

Water in mesoporous materials: Investigating capillary flow, elastocapillarity, and phase transitions with molecular dynamics simulations

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ABSTRACT

Water-driven mesoporous materials exhibit significant potential for sustainable applications. To realize these applications, a thorough understanding of the effects of interactions between water and the mesoporous materials is essential. This thesis contributes to the understanding of water-driven mesoporous materials in three aspects. First, capillary flow dynamics of water in ordered, cylindrical silica mesopores were investigated by molecular dynamics (MD). The analysis of the simulations provided insights into the analytical modeling of capillary flow processes on nanosecond timescales. Specifically, the analysis determined that inertia-dominated and viscosity-dominated capillary flow regimes should be modeled separately. Additionally, an explicit consideration of an evolving contact angle is required to model the viscosity-dominated flow dynamics. Second, an analytical model of imbibition-induced elastocapillarity in ordered, cylindrical mesopores was formulated. By comparing the model with imbibition-induced elastocapillarity observed in MD simulations the model's capacity to predict key aspects of elastic deformation was demonstrated. The deformation dynamics of the porous matrix scales directly with the imbibition length of the liquid column and is typically expansive. After complete filling, the pore matrix expands laterally as the Laplace pressure in the liquid vanishes. These findings could serve as a basis for future applications in the field of actuator or sensor technology. Finally, a method was proposed that incorporates information from measurable radial distribution functions into MD simulations through the principle of maximum relative entropy. It was demonstrated that the method can be employed to mediate liquid-to-solid phase transitions in MD simulations. Consequently, the method could be used in future MD simulations to study liquid-to-solid phase transitions in mesoporous materials.

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Chapter 1

WATER-DRIVEN MATERIALS AS SUSTAINABLE AND SCALABLE SOLUTIONS FOR GLOBAL PROBLEMS

IF THERE IS MAGIC ON THIS PLANET, IT IS CONTAINED IN
WATER.

— Loren Eiseley

In the current era, humanity faces unprecedented global challenges. In response, the United Nations (UN) members defined 17 Sustainable Development Goals (SDGs) in 2015, thereby establishing the sustainable development agenda for 2030.¹ The 17 SDGs are depicted in Fig. 1.1. Many of these goals, such as "Affordable and Clean Energy" (SDG 7), "Industry, Innovation, and Infrastructure" (SDG 9), "Sustainable Cities and Communities" (SDG 11), and "Climate Action" (SDG 13), require a rapid, large-scale societal transformation and technological innovation. Consequently, the development of new technology that enables achievement of these goals is of high importance for us and the future of the planet. Given the nature of the SDGs, any technology created to support these goals must satisfy two requirements. First, because the challenges are global, the technology must exhibit high scalability. However, if scalability is prioritized over sustainability, this may lead to new sustainability challenges. Therefore, the second requirement is that any new technology created to address global challenges must be sustainable. Many definitions of sustainability exist. Harrington² defines sustainability as: "... the capacity to maintain or improve the state and availability of desirable materials or conditions over the long term." With regard to the scalability and sustainability requirements, it is evident that future technology supporting the SDGs has to rely on substances that are readily available in large quantities. Furthermore, the manufacturing process for this technology must avoid environmental damage.



Figure 1.1: The 17 Sustainable Development Goals of the UN.ⁱ

Water is one of the most abundant materials on the planet, which is why Earth is sometimes referred to as the blue planet. Consequently, technology based on water-driven materials satisfies the scalability and sustainability requirements needed to support the SDGs. This rationale underpins the Cluster of Excellence "BlueMat: Water-Driven Materials", which concentrates on the development of nature-inspired, sustainable, water-driven materials that obtain their functionality from the interaction of water with multiscale structures. The BlueMat cluster investigates four classes of water-driven materials tailored for distinct applications. These categories are mechanical materials, fluid transport materials, photonic materials, and energy materials. Mechanical materials comprise nanostructured solids whose mechanical behavior arises from material–water interactions. Research on fluid transport materials seeks to tune water–solid interactions to enhance capillarity-driven liquid transport and to optimize water vapor and solute ion sorption. Photonic materials are engineered to modify the electromagnetic properties of water-driven materials within the optical and microwave frequency range. Lastly, energy materials rely on porous frameworks impregnated with water or aqueous solutions to store and convert energy. To realize these sustainable and scalable applications, a comprehensive understanding of water-driven materials is essential, and suitable methods must be developed to obtain this understanding.

The objective of this thesis is to contribute to a deeper understanding of water-driven

ⁱThe content of this publication has not been approved by the United Nations and does not reflect the views of the United Nations or its officials or Member States. See <https://www.un.org/sustainabledevelopment>. See https://www.un.org/sustainabledevelopment/wp-content/uploads/2019/01/SDG_Guidelines_AUG_2019_Final.pdf for the guidelines on how to use the SDG branding.

materials, particularly water-driven mesoporous materials. Specifically, two processes are investigated in this thesis at the atomic scale with Molecular Dynamics (MD) simulations. In Ch. 4, the capillary flow dynamics of water into ordered, cylindrical nanopores are investigated. As a result, the findings of this chapter fall within the scope of research on fluid transport materials. Subsequently, in Ch. 5, the imbibition-induced elastocapillarity effects on the pore matrix during and after the capillary flow process are investigated. As this chapter addresses material deformation, it falls within research on mechanical materials. Both studies are based on the capillarity-driven flow of water into an identically simulated porous structure. The properties of this structure and details on simulating the imbibition process are discussed in Ch. 3. Elastocapillarity effects are also observed for liquid-to-solid phase transitions of water in nanoconfinement³, but they are not yet fully understood. Consequently, this effect would be another interesting topic to study with MD simulations. However, as discussed in Sec. 6.1.2, investigating phase transitions with MD simulations is challenging. Therefore, Ch. 6 presents a method that facilitates liquid-to-solid investigations in MD simulations in general, and for future studies of water phase transitions in confinement, specifically. Finally, Ch. 7 provides conclusions regarding the contributions of this thesis and future possibilities in research and applications. Before the results of the scientific studies are presented in the subsequent chapters, the next chapter provides an overview of the fundamental physics required for an in-depth understanding of the topics discussed in this thesis.

Chapter 2

FUNDAMENTALS OF WATER IN MESOPOROUS MATERIALS

As detailed in Ch. 1, the objective of this thesis is to enhance our understanding of water-driven mesoporous materials. In preparation for the presentation of the results, this chapter summarizes the theoretical fundamentals necessary to comprehend the contributions of this thesis. First, the definition of mesoporous materials is provided in Sec. 2.1. The subsequent section Sec. 2.2 provides a concise overview of elastic deformation. Sec. 2.3 examines capillarity and surface effects of liquids in mesoporous materials. Afterwards, a concise overview of molecular dynamics simulations is presented in Sec. 2.4. Finally, Sec. 2.5 addresses the key aspects of classical nucleation theory (CNT). It is important to note that each topic can only be discussed as a very brief overview and provides the minimum of information necessary to follow the thesis at hand. For readers that seek a more in-depth explanations of the topics, the provided references offer further insight.

2.1 Liquids in mesoporous materials

Porous materials are materials that are interspersed with voids. Porous materials can occur in a variety of pore diameter distributions, pore arrangements, and porosities. The porosity is defined as $\phi = \frac{V_{\text{void}}}{V_{\text{total}}}$, i.e., the ratio of void volume V_{void} to material volume V_{total} . The International Union of Pure and Applied Chemistry (IUPAC) has established a classification system for porous structures, which are divided into three categories based on their pore diameters⁴. These are:

- Microporous materials: < 2 nm diameter
- Mesoporous materials: 2 nm – 50 nm
- Macroporous materials: 50 nm – 1000 nm

In this thesis, the terms *mesoporous* and *nanoporous* materials are used interchangeably. The focus of this thesis is on mesoporous materials with ordered, cylindrical pores. A

well-known example of this class of materials is Mobil Composition of Matter No. 41 (MCM-41). MCM-41 consists of mesoporous silica (SiO_2) with an ordered, cylindrical pore structure. Fig. 2.1 depicts a transmission electron microscope image of MCM-41 particles. The image was originally published by Ajumobi et al.⁵ Another example of a

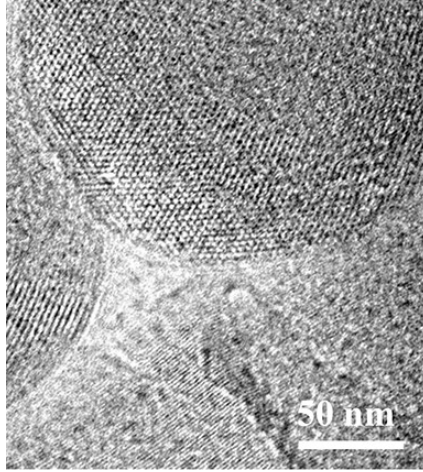


Figure 2.1: Transmission electron microscopy image of MCM-41 particles. The image is a cropped version of the original image published by Ajumobi et al.⁵ under the CC-BY 4.0 license.

nanoporous material with ordered, cylindrical pores is anodic aluminum oxide (AAO). When substances are infused within small pore structures, they often exhibit peculiar confinement effects.⁶ Additionally, nanoporous materials feature a very large surface-to-volume ratio ζ . For instance, for MCM-41 with pore diameters of 3 nm, a pore matrix that plays an important role in this thesis, Kruk et al.⁷ measured a surface-to-volume ratio of $\zeta \approx 1.8 \times 10^9 \text{ m}^{-1}$. The large surface-to-volume ratio promotes surface effects between the porous material and potentially infused fluids. As a result, many potential applications of mesoporous materials rely on these surface effects. One important phenomenon originating from surface effects is imbibition-induced elastocapillarity. Elastocapillarity leads to elastic deformations of the mesoporous materials. To better discuss elastocapillarity, the following section provides a brief introduction to elastic deformations.

