functionality on a wide range of scales. There are chemical bonds within



Figure 2.1: An example of a cationic surfactant, cetyltrimethylammonium bromide (CTAB), with a hydrophilic quaternary ammonium head group, hydrophobic hydrocarbon tail, and a Br⁻ counter ion. This prototypical surfactant is used in paper III.

the surfactants and the surface, respectively, around which the atoms vibrate. Furthermore, surfactants are generally organic molecules, often with hydrophilic head groups and hydrophobic tails (Fig. 2.1). This means that surfactants, in pure water, collectively order into liquid-crystal like phases due to the hydrophobicity of the tails, with the head groups pointing towards the water [29]. This ordering is called self-assembly and the resulting phases, depending on the surfactant concentration, include micelles, cylinders, and lamellar structures, to name a few. A common measure of characterization for a surfactant is the critical micelle concentration (CMC), i.e., the concentration at which micelles begin to form.

When aqueous surfactant solutions also include surfaces, made up of, e.g., metals or other inorganic materials, the situation becomes even more complex. Now, there is not just the hydrophobicity of the tails driving the formation of supramolecular surfactant structures, but also the interaction between the head groups and the surface. This is an electrostatic interaction due to the small counter-ion diffusing around much more than the comparatively sluggish head group and its hydrocarbon tail, leaving the charged head group bare. There are thus two competing mechanisms, the hydrophobicity of the tails and the electrostatic interaction between the head group and the surface. These types of interactions lead to surfactants accumulating on the surface even below



Figure 2.2: Schematic examples of surfactant surface-phases for CTAB on silica, encountered in paper III. The surface-phases, from left to right, are a bilayer, a hemispherically capped bilayer, and cylindrical micelles.

the CMC, in for example bilayers, hemispherically capped bilayers, or cylindrical micelles (Fig. 2.2). Two models exist in the literature for *how* this adsorption progresses with increasing surfactant concentration: the two-step and four-region models [29, 30]. The first step in both of the models, at low concentration, is the adsorption of single surfactant molecules due to the electrostatic interaction. In the two-step model the electrostatic interaction dominates, causing the formation of aggregates of adsorbed surfactants with bare tails pointing towards the water. Only at higher surfactant concentrations, these tails are covered by other surfactants with their head groups pointing towards the water, forming closed structures such as bilayers or micelles. In the fourregion model the hydrophobic interaction governs the behavior, such that the tails of adsorbed surfactants are covered by other surfactants with their head group pointing towards the water early on, forming small clusters which at sufficiently high concentrations fuse into a bilayer of form close-packed micellar structures. Which of the two models best describes the actual adsorption process is still debated, and depending on the type of surface, the surfactant, the temperature and other variables, one of them might seem more likely than the other on a case-to-case basis [29–33].

The lack of a unified picture of the surfactant surface-phases is unfortunate, as surfactants have large implications for the structure and dynamics of a system due to their reduction of the surface tension at interfaces. In particular, these models do not capture the qualitative difference between the bilayer-like and micellar phase at higher concentrations, which can affect the functionality in distinct ways due to one being surface-covering while the other is not. An example of where this is believed to be relevant is during NP growth, where surfactants play a crucial yet elusive role for the morphology of the resulting NPs [34–38]. Changes in structure and dynamics affect the functionality, so to be able to understand and control the functionality of a system containing surfactants, it is desirable to gain insight into their surface-phase behavior. This includes understanding when the different surface phases occur, but also the dynamics of the phase transitions between them, as these can be expected to be slow due to the large rearrangements involved. Thus, surfactant-surface complexes are interesting yet challenging systems exhibiting dynamics on multiple spatio-temporal scales, calling for the application of a multi-scale approach to gain deeper insight into their behavior.

Theory of Material Response

When setting out to understand the structure and dynamics of a material the general approach is to study how the material responds to its environment, which could entail anything from changes in temperature or pressure to variations in solvation condition. To record the material response, observables must be measured or calculated. Experimentally, this is done by employing some sort of probe that interacts with the system of interest. Common probes include neutrons, electrons, X-rays, visible light or other forms of electromagnetic radiation. Each interacts in a unique way with the material, providing access to, e.g., atomic or electronic structure and dynamics depending on the type of interaction. In this chapter, theory of material response relevant to the included papers is introduced, split by spatio-temporal scale, and theoretical concepts are connected to experimental observables.

3.1 Separation of Scales

The structure and dynamics of a material depend on the positions and movements of its constituents, i.e., the electrons and nuclei. The total energy of the system is captured by the Hamiltonian \mathcal{H} , which (non-relativistically) reads [39, Chapter 3]

$$\mathcal{H} = -\frac{\hbar^{2}}{2m_{e}}\sum_{i}\nabla_{i}^{2} + \frac{1}{2}\sum_{i\neq j}\frac{e^{2}}{4\pi\varepsilon_{0}|\mathbf{r}_{i} - \mathbf{r}_{j}|} - \sum_{i,I}\frac{Z_{I}e^{2}}{4\pi\varepsilon_{0}|\mathbf{r}_{i} - \mathbf{R}_{I}|} - \sum_{I}\frac{\hbar^{2}}{2M_{I}}\nabla_{I}^{2} + \frac{1}{2}\sum_{I\neq J}\frac{Z_{I}Z_{J}e^{2}}{4\pi\varepsilon_{0}|\mathbf{R}_{I} - \mathbf{R}_{J}|}.$$
(3.1)

The first and fourth term describe the kinetic energies \mathcal{T}_e and \mathcal{T}_n of the electrons and nuclei (also called ions), respectively, and the other terms describe, in turn, the Coulomb

interactions \mathscr{V}_{ee} for electron pairs, \mathscr{V}_{ne} between the nuclei and the electrons, and \mathscr{V}_{nn} for nucleus pairs.

Solving the Schrödinger equation $\mathscr{H} |\Psi\rangle = E |\Psi\rangle$ with this general Hamiltonian yields the allowed energies *E* and eigenstates $|\Psi\rangle$. With $|\Psi\rangle$ as a basis, any many-body state $|\Psi(t)\rangle$ can be constructed, which in principle contains information about every property of the system. Finding a solution is, however, no easy task for any but the very simplest systems. Luckily, we can simplify matters due to the large mass difference between the electrons and nuclei, which means that it is possible to treat them separately. This is called the Born-Oppenheimer approximation [40], and the electronic Hamiltonian reads

$$\mathcal{H}_{e} = \mathcal{T}_{e} + \mathcal{V}_{int} + \mathcal{V}_{ext}, \qquad (3.2)$$

where \mathcal{V}_{int} is the potential energy between electrons, i.e., \mathcal{V}_{ee} , while \mathcal{V}_{ext} is the static potential from the fixed ions. The corresponding Hamiltonian for the nuclei reads

$$\mathscr{H}_{n} = \mathscr{T}_{n} + \mathscr{U}, \tag{3.3}$$

where $\mathcal{U} = \mathcal{V}_{nn} + E_e^0$ is the effective potential energy from combining the nucleusnucleus interactions with E_e^0 , which is the ground-state energy of the electrons for a fixed position of the ions obtained by solving Schrödinger's equation with Hamiltonian \mathcal{H}_e in Eq. (3.2). This means that the nuclei can be thought of as moving on the potential energy surface (PES) generated by the electrons.

When computationally studying complex systems such as amorphous or mixed solidliquid materials, the number of atoms that must be included often reaches far into the tens of thousands or even higher. Therefore, the starting point in this thesis is the atomic scale, as treating such systems at the electronic level quickly becomes unfeasible. We thus concern ourselves with \mathcal{H}_n in Eq. (3.3). In fact, we can simplify matters even further by describing the ions classically, which is a good approximation, especially for heavier atom types and at high temperatures. Having motivated a classical treatment of the atoms, we are now ready to ask the question: What are suitable observables for studying material response at this scale?