2.2 Elastic deformation of materials

The induction of stress into a material results in deformation of that material. In general, two types of deformation are distinguished, elastic deformation and plastic deformation. A material undergoes elastic deformation when it is subject to minor deformations. Elastic deformations are reversible if the applied stress vanishes. If the magnitude of a deformation

exceeds the material's elastic limit, plastic deformation occurs. This form of deformation is not reversible by removing the applied stress. This thesis focuses exclusively on elastic deformations of materials that can be described by continuum mechanics. The following constraints are satisfied in elastic deformations:

- The deformations are small.
- The deformation is reversible, meaning that it disappears once the stress is released.
- The relationship between the imposed stresses and the observed deformations is linear.

Below, a brief theoretical overview is provided that contains the most important aspects of elastic deformations. The content of this section can be found in the textbook "Introduction to Continuum Mechanics" from Lai, Rubin, and Krempel⁸.

To fully describe the deformation of an object, the displacement of every mass coordinate $\mathbf{r}^T = (r_x \ r_y \ r_z)$ inside the body has to be considered. Towards this goal, a so called displacement field $\mathbf{u}(\mathbf{r})$ is introduced, that relates a displacement vector to every mass coordinate contained in the object. After deformation the mass coordinate $\mathbf{r}$ is situated at

$$\mathbf{r}' = \mathbf{r} + \mathbf{u}(\mathbf{r}) . \quad (2.1)$$

The change of the mass coordinate relative to an infinitesimal close neighboring point at $\mathbf{r} + d\mathbf{r}$ can be calculated by

$$d\mathbf{r}' = d\mathbf{r} + \frac{\mathbf{u}(\mathbf{r} + d\mathbf{r}) - \mathbf{u}(\mathbf{r})}{d\mathbf{r}} d\mathbf{r} = d\mathbf{r} + (\nabla \mathbf{u}) d\mathbf{r} = (\mathbf{I} + \nabla \mathbf{u}) d\mathbf{r} = \mathbf{F} d\mathbf{r} , \quad (2.2)$$

where $\mathbf{I}$ is the identity matrix. $\mathbf{F}$ is known as the so called deformation gradient. The infinitesimal distances in the object before and after the deformation are related by

$$d\mathbf{r}' d\mathbf{r}' = d\mathbf{r} (\mathbf{F}^T \mathbf{F}) d\mathbf{r} = d\mathbf{r} \mathbf{G} d\mathbf{r} . \quad (2.3)$$

$\mathbf{G}$ is the so called right Cauchy-Green deformation tensor and defined as

$$\mathbf{G} = \mathbf{F}^T \mathbf{F} = (\mathbf{I} + \nabla \mathbf{u})^T (\mathbf{I} + \nabla \mathbf{u}) = \mathbf{I} + \nabla \mathbf{u} + (\nabla \mathbf{u})^T + (\nabla \mathbf{u})^T (\nabla \mathbf{u}) . \quad (2.4)$$

Note that if $\mathbf{G} = \mathbf{I}$, the infinitesimal distance $d\mathbf{r}' d\mathbf{r}' = d\mathbf{r} d\mathbf{r}$ remains unchanged. Therefore, $\mathbf{G} = \mathbf{I}$ can be related to a rigid body displacement, i.e., a translation or rotation of the object. Deformation, arising from a change in the distances between mass coordinates within the

material, is calculated from the final terms of the Cauchy-Green deformation tensor

$$\mathbf{E}^* = \frac{1}{2} \left[\nabla \mathbf{u} + (\nabla \mathbf{u})^T + (\nabla \mathbf{u})^T (\nabla \mathbf{u}) \right]. \quad (2.5)$$

$\mathbf{E}^*$ is called the Lagrange strain tensor. If elastic deformations are considered, as is the case in this thesis, the partial derivatives of the displacements are small. Hence, the Lagrange strain tensor can be approximated as the infinitesimal strain tensor $\mathbf{E}$ through

$$\mathbf{E}^* = \frac{1}{2} \left[\nabla \mathbf{u} + (\nabla \mathbf{u})^T + (\nabla \mathbf{u})^T (\nabla \mathbf{u}) \right] \approx \frac{1}{2} \left[\nabla \mathbf{u} + (\nabla \mathbf{u})^T \right] = \mathbf{E}. \quad (2.6)$$

In three dimensional euclidean coordinates (x, y, z), the explicit representation of the infinitesimal strain tensor is

$$\begin{aligned} [\mathbf{E}] &= \begin{bmatrix} \varepsilon_x & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{yx} & \varepsilon_y & \varepsilon_{yz} \\ \varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_z \end{bmatrix} \\ &= \begin{bmatrix} \frac{\partial u_x}{\partial r_x} & \frac{1}{2} \left(\frac{\partial u_x}{\partial r_y} + \frac{\partial u_y}{\partial r_x} \right) & \frac{1}{2} \left(\frac{\partial u_x}{\partial r_z} + \frac{\partial u_z}{\partial r_x} \right) \\ \frac{1}{2} \left(\frac{\partial u_x}{\partial r_y} + \frac{\partial u_y}{\partial r_x} \right) & \frac{\partial u_y}{\partial r_y} & \frac{1}{2} \left(\frac{\partial u_y}{\partial r_z} + \frac{\partial u_z}{\partial r_y} \right) \\ \frac{1}{2} \left(\frac{\partial u_x}{\partial r_z} + \frac{\partial u_z}{\partial r_x} \right) & \frac{1}{2} \left(\frac{\partial u_y}{\partial r_z} + \frac{\partial u_z}{\partial r_y} \right) & \frac{\partial u_z}{\partial r_z} \end{bmatrix}. \end{aligned} \quad (2.7)$$

The diagonal components of the infinitesimal strain tensor determine the normal strain, i.e., the infinitesimal change of length in an object. In contrast, the off-diagonal components define the infinitesimal shear strain.

For deformation of a material to occur, the material has to be subject to internal stress. Stress is defined as the internal force across a small interface per unit area of this interface. Since stress is determined by the relation of a three-dimensional force vector to a considered surface normal vector, the stress in a body has to be described by a second rank tensor

$$[\mathbf{S}] = \begin{bmatrix} \sigma_x & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_y & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_z \end{bmatrix}, \quad (2.8)$$

where the diagonal elements denote the tensile and the off-diagonal elements the shear stress.

The mesoporous material examined in this thesis, can be described in good approximation as an array of ordered, cylindrical pores. To exploit the cylindrical symmetry of the pores, it is advantageous to define strain and stress in cylindrical coordinates, where ρ , φ and z denote the radial, azimuthal and axial coordinates, respectively. The corresponding transformed

infinitesimal strain tensor is defined as

$$\begin{aligned}
 [\mathbf{E}] &= \begin{bmatrix} \varepsilon_\rho & \varepsilon_{\rho\varphi} & \varepsilon_{\rho z} \\ \varepsilon_{\varphi\rho} & \varepsilon_\varphi & \varepsilon_{\varphi z} \\ \varepsilon_{z\rho} & \varepsilon_{z\varphi} & \varepsilon_z \end{bmatrix} \\
 &= \begin{bmatrix} \frac{\partial u_\rho}{\partial r_\rho} & \frac{1}{2} \left(\frac{1}{\rho} \frac{\partial u_\rho}{\partial r_\theta} - \frac{u_\theta}{\rho} + \frac{\partial u_\theta}{\partial r_\rho} \right) & \frac{1}{2} \left(\frac{\partial u_\rho}{\partial r_z} + \frac{\partial u_z}{\partial r_\rho} \right) \\ \frac{1}{2} \left(\frac{1}{\rho} \frac{\partial u_\rho}{\partial r_\theta} - \frac{u_\theta}{\rho} + \frac{\partial u_\theta}{\partial r_\rho} \right) & \frac{1}{\rho} \frac{\partial u_\theta}{\partial r_\theta} + \frac{u_\rho}{\rho} & \frac{1}{2} \left(\frac{\partial u_\theta}{\partial r_z} + \frac{1}{\rho} \frac{\partial u_z}{\partial r_\theta} \right) \\ \frac{1}{2} \left(\frac{\partial u_\rho}{\partial r_z} + \frac{\partial u_z}{\partial r_\rho} \right) & \frac{1}{2} \left(\frac{\partial u_\theta}{\partial r_z} + \frac{1}{\rho} \frac{\partial u_z}{\partial r_\theta} \right) & \frac{\partial u_z}{\partial r_z} \end{bmatrix}. \quad (2.9)
 \end{aligned}$$

The transformed stress tensor is given by

$$[\mathbf{S}] = \begin{bmatrix} \sigma_\rho & \sigma_{\rho\varphi} & \sigma_{\rho z} \\ \sigma_{\varphi\rho} & \sigma_\varphi & \sigma_{\varphi z} \\ \sigma_{z\rho} & \sigma_{z\varphi} & \sigma_z \end{bmatrix}. \quad (2.10)$$