3.2 Atomistic Response

To address the question regarding which observables are suitable for studying material response at the atomic scale, we must take a moment to reflect on what we actually mean by atomistic response. At any given time t, the N atoms in a material reside at some positions $\mathbf{R}(t)$. Each atom I has a position $\mathbf{R}_I(t)$ and an associated velocity $\mathbf{v}_I(t)$. Together, these positions and velocities make up the 6N-dimensional phase space, in which the state of the system at time t is a point [41, 42]. When atoms move, the state changes, generating a trajectory in phase space. Observables O are determined by the state and can be expressed as a function of the point or curve in phase space, i.e., $O(\mathbf{R}(t), \mathbf{v}(t))$.

In this context, statics and dynamics are two common terms. When discussing statics, it is the structural arrangement of the atoms in the system that is of interest. Many material properties are directly determined by the ordering of its atoms. In thermodynamic equilibrium, there is in general one macroscopic phase that minimizes the free energy, which is thus the stable structure. In solids, these stable structures often form high-symmetry ordered arrangements, which are phases with well-known names such as body-centered cubic (BCC), face-centered cubic (FCC), and hexagonal close-packed (HCP). In more complex systems, for example the structure of organic molecules in solution, the phases formed are supramolecular assemblies like bilayers and micelles. Some of these supramolecular assemblies can, in turn, order into larger-scale collections, forming, e.g., a BCC-structure made up of micelles. Based on external stimuli, the system might change from one equilibrium structure to another, which signifies a phase transition. Understanding phase transitions is a cornerstone of describing the behavior of a material. In fact, paper I contains several examples of understanding the phase transition behavior through MD-based correlation functions and in paper III phase transitions of supramolecular surfactant arrangements are studied.

Dynamics is a term referring to the time dependence of material properties. It describes how a system changes in time in response to, e.g., stresses or temperature fluctuations. Even in equilibrium, for a system at a finite temperature, atoms vibrate around their equilibrium positions in a periodic manner, commonly seen in solids, or move around on larger scales, such as atoms diffusing in a liquid. In a soft matter system, like organic molecules in solution, there can also, for example, be folding or breathing modes. Vibrations are commonly understood through phonons, which are quasiparticles describing the atomic dynamics.

So, atomistic response covers the structural rearrangements and dynamical processes that make up the atomic-scale behavior of a material. With this sorted out, we can return to the observables $O(\mathbf{R}(t), \mathbf{v}(t))$. An example is the density of the system, which can be expressed as

$$n(\mathbf{R},t) = \sum_{I}^{N} \delta(\mathbf{R} - \mathbf{R}_{I}(t))$$
(3.4)

and thus is a direct function of the atomic positions. At a given time, many physical quantities depend on the collective behavior of the atoms, and the individual atomic positions and velocities are not necessarily relevant. It is rather the expectation value or ensemble average of an observable $\langle O(t) \rangle$ that is related to a multitude of physical quantities such as temperature, kinetic energy, and pressure.

In practice, it is not usually the instantaneous value as a function of the 6*N*-dimensional space that is measured, but an average collected over time. As mentioned, dynamics occurs even in thermal equilibrium. Thus, quantities of interest are commonly expressed as expectation values of the time development of the observable, $\langle O(t) \rangle_t$. When a sys-

tem is ergodic, which is usually assumed when computationally investigating a material, such a time average equals the ensemble average.

For studying structure and dynamics, many common properties might actually be expressed as spatial, temporal, or spatio-temporal correlation functions of observables. The general form of such a two-point correlation function reads

$$C(\mathbf{R}',\tau) = \langle O_1(\mathbf{R},t) \cdot O_2(\mathbf{R}+\mathbf{R}',t+\tau) \rangle.$$
(3.5)

When O_1 and O_2 are the same, Eq. (3.5) is referred to as an autocorrelation function (ACF). Many transport properties, such as viscosity or conductivity, are also closely related to ACFs, as described by the fluctuation-dissipation theorem and linear response theory [43, 44].

A common ACF for describing structure is the radial distribution function (RDF)

$$g(\mathbf{R}') = \langle n(\mathbf{R}, t) \cdot n(\mathbf{R} + \mathbf{R}', t) \rangle, \qquad (3.6)$$

which captures the spatial correlation between atoms. For example, solvation shells in



Figure 3.1: The dynamic structure factor S(q, w) for a) solid Ni₃Al and b) liquid Ni₃Al. Note the spherical averaging in the liquid case. Slices in the c) liquid intermediate scattering function F(q, t) and d) liquid structure factor. Current correlations for the same material are shown in Fig. 3 in paper I.

liquid systems are clearly seen as areas of higher density followed by areas of lower density (see the dashed lines in Fig. 3.2 for an example). There is a generalized version of the RDF called the van Hove function $G(\mathbf{r}', \tau) = \langle n(\mathbf{R}, t) \cdot n(\mathbf{R} + \mathbf{r}', t + \tau) \rangle$, which also captures time dependence. Instead of working in real space, it can be beneficial to Fourier transform correlation functions, which, if done for the van Hove function in space, yields the so-called intermediate scattering function

$$F(\boldsymbol{q},\tau) = \langle n(\boldsymbol{q},t) \cdot n(-\boldsymbol{q},t+\tau) \rangle.$$
(3.7)

Moreover, Fourier transforming in time yields the dynamic structure factor

$$S(\boldsymbol{q},\omega) = \int_{-\infty}^{\infty} F(\boldsymbol{q},t) e^{-i\omega t} \mathrm{d}t.$$
(3.8)

An example of $S(q, \omega)$ for solid and liquid Ni₃Al is shown in Fig. 3.1ab, as well as slices in *q*-space of F(q, t) and $S(q, \omega)$ for the liquid phase in Fig. 3.1cd. This illustrates the difference between the solid, exhibiting vibrational motion in the form of a phonon dispersion, and the liquid, which has a diffusional motion at low frequencies and vibrational motion at higher frequencies. The low-frequency diffusional part resembles that of a gas, while the vibrational part at higher frequencies is solid-like, as it resembles the acoustic branch in the solid dispersion [45].

The structure factor has strong ties to experiment, as this quantity is directly probed in neutron, X-ray or electron scattering and diffraction measurements. However, each probe interacts in its unique way with the sample, meaning that only distinct parts of the dynamics can be picked up depending on the type of measurement. The fundamental mechanism through which neutrons interact with a material is the short-range strong nuclear force, whereas X-rays sense the electron cloud through electromagnetic forces, and electrons interact with a material via long-range electrostatics. The scattering cross section of an atom describes its scattering strength and the value varies depending on the type of probe, due to the different interaction mechanisms. The theoretical structure factor in Eq. (3.8) contains information about the full dynamics of the system, but to compare with experimental results it needs to be weighted by probe-specific crosssections for each atom type (*A* and *B*)

$$S_{w}(q,\omega) = \sum_{A} \sum_{B} w_{A}(q) w_{B}(q) S_{AB}(q,\omega).$$
(3.9)

Being able to obtain probe-weighted structure factors allows for direct comparison between theory and experiment, which is very useful, especially in the study of complex materials. If $S_w(q, \omega)$ is computed, this comparison allows for validation of the underlying simulation components, such as the interatomic potential that is discussed in Sect. 4.1.1-4.1.2. It is, on the other hand, also beneficial for interpreting experimental results. Computed dynamic structure factors and the underlying simulations can aid in disentangling microscopic processes. An example is to understand what drives certain phase transitions, which is studied for a few perovskites in paper I, contributing to the explanation of experimental results. Eventually, this can even aid the prediction and design of experiments, see, e.g., Ref. [46].

The dynamic structure factor is an example of an important spatially-resolved correlation function, but there are many others. Among these, we find current correlations, which are calculated from the velocity instead of the density. While structure factors are limited to longitudinal modes, current correlations also contain transversal modes of vibration (compare, e.g., Fig. 3 in paper I and Fig. 3.1). How to efficiently compute correlation functions from atomic simulations is the topic of paper I and is described in the next chapter.

To conclude this section, we can note that atomic response encompasses both how the atoms respond to changes in the environment, be it a phase transition from one equilibrium structure to the next or a change in the dynamics, as well as how the atoms interact with the probes used to measure the structure and dynamics.

3.3 Nuclear Quantum Effects

Everything in Sect. 3.2 relied on the approximation that the atoms could be treated classically. When a complex material contains lighter atoms, such as hydrogen, or when lower temperatures are relevant, this approximation can turn out to be insufficient. In this regime, NQEs come into play, which can drastically alter material response.

NQEs capture the quantum nature of the nuclei, and describe the differences arising from treating the nuclei as quantum particles when applying the Hamiltonian in Eq. (3.3). Instead of a fixed position, the location of the nuclei is then described by a distribution, which alters the value of a wide range of observables, including, in particular, correlation-function based observables. Changes can be seen in properties such as diffusion and viscosity [16], elastic constant, and consequently bulk modulus [17], as well as RDFs and hopping rate [47], to name a few.

Whether a quantum description is required can be determined by the de Broglie wavelength of the nucleus. For a non-interacting particle, the de Broglie wavelength relates to temperature *T* and mass *m* via [41, chapter 7]

$$\lambda = \frac{h}{\sqrt{2\pi m k_{\rm B} T}}.$$
(3.10)

Inserting numbers for a quick "back-of-the-envelope" calculation yields $\lambda \approx 1$ Å for a hydrogen atom at room temperature. This is on the order of the interatomic distance, e.g., the O – H bond length in water is just below this value, and it thus suggests that a quantum mechanical treatment might be warranted. Indeed, in paper II, we see that partial RDFs (Eq. (3.6)) for water are drastically altered when including NQEs, compared to the classical treatment (Fig. 3.2). When the temperature decreases, the de Broglie wavelength becomes even larger, further emphasizing the importance of accounting



Figure 3.2: Example from paper II, illustrating the difference between classical (dashed lines) partial RDFs compared to those (solid lines) taking NQEs into account, for water at three different temperatures. (a) shows the partial oxygen-hydrogen RDF and (b) the partial hydrogen-hydrogen RDF.

for NQEs. Continuing with our hydrogen example, this is illustrated by the de Broglie wavelength reaching $\lambda \approx 5.5$ Å at 10 K. For atoms with increasing mass, the de Broglie wavelength instead decreases, eventually becoming smaller than the typical scale of interatomic interactions, and a classical treatment works well. Already for helium at room temperature, the de Broglie wavelength is $\lambda \approx 0.5$ Å.

The topic of efficiently accounting for NQEs in simulations, which allows for studying how they influence different observables, is treated in the next chapter and is the subject of paper II.

3.4 Optical Response

X-rays, which is one of the probes that we encountered in Sect. 3.2 for measuring material behavior, interacts with materials through electromagnetic forces. Another commonly used material probe is light with optical frequencies, which interacts with the probed material through the same mechanisms. Due to the differences in frequency between these types of electromagnetic radiation, optical light is useful for studying other types of dynamics in a material. It is usually not employed as a probe to gain insight



Figure 3.3: Schematic view of the complex, frequency-dependent dielectric function. Resonances are observed in several frequency ranges, with the imaginary part of the dielectric function indicating absorption of the electromagnetic radiation. The highest resonance peak to the right indicates electronic absorption. The next indicates absorption by atomic vibrations. The third one from the right stems from dipolar (also called reorientational) motion, and the lowest frequency peak is due to space charge polarization or (direct current) conductivity.

in the overall atomic structure in diffraction or scattering measurements, but instead the degree of reflected and absorbed light reveals how the electronic degrees of freedom respond to the radiation. Understanding the interactions between light and matter is thus of importance and, in fact, plays a central role in paper III. While it is entirely possible from a theoretical point of view to study light-matter interaction microscopically, the complex materials of interest in this thesis, such as surfactant surface-phases on NP surfaces in paper III, are way beyond the sizes where this is a feasible approach. Instead, a mesoscopic view of the optical response is required. The interplay between light and matter is described by Maxwell's equations [48, 49]

$$\frac{\partial D}{\partial t} = \nabla \times H - J, \tag{3.11}$$

$$\frac{\partial B}{\partial t} = -\nabla \times E - M, \qquad (3.12)$$

$$\nabla \cdot \boldsymbol{D} = \boldsymbol{\rho},\tag{3.13}$$

$$\nabla \cdot \boldsymbol{B} = \boldsymbol{0}. \tag{3.14}$$

Here, *E* and *B* are the electric field and magnetic flux density, respectively. The corresponding derived fields, *D* and *H*, are called the electric displacement field and the magnetic field, and are related to *E* and *B* through the constitutive relations

$$D = \varepsilon E, \tag{3.15}$$

$$\mathbf{B} = \mu \mathbf{H}.\tag{3.16}$$

In vacuum, $\varepsilon = \varepsilon_0$ is the vacuum permittivity and $\mu = \mu_0$ is the vacuum magnetic permeability. In matter, however, these are complex, frequency-dependent functions that describe the response of a material to the incoming radiation. In this thesis, magnetic response is not considered (so $\mu \approx \mu_0$), and the optical response of a system to applied electromagnetic radiation is captured through the permittivity. This is also known as the dielectric function, and a schematic view of the frequency-dependent response $\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$ over a wide frequency range is seen in Fig. 3.3. At certain frequencies, the radiation matches characteristic material degrees of freedom, e.g., atomic or electronic vibrational motion, causing the resonance peaks in the dielectric function that indicate strong absorption.

One resonance is when free electrons are collectively excited by the external electric field, moving in opposite directions to the field to screen it. This is called a plasmon. In small geometries, such as a NP with a volume V that is small compared to the wavelength of light, the electron cloud is confined, leading to a special case of this phenomenon called localized surface plasmon resonance (LSPR), which is visualized in Fig. 3.4. The dynamics of this electron cloud can be described classically through the equation of motion

$$m\ddot{x} + \gamma m\dot{x} = -eE, \qquad (3.17)$$

where *m* is the mass of the electrons, *x* their displacement, γ a damping factor, *e* the elementary charge, and *E* the total electric field as a sum of the external and the internal electric field created by the displacing electrons. Looking from the outside, these displacing electrons (with charge density *n*) generate a dipole with dipole moment p = -Vnex. Inside the NP they result in a uniform electric field $E_{int} = nex/3\varepsilon_0$ [50, Chapter 4], which makes it possible to rewrite Eq. (3.17) as

$$m\ddot{x} + \gamma m\dot{x} = -e\left(\frac{ne}{3\varepsilon_0}x + E_{\text{ext}}\right),\tag{3.18}$$

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Figure 3.4: Schematic view of a localized surface plasmon resonance. When the electric field oscillates, the electron cloud of the nanoparticle oscillates with it, canceling the external field inside the nanoparticle.