As stated above, elastic deformations are reversible and scale linear with the applied stress. Therefore, the strain tensor is linearly related to the stress experienced by the material. Mathematically, the linear relation between stress and strain is described by Hooke's law

$$\mathbf{E} = \mathbf{C}\mathbf{S}, \quad (2.11)$$

where $\mathbf{C}$ is known as the *compliance* of the material and its inverse $\mathbf{C}^{-1}$ as the *stiffness*. In the most general notation, $\mathbf{C}$ is a fourth rank tensor, however, due to the existing symmetries in stress and strain tensor, Hooke's law can be contracted into the so called Voigt notation

$$\boldsymbol{\varepsilon} = \mathbf{c}\boldsymbol{\sigma}, \quad (2.12)$$

where stress and strain are described as a six-dimensional vectors

$$[\boldsymbol{\sigma}] = \begin{bmatrix} \sigma_\rho \\ \sigma_\varphi \\ \sigma_z \\ \sigma_{\varphi z} \\ \sigma_{\rho z} \\ \sigma_{\rho\varphi} \end{bmatrix} \quad (2.13)$$

and

$$[\boldsymbol{\varepsilon}] = \begin{bmatrix} \varepsilon_\rho \\ \varepsilon_\varphi \\ \varepsilon_z \\ 2\varepsilon_{\varphi z} \\ 2\varepsilon_{\rho z} \\ 2\varepsilon_{\rho\varphi} \end{bmatrix}. \quad (2.14)$$

The contracted compliance tensor $\mathbf{c}$ is a 6x6 rank two tensor. The array of ordered, cylindrical pores considered in this thesis is not anisotropic in every direction. Instead, the mesoporous material can be divided into one isotropic plane perpendicular to the cylinder and another direction along the cylindrical axis. Materials that exhibit this symmetry are called transversely isotropic. The compliance tensor for the transversely isotropic materials in contracted notation and cylindrical coordinates can be written as

$$[\mathbf{c}] = \begin{bmatrix} 1/E_\perp & -\nu_\perp/E_\perp & -\nu_{\parallel\perp}/E_\parallel & 0 & 0 & 0 \\ -\nu_\perp/E_\perp & 1/E_\perp & -\nu_{\parallel\perp}/E_\parallel & 0 & 0 & 0 \\ -\nu_{\perp\parallel}/E_\perp & -\nu_{\perp\parallel}/E_\perp & 1/E_\parallel & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/G_{\perp\parallel} & 0 & 0 \\ 0 & 0 & 0 & 0 & 1/G_{\perp\parallel} & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/G_\perp \end{bmatrix}. \quad (2.15)$$

In this context, the subscripts denote the direction of the parameters. $\parallel$ denotes the axial coordinate z of the cylindrical pores and $\perp$ denotes the isotropic ρ - φ plane perpendicular to the cylindrical pore. In this thesis, the direction perpendicular to the cylindrical pore is also referenced as the lateral direction. The parameters $E_\perp$ and $E_\parallel$ are Young moduli perpendicular and parallel to the cylindrical pores, respectively. The Young modulus is a measure of the materials tensile stiffness. In other words, it is a quantitative indicator of the stress induced within the material per unit of deformation. $G_{\perp\parallel}$ is the shear modulus that defines the shear stiffness between the lateral and the axial directions. $\nu_\perp$, $\nu_{\parallel\perp}$ and $\nu_{\perp\parallel}$ are the Poisson ratios, that determine the strength of the so called Poisson effect. The Poisson effect is explained in detail below. Due to symmetry constraints of elastic deformations, the compliance tensor has to satisfy

$$\nu_{\perp\parallel}/E_\perp = \nu_{\parallel\perp}/E_\parallel. \quad (2.16)$$

In experiments and simulations, it is often challenging to determine the infinitesimal strain. Hence, often the macroscopic engineering strain $\bar{\varepsilon}_\alpha$ of a body is determined in experiment

instead. In this context, $\alpha \in \{\perp, \parallel\}$ denotes the direction of the strain. When a body of length L_α is strained by a length ΔL_α , the macroscopic engineering strain is calculated as

$$\bar{\varepsilon}_\alpha = \frac{\Delta L_\alpha}{L_\alpha}. \quad (2.17)$$

The macroscopic engineering strain $\bar{\varepsilon}_\alpha$ can also be determined from the averaged integral of the derivative of the displacement function along direction α as

$$\bar{\varepsilon}_\alpha = \frac{1}{L_\alpha} \int_{r'_\alpha}^{r'_\alpha + L_\alpha} \frac{\partial u_\alpha}{\partial r_\alpha} dr_\alpha = \frac{u_\alpha(r'_\alpha + L_\alpha) - u_\alpha(r'_\alpha)}{L_\alpha} = \frac{\Delta L_\alpha}{L_\alpha}, \quad (2.18)$$

where r'_α is a specific coordinate on the axis α , e.g., one end of the considered object. A sketch that depicts the relation of the displacement functions and the engineering strain is displayed in Fig. 2.2.

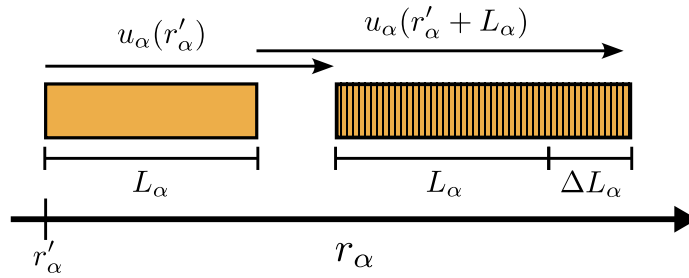


Figure 2.2: Relation between engineering strain and displacement. The unstrained material (left) is displaced along the direction r_α . The displaced body (right) is translated and strained.

The values of the Poisson ratio, which define the strength of the Poisson effect, can be determined from small engineering strains of an object. The Poisson effect is the phenomenon that if a stress is applied along one axis α , e.g., along the lateral direction $\perp$, a deformation of the material is not only observed along direction α but also along the direction β , that is perpendicular to α , e.g., along the axial direction $\parallel$. The Poisson ratio $\nu_{\alpha\beta}$ is for small deformations in good approximation determined from the negative magnitude of the elastic deformation $\bar{\varepsilon}_\alpha$ along α , relative to the observed deformation $\bar{\varepsilon}_\beta$. To be more precise, when a stress σ_α is applied to a material, the material deforms along axis α from L_α to $L_\alpha + \Delta L_\alpha$. Simultaneously, the material deforms along axis β from L_β to $L_\beta + \Delta L_\beta$. The Poisson ratio can be determined from the relation

$$-\nu_{\alpha\beta} \int_{L_\alpha}^{L_\alpha + \Delta L_\alpha} \frac{dr_\alpha}{r_\alpha} = \int_{L_\beta}^{L_\beta + \Delta L_\beta} \frac{dr_\beta}{r_\beta}, \quad (2.19)$$

that connects the infinitesimal relative changes in length. Solving the integrals and subsequent

exponentiation, the relation can be expressed as

$$\left(1 + \frac{\Delta L_\alpha}{L_\alpha}\right)^{-\nu_{\alpha\beta}} = 1 + \frac{\Delta L_\beta}{L_\beta}, \quad (2.20)$$

where $\bar{\varepsilon}_\alpha = \frac{\Delta L_\alpha}{L_\alpha}$ and $\bar{\varepsilon}_\beta = \frac{\Delta L_\beta}{L_\beta}$ are identified to be small engineering strains along the direction α and β , respectively. Since only small deformations are considered, Eq. (2.20) can be approximated by the first-order truncation of the binomial series as

$$1 - \nu_{\alpha\beta}\bar{\varepsilon}_\alpha = 1 + \bar{\varepsilon}_\beta. \quad (2.21)$$

Accordingly, the Poisson ratio for an induced stress σ_α , can be approximated from the small observed engineering strains along the axes α and β through

$$-\nu_{\alpha\beta}\bar{\varepsilon}_\alpha \approx \bar{\varepsilon}_\beta. \quad (2.22)$$

Typically, materials exhibit a Poisson ratio ranging from 0.0 to 0.5.

This thesis investigates elastic deformations of mesoporous materials that are the result of surface effects that induce stress into the porous materials. The following section will provide a concise overview of some of the surface effects between an adsorbed liquid and the porous host material.

2.3 Capillarity in mesoporous materials

In the field of interface science, the term *capillarity* is used to describe the mechanics of interfaces between different phases. The mechanics of interfaces play a crucial role in describing the behavior of a liquid phase in contact with the surface of a solid phase. The subsequent sections offer a concise overview of the theory behind capillarity. Unless otherwise stated, the discussed relations are extracted from the textbook "Physics and Chemistry of Interfaces", written by Butt, Graf, and Kappl⁹.

2.3.1 Surface tension, surface energy and surface stress

For a liquid (l) to form a stable bulk phase, intermolecular attraction is required. It is therefore energetically favorable for each molecule to be fully surrounded by other molecules. Consequently, work has to be performed to move molecules from the bulk to form a surface against a vapor phase (v). This property of a liquid is known as surface tension. At the macroscopic level, the surface tension of a liquid can be quantified by a proportionality

factor $\gamma_{lv} = \gamma$, which relates the performed work ΔW to the change of the surface of a liquid ΔA through $\Delta W = \gamma \Delta A$. For fluids, the work required to create a surface area of size ΔA is equivalent to the work required to deform an existing surface area by the same amount. This is due to the fact that fluid molecules can freely rearrange. However, this is not the case for solid phases (s). Consequently, for solids, it is essential to distinguish between creating a new solid–vapor interface by breaking atomic bonds or by stretching the atomic bonds through deformation. The proportionality factor that determines the work required to form a new surface by the breaking of bonds is characterized by the surface energy γ_{sv} . Conversely, the proportionality factor that determines the work required for the creation of a surface by elastic deformation is characterized by the surface stress f_{sv} . Surface energy γ_{sv} and surface stress f_{sv} are related through the so called Shuttleworth equation¹⁰

$$f_{sv} = \gamma_{sv} + \frac{d\gamma_{sv}}{d\varepsilon}, \quad (2.23)$$

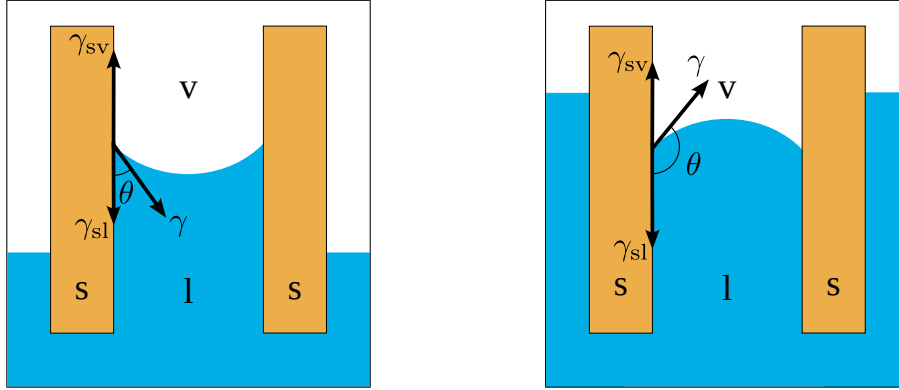
where ε is the elastic strain of the solid (see Sec. 2.2). Therefore, the term $\frac{d\gamma_{sv}}{d\varepsilon}$ determines the change in surface energy due to the elastic deformation of the solid surface. Note that the scalar representation of Eq. (2.23) used in this thesis is only valid when the solid surface is isotropic, a constraint that is satisfied for the systems considered in this thesis.

2.3.2 Capillary rise and depression

When a cylindrical pore is placed in a liquid reservoir, the liquid may behave in one of two ways. If the surface energy of the solid-vapor interface exceeds that of the solid-liquid interface, i.e., $\gamma_{sv} - \gamma_{sl} > 0$, it is energetically favorable for the liquid to wet the walls of the pore. Consequently, the liquid will rise inside the pore above the water level to a certain height. As the liquid rises, a convex meniscus forms. If the liquid rises against gravity, the upward movement of the liquid will eventually come to a halt. However, the meniscus remains. This situation is depicted in Fig. 2.3a. Conversely, if the surface energy of the solid-liquid interface is larger than the surface energy of the solid-vapor interface, i.e., $\gamma_{sv} - \gamma_{sl} < 0$, it is energetically favorable for the liquid to minimize the wetting of the pore walls. As a result, the liquid will fall inside the pore, and a concave meniscus forms, as depicted in Fig. 2.3b.

■ Equilibrium contact angle θ

In equilibrium with gravity, that is, when the liquid does not rise or fall any further, the angle of the meniscus at the solid-liquid-vapor contact point is called equilibrium contact



(a) Capillary rise. The liquid rises above the surface level of the liquid reservoir and forms a concave meniscus at the liquid-vapor interface. The contact angle is $\theta < 90^\circ$ because $\gamma_{sv} > \gamma_{sl}$. **(b)** Capillary depression. The liquid falls below the surface level of the liquid reservoir and forms a convex meniscus at the liquid-vapor interface. The contact angle is $\theta > 90^\circ$ because $\gamma_{sv} < \gamma_{sl}$.

Figure 2.3: Depiction of the capillary rise and depression phenomenon.

angle θ . The equilibrium contact angle is a function only of the surface energy of the solid-vapor interface γ_{sv} , the surface energy of the solid-liquid interface γ_{sl} and the surface tension of the liquid γ and can be calculated by Young's equation

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma} = -\frac{\Delta\gamma}{\gamma}, \quad (2.24)$$

where $\gamma_{sl} - \gamma_{sv} = \Delta\gamma$ denotes the change in surface energy. In the case of capillary rise, the contact angle is always $\theta < 90^\circ$ while in the case of capillary depression the contact angle $\theta > 90^\circ$. A sketch of the equilibrium contact angle is provided for the case of capillary rise and depression in Fig. 2.3. It is important to note that in a non-equilibrium situation, such as during the active movement of the liquid column, the contact angle is not necessarily equal the equilibrium contact angle. To distinguish both contact angles, the contact angle observed during the movement of the liquid column is denoted as the dynamic contact angle θ_{dyn} in this thesis.

■ Laplace pressure effect

The occurrence of capillary rise or depression can be explained through the so called Laplace pressure. The Laplace pressure originates from the formation of a meniscus at the liquid-vapor interface. In the event that the surface of a liquid is curved, a difference in pressure $p = p_l - p_v$ exists across the liquid-vapor interface. The magnitude of the pressure difference is dependent on the curvature of the liquid and on the surface tension γ . In the

event that the liquid is curved convexly, as is the case for the meniscus at capillary depression or for a liquid droplet, the pressure in the liquid p_l is higher than the pressure in the vapor phase p_v . Conversely, the pressure in the liquid is lowered if the liquid is curved concavely, as is the case for capillary rise or for a vapor bubble in a liquid reservoir. The pressure difference at the liquid-vapor interface can be calculated using the Young-Laplace equation

$$p = -2\gamma\kappa = -\gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right), \quad (2.25)$$

where κ denotes the curvature of the liquid-vapor interface and R_1 and R_2 denote the two principal radii of curvature of the interface. In a small cylindrical capillary, the curvature of the liquid is isotropic in every direction and, consequently, the principal radii of curvature are equal, i.e., $R_1 = R_2 = R$. In this case, the capillary pressure condenses to

$$p_L = -\frac{2\gamma}{R}. \quad (2.26)$$

The curvature of the menisci in the cylindrical pore can be determined from the pore radius r and the equilibrium contact angle θ with

$$R = \frac{r}{\cos \theta}. \quad (2.27)$$

By substituting Eq. (2.27) into Eq. (2.26) one arrives at

$$p_L = -\frac{2\gamma \cos \theta}{r}, \quad (2.28)$$

which will be referred to as Laplace pressure during the remainder of this thesis. Mesoporous materials are characterized by their small pore sizes, which result in substantial Laplace pressures within infused liquids. For instance, assuming a water column with a surface tension of $\gamma = 72 \text{ mN m}^{-1}$ in cylindrical nanopores of $r = 1.5 \text{ nm}$ pore radius and a contact angle of $\theta = 0^\circ$ the Laplace pressure is $p_L = -960 \text{ bar}$.

■ Jurin's law

As mentioned above, the liquid column within the cylindrical pore eventually reaches a state of equilibrium if the capillary rise or depression is in opposition to gravitational forces. The equilibrium is reached when the driving Laplace pressure is balanced by the hydrostatic pressure $p_{\text{hydro}} = \rho gh$ in the liquid column. Here, ρ is the density of the liquid, g the gravitational acceleration and h the height of the liquid column. Therefore, the equilibrium

height of the liquid column in the cylindrical pore is determined by Jurin's law

$$p_L = -p_{\text{hydro}} \implies h_{\text{equil}} = \frac{2\gamma \cos \theta}{r \rho g}. \quad (2.29)$$

Given that the equilibrium height is inversely proportional to the radius of the cylinder, the equilibrium height in porous media with pore radii in the nanometer range will be very large. For example, considering water with a density of 997 kg m^{-3} , a surface tension of $\gamma = 72 \text{ mN m}^{-1}$ and a contact angle of $\theta = 0^\circ$ in cylindrical nanopores of $r = 1.5 \text{ nm}$ pore radius with a gravitational acceleration of 9.81 m s^{-2} , the equilibrium rise height at equilibrium amounts to around $h_{\text{equil}} \approx 9.82 \text{ km}$. This equilibrium height is significantly larger than the typical length of porous structures discussed in this thesis, which are approximately 10 nm . It is also significantly larger than typical centimeter sized macroscopic samples used in capillary rise experiments. Therefore, the impact of hydrostatic pressure on imbibition processes in nanoporous media can be considered negligible in relation to the capillary rise phenomena examined in this thesis.

Later, it is demonstrated that the Laplace pressure plays a vital role for the observed deformations of mesoporous materials during the imbibition of liquids into the material. Another very important effect for the deformation of mesoporous materials is the Bangham effect, which is discussed in the next section.