The solution in Fourier space reveals the dynamics of the electron cloud

$$\mathbf{x}(\omega) = \frac{e/m}{\omega^2 + i\gamma\omega - \omega_p^2/3} E_{\text{ext}}(\omega), \qquad (3.19)$$

where $\omega_p = \sqrt{ne^2/m\varepsilon_0}$ denotes the plasma frequency. Dividing the dipole moment and the external electric field yields the polarizability

$$\alpha(\omega) = \frac{\boldsymbol{p}(\omega)}{\boldsymbol{E}_{\text{ext}}(\omega)} = -V\varepsilon_0 \frac{\omega_p^2}{\omega^2 + i\gamma\omega - \omega_p^2/3},$$
(3.20)

which is a measure of how easily the NP is polarized. Exploiting the Drude model for the dielectric function [51, Chapter 9]

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega},\tag{3.21}$$

the polarizability can be rewritten as

$$\alpha(\omega) = 3V\varepsilon_0 \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 2}.$$
(3.22)

In we, instead of vacuum, assume that the surrounding medium has permittivity ε_m , this takes the form

$$\alpha(\omega) = 3V\varepsilon_m \frac{\varepsilon(\omega) - \varepsilon_m}{\varepsilon(\omega) + 2\varepsilon_m}.$$
(3.23)

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This form of the polarizability reveals the resonance criterion for a LSPR, i.e., it occurs if $\Re(\varepsilon(\omega)) = -2\varepsilon_m$ (if $\Im(\varepsilon(\omega))$) is small). Furthermore, the polarizability dictates the scattering and absorption cross sections of the NP [51, Chapter 5]

$$\sigma_{\rm sca}(\omega) = \frac{1}{6\pi\varepsilon_m^2} \left(\frac{\omega}{c}\right)^4 |\alpha(\omega)|^2, \qquad (3.24)$$

$$\sigma_{abs}(\omega) = \frac{\omega}{\varepsilon_m c} \Im(\alpha(\omega)). \tag{3.25}$$

Summing these yields the cross section for total extinction

$$\sigma_{\text{ext}}(\omega) = \sigma_{\text{sca}}(\omega) + \sigma_{\text{abs}}(\omega). \tag{3.26}$$

Since the polarizability is maximized at the LSPR, the extinction is maximized there



Figure 3.5: Schematic view of the basic principle of plasmonic sensing. When the dielectric environment of the plasmonic particle changes, the extinction spectrum is shifted, allowing this mechanism to be used as a probe of the dielectric environment. Magnitude of shift exagerrated for clarity.

as well, providing a large signal that is very sensitive to small changes in the dielectric function ε_m of the environment. This fact is exploited in plasmonic sensing (Fig. 3.5). Since the permittivity of the system changes if something adheres to the surface of the nanoparticle, the plasmonic response changes along with it. This allows for a very sensitive probe of the immediate surrounding of a nanoparticle, which has been used to, for example, measure antibody-antigen binding [52] or to detect hydrogen [53]. In paper III, plasmonic sensing is proposed as a method for measuring surfactant surfacephases and the dynamics of the transitions between them. In this context, computationally solving Maxwell's equations to obtain extinction spectra is needed, which is discussed in detail in the next chapter.

4

Computational Methods for Studying Material Response

Equipped with the theory of material response at different spatio-temporal scales from Chapter 3, the question remains how to actually perform computations at each of these scales. This chapter is devoted to precisely that, covering MD for simulations at the atomic level, PIMD for those including NQEs, and electrodynamics simulations for computing the optical response at the continuum level.

4.1 Molecular Dynamics

Computationally, it is possible to study the structure and dynamics at the atomic level through a technique called molecular dynamics (MD), in which the time evolution of a system of atoms is determined by integrating Newton's equations of motion [42, 44]. The force on each atom is given by an interatomic potential $\mathcal{U}(\mathbf{R}(t))$, which we already encountered in Eq. (3.3). As from any other classical potential, the force acting on an atom (with index *I*) is thus

$$F_I(t) = -\nabla_I \mathcal{U}(\mathbf{R}(t)). \tag{4.1}$$

Knowing the force on each atom, Newton's equations of motion can be numerically integrated using a time step Δt , to update the current atomic positions R(t) to the new positions $R(t + \Delta t)$. For this, a symplectic integrator is needed, which preserves the phase space volume and, thus, permits near conservation of the total energy during very long simulation times [44, 54]. In practice, a common method of choice is velocity Verlet [55]. In this algorithm, the new positions $R(t + \Delta t)$ are Taylor expanded and expressed in terms of the current positions R(t), forces F(t), and velocities v(t). This allows for the computation of the new forces $F(t + \Delta t)$ using Eq. (4.1) and, subsequently the velocities $v(t + \Delta t)$, which both go into the computation of the positions at the next time $t + 2\Delta t$, and so forth. For atom *I* this can be expressed as

$$\boldsymbol{R}_{I}(t+\Delta t) = \boldsymbol{R}_{I}(t) + \boldsymbol{v}_{I}(t)\Delta t + \frac{F_{I}(t)}{2m_{I}}\Delta t^{2}, \qquad (4.2)$$

$$\mathbf{v}_I(t+\Delta t) = \mathbf{v}_I(t) + \frac{F_I(t+\Delta t) + F_I(t)}{2m_I} \Delta t.$$
(4.3)

Note that to perform the computation in Eq. (4.3) for atom *I*, *all* new positions must be calculated with Eq. (4.2) to know the total force on atom *I*. Using this approach, the positions and velocities are incrementally generated for the simulated system, forming a so-called trajectory. There is a mathematically equivalent algorithm called leap-frog [56], which in principle generates identical trajectories but where the positions and velocities are instead stored with a time difference of $\Delta t/2$, with the disadvantage that, e.g., kinetic and potential energy are not known at the same times.

Apart from integrating Newton's equation of motion, there are other considerations when performing MD simulations. Despite our best efforts to apply suitable approximations to reach sufficient scales, we are no where near the approximately 10²³ atoms in a real material. Luckily, we do not have to simulate this many, partly because we apply periodic boundary conditions to our simulation cell, which allows for using a smaller cell that is representative of the structure and dynamics of the larger system. For complex systems, these cells can still be rather large, but nonetheless the periodic boundary conditions assist in reducing the required simulation size.

In practice, the user also needs to supply an initial condition for the MD simulation, from which the integration of Newton's equation of motion begins. As discussed in Sect. 3.2, this is a point in phase space. However, from a physical perspective, exactly how the initial value is chosen has consequences for how the MD simulation is conducted. Note that, when integrating Newton's equation of motion as discussed above, the energy of the system is preserved (up to small oscillations from the symplectic integrator), i.e., it is the microcanonical (*NVE*) ensemble that is sampled. The initial state is often supplied from, e.g., electronic structure calculations, experiment, or it is simply randomized within the space of "reasonable" starting points for the system. Running MD directly from such an initial condition results in the Newtonian dynamics on an isosurface of fixed N, V, and E, where the energy of the system does not change from the initial one. If the desire is to compute structural or dynamical observables at a specific thermodynamic condition, such as room temperature, the simulation must instead be performed in the NVT ensemble, keeping the number of atoms, volume and temperature fixed. If we aim to closely match experimental conditions, it is the NPT ensemble that most closely adheres to the situation in the lab, keeping the number of atoms, pressure and temperature constant. To sample other ensembles than NVE, the equations of motion must be altered, which is done by applying a thermostat for the temperature and

a barostat for the pressure. However, this way of keeping the temperature or pressure fixed directly influences the dynamics of the atoms, for example leading to an artificial decorrelation of the velocities. As such, it is generally not a good idea to immediately calculate observables from a simulation performed under such conditions. To both be able to sample the desired thermodynamic state and obtain observables that reflect the true dynamics of the system, equilibration is generally first performed in, e.g., the *NPT* ensemble. When the target pressure and temperature are reached, we switch to the *NVE* ensemble to generate trajectories that reflect the unperturbed dynamics of the system.