2.3.3 Bangham effect

Almost a century ago, Bangham and colleagues discovered that the adsorption of molecules on the surface of a solid results in an expansive deformation of the solid material.^{11,12} This phenomenon is now recognized as the Bangham effect. At the time of discovery, Bangham stated the assumption that the adsorption-induced strain of the solid ε is proportional to the change in surface energy $\Delta\gamma = (\gamma_{\text{sl}} - \gamma_{\text{sv}})$, i.e., $\varepsilon \propto \Delta\gamma$. However, this result holds only approximately. More precisely, the adsorption of molecules at a surface, causes a surface stress release $\Delta f = f_{\text{sl}} - f_{\text{sv}}$. The energy, that is released from the change of surface stress, is balanced by an expansion of the adsorbing solid. Consequently, the deformation of the solid is actually proportional to the surface stress release $\Delta f = f_{\text{sl}} - f_{\text{sv}}$ upon wetting, i.e., $\varepsilon \propto \Delta f$. A sketch of the Bangham effect is depicted in Fig. 2.4. The surface stress release can be related to the change in surface energy through Eq. (2.23) as

$$\Delta f = (\gamma_{\text{sl}} - \gamma_{\text{sv}}) + \left(\frac{d\gamma_{\text{sl}}}{d\varepsilon} - \frac{d\gamma_{\text{sv}}}{d\varepsilon} \right) = \Delta\gamma + \frac{d\Delta\gamma}{d\varepsilon}. \quad (2.30)$$

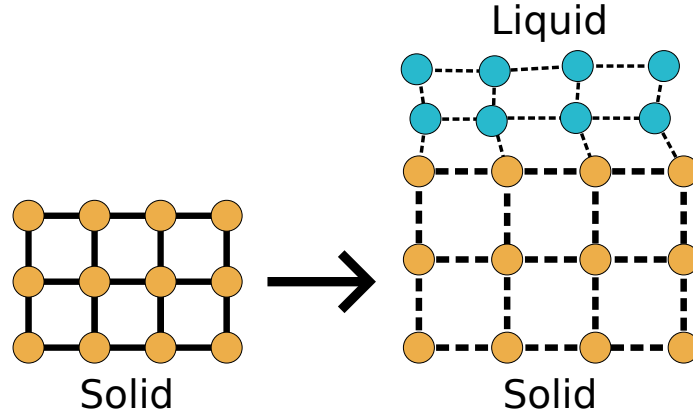


Figure 2.4: Sketch of the Bangham effect. The adsorption of molecules at a solid surface leads to surface stress release. The release of surface stress is compensated by an expansion of the adsorbing solid.

The term $\frac{d\Delta\gamma}{d\varepsilon}$ originates from the increase of adsorbed molecules per solid surface atom due to the expansion of the material. Therefore, typically the term counteracts the release of surface energy from the adsorption process of the surface. Eq. (2.30) indicates that the surface stress release can be approximated by the surface energy release $\Delta f \approx \Delta\gamma$ if the so called Bangham approximation $\frac{d\Delta\gamma}{d\varepsilon} \approx 0$ holds. Gor and Bernstein¹³ suggest that the Bangham approximation is reasonable under the assumption of small induced strains and small molecules with non-specific interactions. However, in certain instances where the Bangham approximation is not applicable, the term $\frac{d\Delta\gamma}{d\varepsilon}$ can even lead to a contractile behavior of the solid.

Since the Bangham effect causes a deformation of the material by releasing surface stress upon molecule adsorption at the solid, the Bangham effect also occurs if a solid is wetted by a liquid. The surface stress release induces a stress $\mathbf{S}$ into the solid underneath the liquid-solid interface. When an curved isotropic surface is considered, the induced stress is uniform and proportional to Δf . The induced stress in the solid directly under the liquid-solid interface along the direction of the surface normal $\mathbf{n}$ of the solid can be determined from the local balance law^{14,15} as

$$\mathbf{nSn} = -p_1 + 2\Delta f\kappa, \quad (2.31)$$

where $-p_1$ is the contribution to the stress originating from the pressure in the liquid. $\kappa = \frac{1}{2} \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$ denotes the mean curvature of the wetted surface with the two principal radii R_1 and R_2 . Due to the close similarity of the term $2\Delta f\kappa$ to the Young-Laplace equation

Eq. (2.25), it is convenient to consider

$$p = 2\Delta f\kappa = \Delta f \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2.32)$$

an effective pressure, that acts on the surface of the solid. However, it is important to note that Eq. (2.32) does not represent a real pressure in the fluid. Assuming a liquid that wets the inner part of a cylindrical surface with radius r , e.g., of a cylindrical nanopore, Eq. (2.32) condenses to

$$p_B = \frac{\Delta f}{r}. \quad (2.33)$$

In this thesis p_B is referred to as Bingham pressure.

The surface effects discussed in this section are the result of interactions between liquid and solid at the atomic level. Consequently, it is of interest to investigate these effects. Molecular dynamics simulations offer the possibility to investigate the described effects and their impact on mesoporous materials on the atomic scale. Therefore, the subsequent section provides a concise overview of molecular dynamics simulations.

2.4 Molecular dynamics (MD) simulations

This section provides a brief overview of the inner workings of molecular dynamics simulations. However, given the complexity of modern molecular dynamics simulations, an exhaustive discussion of the subject is beyond the scope of this thesis. Instead, the discussion is confined to the fundamental principles. If not stated otherwise, the information contained in this chapter are extracted from the textbooks "Understanding Molecular Simulation: From Algorithms to Applications" authored by Frenkel and Smit¹⁶ and "Simulating the physical world: Hierarchical modeling from quantum mechanics to fluid dynamics" authored by Berendsen¹⁷.

MD simulations are a powerful tool to conduct *in silico* studies of materials at the atomic scale. Many software packages are currently available for performing MD simulations. These MD simulation codes include the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)¹⁸, Groningen Machine for Chemical Simulations (GROMACS)¹⁹, Nanoscale Molecular Dynamics (NAMD)²⁰, and Open Molecular Mechanics (OpenMM)²¹. In this thesis, MD simulations are exclusively conducted with LAMMPS. This thesis presents multiple snapshots of the conducted MD simulations. These snapshots were generated with Visual Molecular Dynamics (VMD)²².

As the name implies, molecular dynamics simulations compute the dynamics of a number

N individual atoms, molecules, or larger particles. This is achieved by successively solving Newtons classical equations of motion for discrete, small time steps. To this end, all particle positions $\mathcal{R} = \{\mathbf{r}_1, \dots, \mathbf{r}_N\}$ and particle momenta $\mathcal{P} = \{\mathbf{P}_1, \dots, \mathbf{P}_N\}$, i.e., all microstates of the system, are explicitly calculated during the simulation. Multiple integration schemes for Newtons equation of motion have been developed. Two of the most popular are the Leap-Frog algorithm²³ and the Verlet algorithm²⁴. By default LAMMPS uses a velocity form of the Verlet time integration algorithm, also called velocity-Verlet algorithm²⁵.

In order to simulate changes in the motion of particles, it is necessary to model the forces between their constituent particles. The force $\mathbf{F}_i$ for every atom i in the simulation is derived for every time step from the potential energy of the system $U(\mathcal{R})$ through

$$\mathbf{F}_i = -\nabla_i U(\mathcal{R}) . \quad (2.34)$$

The potential energy is determined through interaction potentials between the N simulated particles. Two key variants of molecular dynamics simulations are distinguished by their method used to derive these interaction potentials. These are ab-initio and classical MD simulations. Ab-initio MD simulations utilize the Born-Oppenheimer approximation to calculate the electronic wavefunctions with density functional theory, and then derive forces from the result. In contrast, classical molecular dynamics simulations utilize fixed interaction potentials. These potentials are derived empirically from data about atomic interactions. In recent times, machine learning models have become a common tool for approximating atomic interactions. While ab-initio MD simulations yield higher accuracy, they are restricted in the number of particles and the time span that can be simulated, whereas classical MD simulations handle larger systems and longer timescales. Machine-learned models occupy an intermediate position between ab-initio and classical methods in terms of precision, system size, and simulateable time spans. For the studies reported in this thesis, only classical molecular dynamics simulations were used.

Due to the explicit integration of Newtons equations of motion, one potential application of MD simulations is to simulate the dynamics of an atomic system in a non-equilibrium situation. The ability to explicitly model the dynamics of non-equilibrium systems is essential for the investigation of the capillary flow of water into MCM-41 and the resulting elastocapillarity effects that are featured in Chs. 3, 4, and 5.

In human-scale systems, such as a glass of water, the impact of individual atoms on the macroscopic system is negligible. Instead, the observed macroscopic behavior arises from the collective behavior of a vast ensemble of atoms, comprising approximately $\tilde{N} \sim 10^{24}$ particles. Every microstate of the system thus consists of $\tilde{N}$ coordinates $\tilde{\mathcal{R}} = \{\mathbf{r}_1, \dots, \mathbf{r}_{\tilde{N}}\}$ and

momenta $\tilde{\mathcal{P}} = \{\mathbf{P}_1, \dots, \mathbf{P}_N\}$. One important application of MD simulations is to compute macroscopic observables Y^{obs} , which arise from the ensemble average of microstates within these systems. The ensemble average is calculated by

$$Y^{\text{obs}} = \int d\tilde{\mathcal{R}} \int d\tilde{\mathcal{P}} Y(\tilde{\mathcal{R}}, \tilde{\mathcal{P}}) P(\tilde{\mathcal{R}}, \tilde{\mathcal{P}}). \quad (2.35)$$

Here, $P(\tilde{\mathcal{R}}, \tilde{\mathcal{P}})$ is the joint probability density of the coordinates and momenta of the particles in the system and Y is the microscopic observable in the thermodynamic system.