We have yet to return to \mathcal{U} required for the force computation. The form of \mathcal{U} in Eq. (3.3) is based on the evaluation of the ground state energy E_e^0 of the electrons for a fixed position of the ions. This can be computed using a technique called ab initio MD [57], but even that quickly becomes too costly for large systems with many electrons, which is an inherent feature when modeling complex materials. This means that we might not be able to reach the time and length scales required to properly study these materials. Instead of the pure ion-ion Coulomb interaction in combination with the ground state energy of the electrons, many different ways of expressing the interatomic potential have been developed to overcome this hurdle.

4.1.1 Interatomic Potentials

There are many ways in which the effective potential \mathcal{U} (Eq. (3.3)) has been traditionally modeled, including so-called classical or empirical interatomic potentials or force fields. Such interatomic potentials have been systematically parametrized and developed for describing the way atoms interact, and different functional forms are suitable for different types of materials. The simplest one is a pair potential, where the energy depends on the interatomic distance between atoms and only interactions between pairs are considered, excluding triplets and higher order terms. Common ones are the Lennard-Jones [58] and Buckingham [59] potentials, which have a repulsive region for very short distances and an attractive region for slightly larger ones. The Lennard-Jones potential, for instance, can be expressed as

$$\mathscr{U}_{LJ}(\mathbf{R}) = \frac{C_{IJ}^{(12)}}{R_{IJ}} - \frac{C_{IJ}^{(6)}}{R_{IJ}} = 4\epsilon \left[\left(\frac{\sigma}{R_{IJ}} \right)^{12} - \left(\frac{\sigma}{R_{IJ}} \right)^{6} \right], \tag{4.4}$$

and is visualized in Fig. 4.1. Pair potentials are suitable for, e.g., noble gases, but are not applicable in systems where many-body effects are important. For metallic systems, embedded atom method (EAM) potentials [60–62] are commonly employed, which in addition to a pair potential term take into account the energetic gain of embedding an atom in the electron density of its neighbors. In covalently bonded systems, where directional bonding must be properly described, bond order potentials [63, 64] are favored. For molecular systems, especially organic ones, non-reactive force fields are popular, and well-known ones include GROMOS [65, 66], OPLS [67, 68], CHARMM [69–71], and AM-BER [72, 73]. Commonly, their functional form can be written ad

$$\mathscr{U}(\mathbf{R}) = \mathscr{U}_{\text{bond}}(\mathbf{R}) + \mathscr{U}_{\text{angle}}(\mathbf{R}) + \mathscr{U}_{\text{dihedral}}(\mathbf{R}) + \mathscr{U}_{\text{vdW}}(\mathbf{R}) + \mathscr{U}_{\text{electrostatic}}(\mathbf{R}), \quad (4.5)$$

where the first three terms describe the two-body (bond), three-body (angle), and fourbody (dihedral) forces, respectively. These three terms together form the bonded forces, and there are a plethora of ways to parametrize each term. A common approach is to use harmonic oscillator-type expressions, or, when needed to properly describe the vibrational behavior, anharmonic ones such as a Morse potential [74]. The last two terms describe non-bonded forces, split by van der Waals (vdW) and electrostatic ones. The former is commonly described using a Lennard-Jones potential (Eq. (4.4)) and the latter describes the Coulomb interaction, based on the (effective) charges of the ions.





For systems where a larger-scale process is of interest, it is common to coarse-grain the highest-frequency vibrations that are not crucial for modeling the property of interest. An example of such a larger-scale process is the surface-phase formation of surfactants. There, one way to coarse-grain is to replace (non-aromatic) hydrocarbons with CH_x superatoms, with suitably modified interaction potentials. Such force fields are called united atom models, as opposed to the all-atom case where no coarse-graining is performed. With united atom potentials, simulations contain fewer particles and longer time steps Δt can be used, reducing the computational cost and making it possible to reach longer simulation times. In paper III, we therefore use a united atom potential for CTAB.

Non-reactive force fields are often very good for the systems for which they have been parametrized and are still widely used today [75]. For complex materials, however, many different components are usually required, and it is rarely the case that an empirical potential has been parametrized for a full complex system. The main system of interest in this thesis comprises an aqueous solution of organic molecules, in combination with an inorganic surface. For each of these components—the water, the surfactant, and the surface—there exist classical interatomic potentials, but what about the full system? In some cases it can be sufficient for the components to only interact with each other through non-bonded forces, as no new bonds are expected to form. The vdW forces between the components are estimated through combination rules. Depending on the functional form of \mathcal{U}_{vdW} , different combination rules are employed, commonly in the form of geometric or arithmetic averages [76–79]. For instance in GROMOS, the interatomic potential used in paper III, the Lennard-Jones parameters are combined through geometric averages

$$C_{IJ}^{(6)} = \sqrt{C_{II}^{(6)} C_{JJ}^{(6)}}, \quad C_{IJ}^{(12)} = \sqrt{C_{II}^{(12)} C_{JJ}^{(12)}}.$$
 (4.6)

This approach for combining potentials into one that works for a full complex system can be skipped by switching to machine-learned interatomic potentials (MLIPs).

4.1.2 Machine-Learned Interatomic Potentials

The parameters in classical potentials are fitted using experimental data to match materials properties such as density, surface tension, or other measurable quantities. MLIPs, on the other hand, are trained on electronic structure data, obtained by solving Eq. (3.2) using for instance DFT [1, 2]. This allows for training one potential specifically for a system of interest, even a complex one with many constituents. Compared to classical potentials, which are limited by the choice of functional form, MLIPs are highly flexible with many more parameters, allowing them to reach the accuracy of the underlying electronic structure data, at a computational cost similar to classical interatomic potentials.

MLIPs exist in many forms, but they can be categorized into two main classes: kernelbased methods and neural-network based ones. Both of these offer highly flexible functional forms that are fitted using a training data set. There exist many different realizations of kernel-based methods, such as GAP [80] and (s)GDML [81–83], as well as neural-network based ones, including BPNN [84, 85], EANN [86], MACE [87], SchNet [88], DeePMD [89], and NequIP [90]. Here, the focus is on a specific type of neuralnetwork based MLIP called neuroevolution potential (NEP), which is implemented in the GPUMD package [91]. The NEP formalism is used to perform all the MD simulations in paper I, as well as being the basis for the efficient implementation of methods accounting for NQEs in paper II, which is discussed in more detail in Sect. 4.3.

In MLIPs, the descriptors of the material are usually not taken to be the atomic positions R, of which the classical potential is a function (Eq. (4.5)). Instead, a descriptor vector q that is a function of interatomic distances R_{IJ} and distance vectors R_{IJ} is used. This descriptor vector captures the environment surrounding each atom and is introduced to make sure that physical symmetries and invariances are fulfilled by the model [92]. There are many different ways of expressing these descriptors, but in NEP the descriptor for atom I consists of $n_{max}^R + 1$ radial components

$$q_n^I = \sum_{J \neq I} g_n(R_{IJ}), \quad 0 \le n \le n_{\max}^R,$$
 (4.7)

and $(n_{\max}^A + 1)l_{\max}^{3b}$ angular ones, which, for three-body interactions, take the form

$$q_{nl}^{I} = \frac{2l+1}{4\pi} \sum_{J \neq I} \sum_{K \neq I} g_n(R_{IJ}) g_n(R_{IK}) P_l(\cos \theta_{IJK}), \quad 0 \le n \le n_{\max}^{A}, 1 \le l \le l_{\max}^{3b}.$$
(4.8)

For the radial descriptors, the summation is taken over all neighbors J to atom I within a cutoff distance R_c^R . Similarly, for the angular descriptor components, the summation is over all neighbors J and K to atom I within a cutoff R_c^A and θ_{IJK} is the angle formed by the IJ and IK distance vectors. P_l denotes the Legendre polynomial of order l. Higher order interactions, such as four-body and five-body descriptor components can be optionally included [91]. Furthermore, both the radial and the angular descriptors contain the radial function $g_n(R_{IJ})$, which in the NEP formalism is given by $N_{bas}^R + 1$ basis functions in the radial case and $N_{bas}^A + 1$ ones in the angular case. Mathematically, it is expressed as

$$g_n(R_{IJ}) = \sum_{k}^{N_{\text{bas}}} c_{nk}^{IJ} f_k(R_{IJ}), \qquad (4.9)$$

$$f_k(R_{IJ}) = \frac{1}{2} \left[T_k \left(2 \left(\frac{R_{IJ}}{R_c} - 1 \right)^2 - 1 \right) + 1 \right] f_c(R_{IJ}), \tag{4.10}$$

with the cutoff function

$$f_c(R_{IJ}) = \begin{cases} \frac{1}{2} \left[1 + \cos\left(\pi \frac{R_{IJ}}{R_c}\right) \right], & R_{IJ} \le R_c, \\ 0, & R_{IJ} > R_c. \end{cases}$$
(4.11)

Here, T_k is the *k*-th Chebyshev polynomial of the first kind and N_{bas} and R_c are either the radial number of basis functions and cutoff $(N_{\text{bas}}^R, R_c^R)$ or the angular ones $(N_{\text{bas}}^A, R_c^R)$

 R_c^A). Crucially, the expansion coefficients c_{nk}^{IJ} are free parameters in the NEP approach, and are optimized alongside the weights of the neural network. The number of radial and angular descriptor components, the cutoff distances as well as the number of basis functions are hyperparameters set during model construction.

On that note, we now introduce the neural network used to predict the atomic energies with the descriptor vector as input. The energy per atom \mathcal{U}_I is obtained as a function of the descriptor vector with its $N_{\text{des}} = (n_{\text{max}}^R + 1) + (n_{\text{max}}^A + 1)l_{\text{max}}^{3b}$ components, following the original approach for a neural-network based MLIP by Behler and Parinello [84]. In the NEP formalism, a single-layer feedforward neural network is employed, with N_{neu} neurons in the hidden layer, yielding the energy of atom *I* through

$$\mathcal{U}_{I}(\boldsymbol{q}) = \mathcal{U}_{I}(\{q_{n}^{I}\}_{n=1}^{N_{\text{des}}}) = \sum_{\mu=1}^{N_{\text{neu}}} w_{\mu}^{(1)} \tanh\left(\sum_{n=1}^{N_{\text{des}}} w_{\mu n}^{(0)} q_{n}^{I} - b_{\mu}^{(0)}\right) - b^{(1)}, \quad (4.12)$$

where the weights w and biases b are trainable parameters. Partial forces are obtained as the derivative of \mathcal{U}_I with respect to R_{IJ} and from this the per-atom force F_I and virial W_I are accessible.

There are many options for how to optimize a loss function, but in the NEP approach the separable natural evolution strategy [93] is employed, which does not require the loss function to be analytical. The loss function in the NEP formalism is

$$L(z) = \lambda_{e} \left(\frac{1}{N_{\text{str}}} \sum_{n=1}^{N_{\text{str}}} \left(\mathcal{U}^{\text{NEP}}(n, z) - \mathcal{U}^{\text{tar}} \right)^{2} \right)^{1/2} + \lambda_{f} \left(\frac{1}{3N} \sum_{i=1}^{N} \left(F_{i}^{\text{NEP}}(z) - F_{i}^{\text{tar}} \right)^{2} \right)^{1/2} + \lambda_{v} \left(\frac{1}{6N_{\text{str}}} \sum_{n=1}^{N_{\text{str}}} \sum_{\mu\nu} \left(W_{\mu\nu}^{\text{NEP}}(n, z) - W_{\mu\nu}^{\text{tar}} \right)^{2} \right)^{1/2} + \lambda_{1} \frac{1}{N_{\text{par}}} \sum_{n=1}^{N_{\text{par}}} |z_{n}| + \lambda_{2} \left(\frac{1}{N_{\text{par}}} \sum_{n=1}^{N_{\text{par}}} z_{n}^{2} \right)^{1/2},$$
(4.13)

where the set of parameters z that optimizes the problem thus minimizes the root mean squared errors for the energies, forces and virials, under the constraint of L_1 - and L_2 regularization. In practice, the training is generally performed using a number of cycles where the training data set is augmented, usually by including structures for which the MLIP has a large error, indicating that such a structure was far outside the training data set. Neural networks in general perform poorly when extrapolating, so this serves to enlarge the space spanned by the training data, reducing the risk of hallucination. This process of iteratively training a MLIP is called active learning and for complex systems it can be expected to take a few more training cycles than for simpler systems to achieve a potential that performs well. In papers I and II, the MD simulations are performed using NEP models that are trained via this approach.

As a final note on the subject of MLIPs, consider the matter of locality, i.e., the descriptors being 0 beyond a cutoff (Eq. (4.11)). This is a cornerstone for being able to apply MLIPs to complex system, as it allows for identifying representative smaller units of the large complex system for which electronic structure calculations can be run and training data can be generated. The MD can then be run for much larger systems. There are, however, a few cases to be aware of, especially for complex materials, where the assumption of locality is a poor one, such as materials containing unscreened Coulomb interactions or other explicitly long-range phenomena. In such cases, additional treatments of long-range interactions are required in the formulation of the MLIP [94, 95].

4.2 Correlation Functions from Molecular Dynamics

To gain some physical insight from the trajectories generated in MD simulations, observables must be computed. As discussed in Sect. 3.2 many of these can be expressed in terms of correlation functions of phase space properties. Such correlation functions can be computed from the trajectory, but because it contains positions and velocities at discrete times, a computed ACF is an approximation of the true one. The intermediate scattering function encountered in Eq. (3.7), for instance, takes the form

$$F(\boldsymbol{q},t) = \frac{1}{N} \sum_{I}^{N} \sum_{J}^{N} \left\langle \exp\left[i\boldsymbol{q} \cdot (\boldsymbol{R}_{I}(t) - \boldsymbol{R}_{J}(0))\right] \right\rangle.$$
(4.14)

How well a computed correlation function approximates the true one depends on how we have sampled phase space during the MD simulation, which might be affected by metastability of the system hindering a thorough sampling of phase space in the available simulation time as well as the time step of the velocity Verlet integration algorithm (Eqs. (4.2)-(4.3)).

The time step, together with the frequency of writing the trajectory to file, determines the limit of resolution for the computed correlation function. According to the Nyquist-Shannon sampling theorem [96, 97], the time between two subsequent entries in the trajectory must be such that the dynamical process with the highest frequency is sampled more than twice per period to not risk aliasing (Fig. 4.2). The length of the trajectory determines the slowest resolvable process, which is relevant to keep in mind for complex systems as they possibly exhibit slow dynamics or rare events. If a generated trajectory is longer than the slowest dynamics of interest, statistics can be improved by not com-



Figure 4.2: Illustration of Nyquist-Shannon's sampling theorem. Consider the black solid line as the highest frequency process that we would like to sample. a) The sampling frequency is too low (less than two per period), resulting in an erroneous reconstruction of the signal (blue dashed line). b) The sampling frequency fulfills the Nyquist criterion, being exactly double the signal frequency. At this sampling frequency the signal can be reconstructed properly (green dashed line), but aliasing can also occur if we happen to sample precisely when the amplitude of the signal is 0, resulting in the reconstruction giving no signal at all (blue dashed line). c) The signal is sampled more than twice per period, fulfilling the theorem and leading to a correct reconstruction of the signal.

puting a single ACF over the full trajectory, but rather windowing the trajectory with some overlap and computing the ACF within each of these windows, after which they can be averaged. Furthermore, the size of the simulation cell sets a limit on the smallest available wave vector q in the computation of, e.g., the intermediate scattering function obtained via Eq. (3.7) or the dynamic structure factor in Eq. (3.8). For certain physical properties it might be the long-wavelength limit that is of interest, in which case the convergence with cell size must be carefully considered.