In MD simulations, the maximum number of particles that can be simulated simultaneously is on the order of $N \sim 10^7$. Hence, the number of simulateable particles is significantly lower than the amount typically observed in the considered thermodynamic system. However, for ergodic systems, the ensemble average can be approximated by a time average of the simulated system. Therefore, the thermodynamic, macroscopic observable Y^{obs} can be estimated by averaging it in an MD simulation over a sufficient number of time steps N_T . Mathematically, this processes can be expressed as

$$Y^{\text{obs}} \approx \frac{1}{N_T} \sum \int d\mathcal{R} \int d\mathcal{P} Y(\mathcal{R}, \mathcal{P}) P(\mathcal{R}, \mathcal{P}). \quad (2.36)$$

To ensure the accuracy of molecular dynamics simulations in approximating the observable Y^{obs} , it is essential that the MD simulations sample the microstates according to how they appear in the real thermodynamic system. Therefore, the probability density function of the MD simulation $P(\mathcal{R}, \mathcal{P})$ has to reflect the distribution of microstates in the thermodynamic system. The total energy E of the simulated system is calculated by summing the potential energy $U(\mathcal{R})$ and kinetic energy $E_{\text{kin}} = \sum_i^N \frac{\mathbf{P}_i^2}{2m_i}$ of the system, i.e., $E = U(\mathcal{R}) + E_{\text{kin}}$. If the MD simulations are computed while conserving particles N , volume V and energy E a microcanonical ensemble (NVE) is simulated. The conservation of these system parameters is satisfied in the integration of Newtons equations of motion and every microstate that possesses the same volume and energy is sampled equiprobable in the MD simulation. Consequently, the probability to encounter a specific state is uniform and inversely proportional to the number of microstates Z^{NVE} , i.e.,

$$P^{\text{NVE}}(\mathcal{R}, \mathcal{P}) = \frac{1}{Z^{\text{NVE}}}. \quad (2.37)$$

The microcanonical ensemble describes a thermodynamic system isolated from the environment. However, typically systems can not be considered isolated from their environment. Often, systems exchange heat with their surroundings under a constant temperature T and

volume under a constant pressure p . In the scenario where only heat is exchanged with the environment, the system is considered a canonical (NVT) ensemble. In canonical ensembles, the distribution of microstates follows the so called Boltzmann distribution

$$P^{\text{NVT}}(\mathcal{R}, \mathcal{P}) = \frac{1}{Z^{\text{NVT}}} e^{-\beta E(\mathcal{R}, \mathcal{P})}, \quad (2.38)$$

In the case that also volume is exchanged with the environment, the system is considered an isothermal–isobaric ensemble (NpT). For isothermal–isobaric ensembles, the distribution of the microstates follows the generalized Boltzmann distribution

$$P^{\text{NpT}}(\mathcal{R}, \mathcal{P}) = \frac{1}{Z^{\text{NpT}}} e^{-\beta(E(\mathcal{R}, \mathcal{P}) + pV(\mathcal{R}))}. \quad (2.39)$$

In Eq. (2.38) and Eq. (2.39), $\beta = \frac{1}{k_{\text{B}}T}$ is the so called coldness of the system, that is defined as $\beta = \frac{1}{k_{\text{B}}T}$ with the Boltzmann constant k_{B} . Z^{NVT} and Z^{NpT} are the so called partition functions that ensure that the respective probability distributions are properly normalized. The Helmholtz free energy F and the Gibbs free energy G can be related to the partition function Z^{NVT} and Z^{NpT} through

$$F = -\frac{1}{\beta} \ln(Z^{\text{NVT}}) \quad (2.40)$$

and

$$G = -\frac{1}{\beta} \ln(Z^{\text{NpT}}). \quad (2.41)$$

To ensure that the microstates of the simulated system are distributed according to the (generalized) Boltzmann distribution, special algorithms, that alter the equations of motion, have to be employed in the MD simulations. These algorithms are referred to as thermostats and barostats. In this thesis, the Nosé-Hoover style thermostat and barostat are used exclusively.^{26–31}

To minimize simulation artifacts caused by the finite number of simulated particles, periodic boundary conditions (PBCs) are frequently employed in MD simulations. Periodic boundary conditions link opposite faces of the simulation box to replicas of that box. This strategy allows the system to interact with itself across its boundaries, thereby simulating the influence of the extended atomic environment. Consequently, the behavior of macroscopic materials can be simulated with a reduced number of particles. PBCs are particularly effective for simulating symmetric materials, such as crystals. In fact, a single unit cell suffices to represent a monocrystal in a MD simulation.

In LAMMPS the instantaneous temperature T of the simulated system is calculated from

the kinetic energy of the individual particles as

$$T = \frac{2E_{\text{kin}}}{3(N-1)k_B} . \quad (2.42)$$

The instantaneous pressure in the simulation is calculated as

$$p = \frac{Nk_BT}{V} + T_{\text{virial}} \quad (2.43)$$

where T_{virial} is the virial of the system. The virial is defined as

$$T_{\text{virial}} = \frac{1}{3V} \sum_i^N \mathbf{F}_i \mathbf{r}_i . \quad (2.44)$$

A challenge inherent to MD simulations is the simulation of liquid-to-solid crystallization events. MD simulations often fail to replicate these transitions because the system has to overcome a Gibbs free energy barrier to form a nucleation seed that initiates the crystallization process. The next section addresses the issue of liquid-to-solid phase transitions in MD simulations on the basis of classical nucleation theory, a theory that describes the formation of nuclei on the atomic scale.

2.5 Classical nucleation theory (CNT)

Classical nucleation theory (CNT) is a widely accepted theory that describes homogeneous nucleation events. In the context of CNT, the term *homogeneous* refers to the absence of foreign phases that could potentially influence the crystallization process, such as the presence of a solid surface. This section offers a concise introduction to the fundamentals of CNT. For a more thorough discussion of this topic, refer to the works of Sosso et al.³² The CNT framework provides a rationale for the challenge of investigating nucleation events using MD simulations.

CNT emerged nearly a century ago from numerous scientific contributions.^{33–36} The theory provides an explanation of the crystallization process of a supercooled liquid and can also be consulted to explain the condensation of supersaturated vapor into the liquid phase. In a crystallization scenario, CNT assumes a spherical nucleus of crystalline atoms of radius r separated from a surrounding liquid in an isothermal-isobaric ensemble. The central element of CNT is the Gibbs free energy surface $G(r)$ as function of the nucleus radius r . In CNT the Gibbs free energy surface is defined by two contributions.

One contribution is the release of free energy per unit volume $\Delta\mu$ from the crystal nucleus.

In a supercooled liquid, the free energy release $\Delta\mu$ from the transition of the atoms or molecules from the liquid phase to the crystalline phase contributes negatively to the Gibbs free energy. Therefore, in a supercooled liquid the larger the volume of the nucleus, the lower the Gibbs free energy.

However, to form the spherical crystal nucleus in the liquid, an interface has to be formed against the surrounding liquid. The nucleus features a solid-liquid interface with a surface energy γ_{sl} . In CNT, this surface energy is approximated by that of a bulk-bulk liquid-solid interface, in what is referred to as the capillarity approximation. The formation of the solid-liquid interface is unfavorable in terms of Gibbs free energy. Consequently, the solid-liquid interface counteracts the release of free energy proportional to its surface area. Combining these two contributions, the Gibbs free energy surface is obtained by

$$G(r) = 4\pi r^2 \gamma_{sl} - \frac{4\pi}{3} r^3 \Delta\mu, \quad (2.45)$$

where the first term is the surface contribution of the spherical nucleus and the second term the volume contribution of the spherical nucleus. The Gibbs free energy surface exhibits a maximum of

$$G^\star = \frac{16\pi \gamma_{sl}^3}{3\mu^2} \quad (2.46)$$

at the nucleus radius

$$r^\star = \frac{2\gamma_{sl}}{\mu}. \quad (2.47)$$

Fig. 2.5 presents a sketch of the free energy as a function of the radius of the nucleus, according to the predictions of CNT. As visible, the Gibbs free energy surface exhibits a free energy barrier that has to be overcome for crystallization to occur. The existence of metastable supercooled liquids in the macroscopic world is a result of this Gibbs free energy barrier.

The Gibbs free energy barrier also poses a challenge to simulate a nucleation event in MD simulations. As discussed in Sec. 2.4, MD simulations sample microstates from the generalized Boltzmann distribution $P^{\text{NpT}}(\mathcal{R}, \mathcal{P})$, as defined in equation Eq. (2.39), to model isothermal-isobaric ensembles. The probability of finding a thermodynamic system in a macroscopic state that exhibits a nucleus of radius r is

$$P(r) = \int d\mathcal{R} \int d\mathcal{P} \delta(r'(\mathcal{R}) - r) P^{\text{NpT}}(\mathcal{R}, \mathcal{P}). \quad (2.48)$$

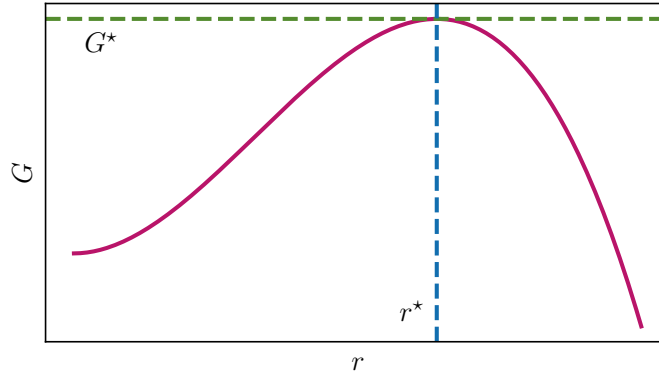


Figure 2.5: Sketch of the free energy G in dependence of the nucleus radius. The maximum of the Gibbs free energy barrier is marked by G^* . The critical radius of the nucleus is marked by r^* .