There are several software packages available for extracting correlation functions from MD, such as NMOLDYN [98–100], MDANSE [101], and FREUD [102], which often target specific ones, for instance the dynamic structure factor in the context of neutron scattering (Eq. (3.9) with neutron scattering lengths). The DYNASOR package, of which the recent developments are presented in paper I, is designed to extract spatially-resolved correlation functions from MD simulations, including the intermediate scattering function,

dynamic structure factor, and current correlations mentioned in Sect. 3.2, but also several others. In addition, the computed correlation functions are not probe-specific in DYNASOR, but there is functionality for weighting them with, e.g., neutron, electron, or X-ray form factors, facilitating comparison with multiple types of experiments.

4.3 Path-Integral Molecular Dynamics

As discussed in Sect. 3.3, the classical treatment in MD does not suffice for light atoms and low temperatures and taking NQEs into account can alter many of the observables available from MD. A solution to this is the PIMD method, where the main idea is that



Figure 4.3: The basic idea behind the PIMD method: representing every quantum particle by a number of replicas connected by springs, which can be treated classically.

every quantum particle is represented by a number of classical replicas connected by springs (Fig. 4.3). The replicas, also called beads, are then evolved separately using the same equations of motion as in classical MD, but with an added term taking into account the interaction with neighboring beads via the springs. Mathematically, this entails that the kinetic and potential energy parts of the Hamiltonian in Eq. (3.3) are replaced with a sum of the kinetic energies of each individual bead and a sum of the potential energy function of the system, e.g., Eq. (4.5) or Eq. (4.12). Additionally, a term for the interaction between the connected beads is added to the Hamiltonian, which for atom with index *I* takes the form

$$\mathscr{V}_{I}^{P,\text{int}} = \sum_{J=1}^{P} \frac{1}{2} m_{I} \omega_{P}^{2} (\boldsymbol{R}_{J} - \boldsymbol{R}_{J+1})^{2}, \qquad (4.15)$$

where the sum runs over the *P* replicas of atom *I* and $\omega_P = k_B T P / \hbar$ is the spring frequency.

In the limit of an infinite number of beads ($P \rightarrow \infty$), the quantum nature of the nuclei is reproduced. During PIMD simulations, we cannot use an infinite number of replicas to denote every atom, so, in practice, the number of beads is a convergence parameter that needs to be carefully considered for accurately capturing the NQEs. This means that a PIMD simulation quickly becomes expensive, especially for complex materials which generally need large simulation cells. For this reason, the PIMD method is implemented into GPUMD, as presented in paper II, which allows for the combination of PIMD with the NEP formalism described in Sect. 4.1.2. This facilitates efficient largescale PIMD simulations, allowing for computation of observables that include NQEs, even for complex systems.



Figure 4.4: The full width at half maximum for the first partial RDF peaks in water at 300 K, as a function of the number of beads used in the PIMD simulation. The H-H and O-H lines are also part of Fig. 7 in paper II.

As an example, the convergence behavior of the full width at half maximum (FWHM) values of the first peak in the partial RDFs of water are shown in Fig. 4.4. This illustrates the larger effect of NQEs on light atoms, discussed in Sect. 3.3, as the difference between a PIMD simulation with 1 beads (classical MD) and 64 beads is the largest for the H-H RDF (~ 0.07 Å), then for the O-H RDF (~ 0.04 Å), and almost nothing for the O-O RDF.

4.4 Electrodynamic Simulations

To study macroscopic light-matter interactions computationally, Maxwell's equations (Eqs. (3.11)-(3.14)) are solved at the continuum level using the FDTD, or Yee, method [103], as implemented in the MEEP software [104]. The Yee method is a finite-difference



Figure 4.5: The Yee grid used for discretization of Maxwell's equations.

approach for solving time-dependent partial differential equations, in which the sixdimensional system in Eqs. (3.11) and (3.12) is solved by integration in time. To do so, a discretization scheme called a Yee grid is used, where the components of the electric field *E* and magnetic field *H* are placed in a staggered fashion (Fig. 4.5). Every magnetic field component is surrounded by the corresponding electric field components, and vice versa. By ordering the field components on this three-dimensional grid and using the leap-frog integration algorithm [56] that was mentioned in Sect. 4.1, the values of *E* are known with a difference of half a time step compared to the values of *H*, meaning that central-differences to second-order can be used to compute the derivatives in Eqs. (3.11) and (3.12).

To perform these computations, a continuum representation of the studied system is needed, which is placed in a finite cell with electrodynamic boundary conditions. There are several different options of boundary conditions, including an artificial absorbing medium with no reflection at its interface, called a perfectly matched layer [104]. This boundary condition is employed in paper III, where a continuum representation of the surfactant- and silica-covered gold NPs are defined as one part of the multi-scale approach, allowing for performing FDTD simulations with MEEP. The continuum repre-



Figure 4.6: Extinction spectra calculated using FDTD in paper III for the different surfactant phases in Fig. 2.2.

sentations are based on the geometry obtained in MD simulations. These simulations yield the computed extinction spectra (Eq. (3.26)), revealing that the plasmonic resonance peak is sensitive to the surfactant-surface phase (Fig. 4.6) and qualitatively matching the observed behavior in plasmonic sensing measurements of the same system.

5

Summary of Papers

Paper I

Dynasor 2: From Simulation to Experiment Through Correlation Functions

We present a substantial development of the DYNASOR software, which is designed for the computation of spatially-resolved correlation functions introduced in Sect. 3.2, such as structure factors $S(q, \omega)$ (Eq. (3.8)) and current correlations $C(q, \omega)$. The paper accompanies version 2.X of the software, which has seen some major developments compared to earlier versions. These developments include a completely new Python interface, added support for weighting with form factors or scattering lengths (Eq. (3.9)) to facilitate comparison with experiment, and the implementation of new correlation functions, such as mode projection ACFs and the spectral energy density method. The paper outlines both the underlying theory as well as the utility of DYNASOR through a comprehensive set of examples that range from ordered solid systems to both disordered solid and liquid systems. This illustrates an advantage of MD-based correlation functions over perturbative methods, which would not be applicable for the latter of these systems. Computed correlation functions are also compared to experiments with X-ray, neutron, and electron probes, showcasing the versatility of the software, being applicable both in fundamental research and for experimental planning.

Paper II

Highly efficient path-integral molecular dynamics simulations with GPUMD using neuroevolution potentials: Case studies on thermal properties of materials

The efficient implementation of PIMD into the open-source MD package GPUMD is presented. Using the NEP framework introduced in Sect. 4.1.2, the resulting computational cost of the PIMD simulations (introduced in Sect. 4.3) is comparatively low. This allows for running large-scale simulations that account for NQEs, which we discussed in Sect. 3.3.

The NEP-PIMD approach is demonstrated in the paper for different types of materials. This includes solids of various degrees of complexity, such as elemental aluminum, lithium hydride, and different metal-organic frameworks, as well as water to showcase its application to a liquid system.

A number of structural and thermal properties are computed for the different materials, including lattice parameters, RDFs (see Fig. 3.2), thermal expansion coefficient as well as phonon frequencies and damping parameters. The simulations confirm or reveal how NQEs affect these systems and pave the way for running large-scale PIMD simulations with MLIPs of the NEP form for other systems in the future.