According to CNT, $P(r)$ is directly related to the Gibbs free energy surface through

$$P(r) = e^{-\frac{G(r)}{k_B T}}. \quad (2.49)$$

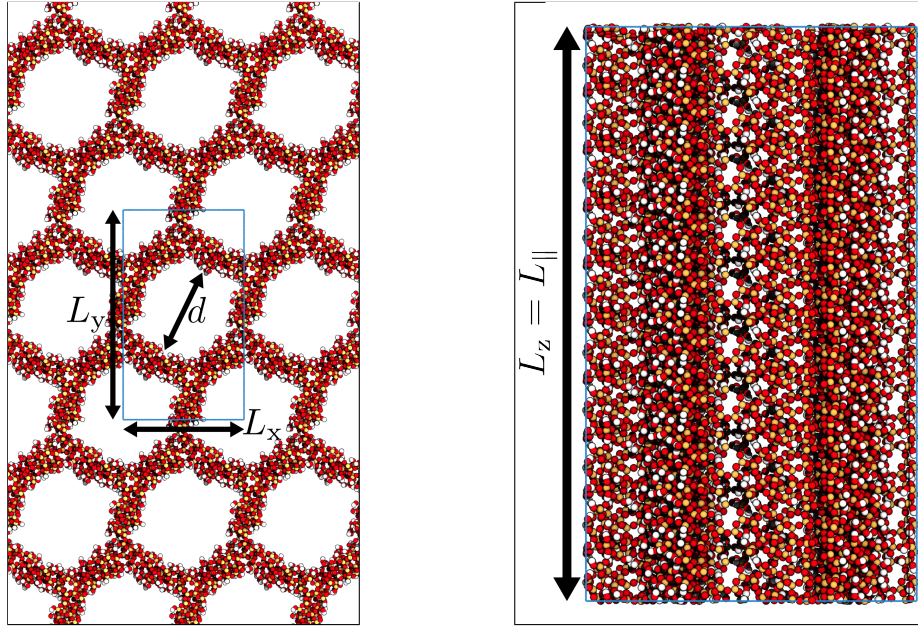
Consequently, the Gibbs free energy maximum dictates that a thermodynamic system rarely occupies a state containing a nucleation seed of a size near radius r^* . In contrast, the system is more likely to occupy a state that is completely liquid or crystalline. The existence of metastable supercooled liquids indicates that the probability of forming a crystal nucleus can be sufficiently low that even large thermodynamic systems with many particles cannot overcome the Gibbs free energy barrier, or equivalently the low probability region of forming a critical crystallization nucleus. Nucleation events therefore occur too infrequently within the accessible time scales and system sizes of MD simulations. This hinders the investigation of liquid-to-solid phase transitions with MD simulations. Consequently, an artificial bias is required to increase the probability of nucleation events during the simulations. A new method that introduces a bias to archive liquid-to-solid phase transitions in MD simulations is presented in Ch. 6 of this thesis.

SIMULATING THE IMBIBITION OF WATER INTO ORDERED, CYLINDRICAL MESOPOROUS SILICA

In this thesis the imbibition of liquid into ordered, cylindrical mesopores and the resulting imbibition-induced elastocapillarity are investigated in Ch. 4 and Ch. 5, respectively. Both effects were investigated by simulating the capillary flow of water into MCM-41 with MD simulations in LAMMPS. This chapter provides details about the simulated MCM-41 structure in Sec 3.1, the setup of the capillary flow simulations in Sec 3.2, and relevant physical properties of the MCM-41 structure in Sec. 3.3.

3.1 The Mobil Composition of Matter No. 41 (MCM-41) pore matrix

The MD simulations of capillary flow were conducted with a matrix of ordered, cylindrical silica mesopores analogous to the structure of MCM-41. The structure was originally created by Ugliengo et al.³⁷ and utilized for the investigation of ibuprofen adsorption by Delle Piane et al.³⁸ In the simulations the axial direction of the cylindrical pores was aligned with the z-axis of the simulation box. Consequently, the directions lateral to the pores were the x- and y-axis. Fig. 3.1 illustrates the structure of the pores along the axial direction (Fig. 3.1a) and the lateral direction (Fig. 3.1b). The matrix featured pores with an approximate pore wall thickness of around 1 nm, which is comparable to experimentally determined wall thicknesses of MCM-41 structures with similar pore diameter.⁷ In the original pore matrix, periodicity in all directions was ensured by employing periodic boundary conditions. Assuming a cylindrical pore geometry, the pore radius was approximated as $r = 1.649$ nm, as detailed in Sec. 3.3.4. The pore surface exhibited a hydroxyl group density of 7.23 nm^{-2} , that rendered the pore surface hydrophilic. The original atomic coordinates of the MCM-41 structure, provided in the format of a Crystallographic Information File (CIF) in a triclinic simulation box, were transformed into an orthogonal simulation box and adapted to the LAMMPS format.



(a) Structure of the MCM-41 pore matrix viewed along the axial direction. The pore diameter d is approximately 3 nm and the wall thickness around 1 nm. The simulation box is indicated by the blue box. The simulation box extensions L_x and L_y are indicated by the black double headed arrows. The extension of the pore matrix beyond the simulation box indicates the simulation of periodic boundary conditions.

(b) Pore matrix viewed along the lateral direction. The length of the pore matrix of $L_z = 12.2$ nm is indicated by the black double headed arrow.

Figure 3.1: Atomic structure of the periodic MCM-41 pore matrix along two axes. The silicon atoms are colored yellow, the hydrogen atoms are white, and the oxygen atoms are red, respectively.

The original CIF file from Ugliengo et al.³⁷ and the corresponding orthogonal structure in LAMMPS format can be obtained at <http://dx.doi.org/10.13140/RG.2.2.19035.99361>. The simulation box extensions were $L_x = 4.06$ nm and $L_y = 7.03$ nm in the x- and y-axis directions, respectively. The simulation box contained the volumes of two pores. To prepare the MCM-41 structure for capillary flow simulations, it was replicated ten times along the axial pore direction (z-axis). This generated a porous matrix of $L_z = L_{||} = 12.2$ nm in length with a total atom number of 11580 atoms. The axially periodic pore matrix was used to determine different properties of the porous system, such as the Poisson ratio (see Sec. 3.3.1) and the Young modulus (see Sec. 3.3.2). However, to perform capillary flow simulations, a water reservoir had to be added to the axial ends of the pore matrix. Hence, the periodicity of the pore matrix in axial direction was broken. The dangling silicon atoms at the ends of the pore structure were removed, and the dangling oxygen atoms were saturated with hydrogen

atoms. The resulting pore structure was then utilized in the capillary flow simulations.

3.2 Simulating the capillary flow process

To simulate the capillary flow process, a water reservoir was added at the axial ends of the pore matrix. The water reservoir consisted of a total of 22,680 water molecules. Since periodic boundary conditions were used on every end of the simulation box, it was essential to ascertain that the water reservoir was large enough to prevent self-interaction of the pore matrix over the periodic axial boundary, even when the pore space was entirely filled and the amount of water in the reservoir was minimal. Additionally, the water reservoir was required to be sufficiently large to simulate water at bulk properties. Note that the water molecules traveled freely over the axial simulation boundary to the two axial ends of the porous matrix during the simulations.

The TIP4P/2005 model, developed by Abascal and Vega³⁹, was utilized to model the water-water interactions. TIP4P water models consist of one oxygen atom, two hydrogen atoms, and one massless "ghost" atom. The ghost atom is positioned at the center of the water molecule and carries the Coulomb charge of the oxygen atom. The relocation of the Coulomb charge to the ghost atom enhances the models representation of the molecular charge distribution. Fig. 3.2 provides a schematic molecular representation of the model. The structure of the TIP4P water models remains fixed during simulations. Consequently, no structural changes of the water molecules can be modeled with TIP4P models. The

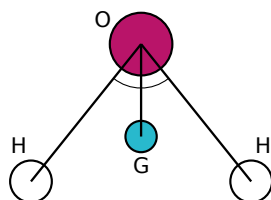


Figure 3.2: Sketch of the TIP4P model structure. The oxygen atom O is depicted in purple, the hydrogen atom H in white and the electric-charge carrying ghost atom G as blue.

TIP4P/2005 model is a widely used water model to simulate liquid water in MD simulations because the TIP4P/2005 model has been shown to accurately replicate many properties of water from experimental observations. Tab. 3.1 presents a comparison of the surface tension, density and shear viscosity of the TIP4P/2005 model at 300 K to experimentally determined values. The properties of the TIP4P/2005 model provided in Tab. 3.1 were utilized in the analysis of the MD simulations presented in this thesis.

The silica-silica interactions were modeled using the interaction potential presented in

Table 3.1: Water properties of the TIP4P/2005 model at 300 K in comparison to experimentally determined water properties.