Paper III

In-situ Plasmonic Sensing of Surfactant Structures

We employ a multi-scale modeling approach to gain insight into a complex material and also connect to experiment by proposing a non-intrusive, *in-situ* method for studying the surface-phase behavior of surfactant structures. These surfactant structures, such as bilayers or micelles, which we discussed in Sect. 2.1, have phase transitions that are inherently slow, due to the large restructuring involved and the competition between entropy and energy that comes with being confined to a surface. Thus, they exhibit complex behavior over long time and length scales, and reside at a solid-liquid interface.

The method we propose for studying the surface-phase behavior of the surfactant structures relies on plasmonic sensing, in which the extinction spectrum (Eq. (3.26)) is measured. As discussed in Sect. 3.4, this spectrum exhibits a peak at the plasmonic resonance of a nanoparticle, which is sensitive to its dielectric environment. The approach offers access to not only structural information, but also the kinetics of the phase transitions between surfactant surface-phases. The multi-scale modeling approach we deploy for showing that it is possible to measure the surfactant structures using plasmonic sensing includes an atomistic level, to find the relevant structures in MD simulations (Sect. 4.1), and an optical response part using FDTD (Sect. 4.4) to show that the surfactant structures are distinguishable using plasmonic sensing. Furthermore, the paper contains experimental results from employing *in-situ* plasmonic sensing of surfactant structures, which are in agreement with the multi-scale modeling outcome.

6

Conclusions and Outlook

Having arrived at the final chapter, we are able to return to the fundamental questions posed in Chapter 1, beginning with the first one.

How can insight be gained into multi-scale dynamics of complex materials? In particular, how can simulation and experiment be connected?

There are many computational techniques for studying multi-scale dynamics of complex materials, and in this thesis we have encountered a selection; MD at the atomic level, PIMD for including NQEs, and FDTD for solving Maxwell's macroscopic equations. To actually understand the dynamics, physically relevant observables must be computed from the simulations. As we have discussed in the case of MD, spatio-temporal correlation functions offer a versatile approach for gaining insight into the dynamics of a material. Computing such correlation functions is the purpose of DYNASOR, the software package of which substantial developments were presented in paper I. Furthermore, when computing such observables from simulations at low temperatures and/or for light atoms, NQEs must be accounted for, as their inclusion can have a drastic effect, which we saw for, e.g., the RDF of water as well as other examples in paper II. In the case of FDTD simulations, spectra for the scattering, absorption, or extinction of light can be extracted, providing information about light-matter interaction and indirectly the atomic structure, such as the LSPR of a NP.

These techniques also offer several possibilities for experimental connection. Dynamic structure factors, i.e., density-density correlation functions, have strong ties to scattering and diffraction experiments, as it is the quantity probed there as well. Weighting computed structure factors with probe-specific cross sections to allow for a more direct comparison is therefore one of the key developments of DYNASOR in paper I. In addition, computed scattering, absorption, or extinction spectra from FDTD can be directly compared with experimental measurements of such optical spectra.

The second fundamental question in Chapter 1 was:

How can these approaches be applied to study a complex system, such as one involving surfactant surface-phases?

In this complex system, a multi-scale modeling approach comprising MD and FDTD proved successful for understanding the change in plasmonic response accompanying a change in surfactant surface-phase. This multi-scale approach in paper III, combined with experimental measurements of the plasmonic response, showed that the structure as well as the dynamics of the phase transitions of surfactant surface-phases are accessible *in situ* by means of plasmonic sensing.

6.1 Outlook

As there is a vast range of scales at which materials in general, and complex materials in particular, can exhibit dynamics of interest, this thesis is in no way comprehensive. We could go to smaller scales than the ones treated here, investigating aspects of, e.g., electronic response. An example of where this would be relevant is the permittivity of the surfactant in paper III, which could be computed at the electronic level through DFT, ideally in combination with methods such as GW [105, 106]. This would go beyond the current approach of scanning a range of permittivities, and would add another level to the multi-scale modeling approach currently containing an atomistic and continuum level.

It would also be possible to go to larger scales. Sticking with the example of surfactant surface-phases, if a surface phase diagram is established, it could be possible to use this information to coarse-grain the surfactants and zoom out to simulate not only surfaces, as currently in paper III, but surfactant-covered NPs to investigate other aspects affecting NP growth and how NPs arrange into larger supramolecular structures.

When determining which scales are of interest for computationally investigating a complex material, the inclusion of certain scales necessitates the exclusion of others. This always comes with a risk of missing some dynamics relevant to the investigation at hand, so when choosing which techniques to combine into a multi-scale modeling approach for a particular system, these aspects must be carefully considered. Additionally, there is a decision to be made about which observables to compute. In this thesis, at the atomic scale, the focus has been on spatially-resolved correlation functions such as the dynamic structure factor. There are many other possible observables, including the conductivity obtainable through the temporal ACF of the ionic current, the IR absorption spectrum available from the temporal ACF of the dipole moment, or the Raman absorption spectrum via the temporal ACF of the polarizability of a system. All of these are very useful correlation functions-based quantities for gaining insight into the dynamics of

a material, each with possibilities for connecting to different experiments, which can elucidate distinct aspects of the dynamics of a complex system.

Computing correlation functions from MD comes with several convergence considerations, some of which are discussed in Sect. 4.2. A possibility to overcome the issues related to sampling would be to employ, e.g., Boltzmann Generators [107] to model the entire PES at once or the Implicit Transfer Operator technique [108] for learning a multiple time-scale surrogate of MD, making much longer time-scales available and providing a platform for accelerating the computation of correlation functions and related observables.

For the complex system of interest in this thesis—aqueous surfactant structures on inorganic surfaces—there are also several other aspects that would be interesting to explore. To begin with, going beyond the classical interatomic potential by training a MLIP for the full system would provide several advantages. This would allow for bonds to form and break during the MD, which is particularly relevant for the system at hand because ionic exchange at the surface is thought to play a role in the adsorption of surfactants [29]. Furthermore, a MLIP with an additional treatment of the long-range contributions discussed at the end of Sect. 4.1.2, could facilitate simulations during which the charge state of the ions is allowed to vary, providing additional insights into the growth mechanism of the underlying NP and possibly aiding in the investigation of why Br⁻ and Cl⁻ appear to have different effects on the surfactant structures and NP growth [35, 109–111].

On a final note, it is important to emphasize that the multi-scale modeling of dynamics in complex systems involves a large methodological "toolbox" and many choices to make on how to combine different techniques. This is not only true for systems containing surfactant surface-phases, but whenever we aim to computationally investigate a complex material with interesting structure and dynamics of multiple spatio-temporal scales. For this reason, the advancement of methodologies in combination with the application of them is crucial, bridging length and time scales and gradually extending the interpretative and predictive possibilities in the direction of complex materials. This is actively pursued, so, for now, the tale of scales is far from concluded.

Acknowledgments

I would like to take this opportunity to express my gratitude to my supervisor Paul for your support, guidance, and for all of the interesting physics that we have studied together during the past years. I could not hope for a better PhD supervisor and I very much look forward to the upcoming years.

I would also like to thank my co-supervisor Aleksandar and my examiner Henrik for your support. Furthermore, I am fortunate enough to be surrounded by fantastic colleagues, who make working at the division a real pleasure. A special thanks to Erik, Fredrik and Eric, for always being up for discussing correlation functions, phonons, and physics in general.

Finally, I would like to thank my family and friends for your encouragement and curiosity about my research, even though it may be far from your own area of expertise. Erik—thank you for everything.

Tot over twee jaar, Esmée Berger, 2025

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