Property	TIP4P/2005 model	Experimental
Surface tension γ ⁴⁰	69.3 mN m ⁻¹	71.3 mN m ⁻¹
Density ρ ^{39,41}	0.9965 g cm ⁻³	0.9965 g cm ⁻³
Shear viscosity η ^{41,42}	0.83 mPa s	0.896 mPa s

Meißner et al.⁴³, which is based on a Morse type potential published by Demiralp⁴⁴. The water-silica interactions were modeled according to Cole et al.⁴⁵ and Butenuth et al.⁴⁶ Bonds and angles involving hydrogen atoms were constrained with the SHAKE algorithm.⁴⁷ Long-range Coulomb interactions were calculated using the Particle-Particle Particle-Mesh (P³M) solver.²³ All simulations were conducted with a time step length of 1 fs. For thermostating and barostating, the Nosé-Hover algorithm was used.²⁸⁻³¹ The temperature was maintained at a constant 300 K with a thermostat damping parameter of 100 fs, while the pressure was maintained at a constant 1 bar with a damping of 1000 fs. In equilibrium simulations, the empty pore matrix exhibited lateral deformations when modeled with classical force fields. The observed effect was produced by the use of classical force fields which differed from the ab-initio calculations of Ugliengo et al.³⁷. To prevent the pore matrix from deforming asymmetrically and to ensure a laterally isotropic strain, the deformations of the x and y axes of the simulation box were coupled in the capillary flow simulations. With the employed coupling, the simulation box extension in the x and y-directions strained at an equivalent rate. Therefore, the relation

$$\bar{\epsilon}_x = \frac{\Delta L_x}{L_x} = \bar{\epsilon}_y = \frac{\Delta L_y}{L_y} = \bar{\epsilon}_\perp \quad (3.1)$$

was satisfied during all simulations. Here, ΔL_x and ΔL_y are the changes in simulation box extension in the x and y directions, respectively, and $\bar{\epsilon}_x$ and $\bar{\epsilon}_y$ are the associated strains of the system. Consequently, $\bar{\epsilon}_\perp$ denotes the strain in the lateral direction of the pore matrix.

The investigation of imbibition dynamics during the capillary flow process necessitated a careful initial preparation of the contact between the pore matrix and the water reservoir. To that end, preliminary simulation runs were conducted. Initially, the system was placed in contact with the water reservoir at the axial ends of the pore matrix and subsequently relaxed by simulating an isothermal-isobaric ensemble for 25 ps. During this period, the formation of a water meniscus within the pore space was actively prevented. Accordingly, molecules exceeding a penetration depth of 5 Å in reference to the outermost Si atoms in the axial direction of the porous matrix, were removed at intervals of 10 fs. Following the initial equilibration, the resulting simulation box extensions were $L_x^0 = 3.96$ nm, $L_y^0 = 6.85$ nm, and

$L_z^0 = L_{\parallel}^0 = 33.90$ nm. The superscript 0 refers to the starting condition of the imbibition simulation.

To measure the dynamically induced strain, 20 independent simulations were conducted to average out thermal motions of the atoms. Distinct initial conditions were required to ensure the independent evolution of the simulations. Additional isothermal simulations with varied durations were conducted to generate these distinct initial conditions. During the isothermal simulations, prevention of water intrusion into the pore space was essential. Therefore, the equations of motion were integrated for the water molecules in the reservoir, except for a 3 Å water layer within the pore space. This static layer effectively prevented water intrusion into the pore space. The isothermal initial simulations were conducted for times ranging from 20 fs, 40 fs, . . . , 400 fs. The resulting 20 system configurations served as initial states for the respective imbibition simulations. Because the pore structure and the initial water layer in the pore space remained static during the isothermal simulations, the simulations were not uncorrelated at the start of the imbibition process. However, the distinct initial states ensured that the simulations evolved uncorrelated after the initial moments of the imbibition process. Fig. 3.3 depicts one of the initial atomic configurations the capillary flow simulations were started from. The simulation of the imbibition process was simulated as a NpT ensemble for a time span of 2 ns. During the simulation, the hydrophilicity of the pore surface led to spontaneous imbibition of the water into the pore space from both ends of the pore matrix. The LAMMPS configuration files of the imbibition simulations are available at <https://doi.org/10.15480/882.13223>.

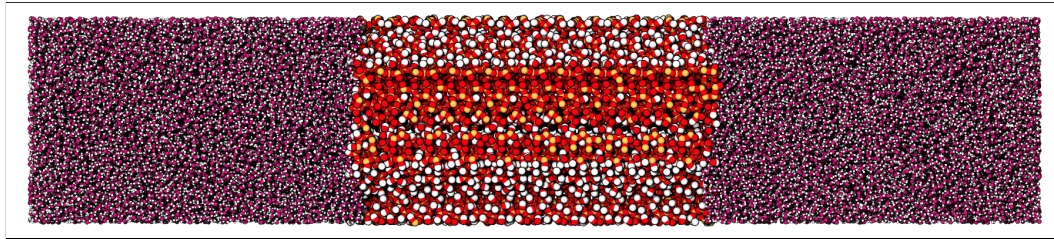


Figure 3.3: One of the 20 initial atomic configurations created for the capillary flow simulations. The silicon atoms are colored yellow, the hydrogen atoms are white and the oxygen atoms bound in the porous solid are red, respectively. To the axial ends of the pore matrix, a water reservoir was added. The oxygen atoms bound in water molecules are purple.

3.3 Properties of the MCM-41 structure

To conduct a comprehensive analysis of the capillary flow and deformation dynamics, it was necessary to determine the Poisson ratios $\nu_{\parallel\perp}$ and $\nu_{\perp\parallel}$, the Young moduli $E_{\perp}$ and $E_{\parallel}$,

the porosity ϕ , and the pore radius r of the pore matrix. The Poisson ratios and Young moduli were obtained from the empty pore matrix, while the porosity and pore radius were determined from the results of the capillary flow simulations. Refer to the following sections for a detailed description of how the pore matrix properties were acquired. The resulting values are displayed in Tab. 3.2. These values were used in the analyses conducted in Ch. 4 and Ch. 5.

Table 3.2: Determined properties of the pore matrix. These properties include the Poisson ratios $\nu_{\parallel\perp}$ and $\nu_{\perp\parallel}$, the axial and lateral Young moduli $E_{\parallel}$ and $E_{\perp}$, the porosity ϕ , and the pore radius r .

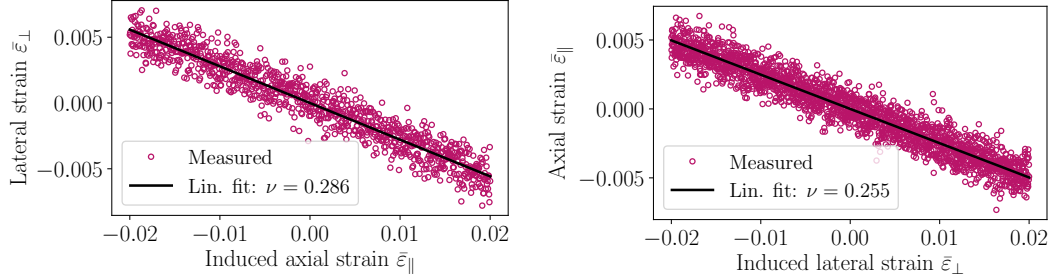
Property	Value
Poisson ratio $\nu_{\parallel\perp}$	0.286
Poisson ratio $\nu_{\perp\parallel}$	0.255
Axial Young modulus $E_{\parallel}$	57.74 GPa
Lateral Young modulus $E_{\perp}$	28.25 GPa
Porosity ϕ	0.706
Pore radius r	1.649 nm

3.3.1 The Poisson ratios

As outlined in Sec. 2.2, the Poisson ratios of the pore matrix are important parameters to understand the relation between induced stress and observed elastic deformation of the pore matrix. Therefore, knowledge about the Poisson ratios is important in the analysis of the imbibition-induced strain effects in the pore matrix. Provided that the pore matrix can be regarded as a transversely isotropic material, the compliance matrix defined in Eq. (2.15) includes three Poisson ratios. These are $\nu_{\parallel\perp}$, $\nu_{\perp\parallel}$ and $\nu_{\perp}$. As demonstrated in Ch. 5, knowledge of the Poisson ratio $\nu_{\perp}$ is not required to analyze the imbibition-induced elastic deformation of the pore matrix. As a result, no further attention is directed toward $\nu_{\perp}$.

To determine the Poisson ratios for $\nu_{\parallel\perp}$ and $\nu_{\perp\parallel}$, simulations with 1 fs time steps were conducted. In these simulations, the axially periodic pore matrix was continuously strained either in the axial direction, denoted as $\bar{\epsilon}_{\parallel}$, or the lateral direction, denoted as $\bar{\epsilon}_{\perp}$. In both directions, the strain was applied over the course of 2 ns from -2% to 2% at a rate of $1 \times 10^{-6} \%$ /fs. During the induced continuous straining process, the strain perpendicular to the induced strain direction was measured at 10 fs intervals. The resulting strain-strain relationships between the induced strain and the observed strain are depicted in Fig. 3.4a and Fig. 3.4b as purple data points. From the data the Poisson ratios were determined by fitting the linear relation of Eq. (2.22) to the obtained strain-strain relationship (black). From the slope of the fit the Poisson ratios were determined as $\nu_{\parallel\perp} = 0.286$ and $\nu_{\perp\parallel} = 0.255$.

Unfortunately, no experimentally determined values for the Poisson ratios were found for comparison in literature.



(a) Measured lateral strain $\bar{\epsilon}_{\perp}$ in dependence of the axially induced strain $\bar{\epsilon}_{\parallel}$ (purple). The linear fit (black) determined as Poisson ratio of $\nu_{\parallel\perp} = 0.286$. **(b)** Measured axial strain $\bar{\epsilon}_{\parallel}$ in dependence of the laterally induced strain $\bar{\epsilon}_{\perp}$ (purple). The linear fit (black) determined as Poisson ratio of $\nu_{\perp\parallel} = 0.255$.

Figure 3.4: Measurement of strain-strain relations of the pore matrix. To determine the values for the Poisson ratio the linear relation defined in Eq. (2.22) was fitted to the measured data.

3.3.2 The Young moduli

The Young moduli are essential for establishing the linear relationship between strain and stress. Consequently, knowledge of the Young moduli is crucial in the analysis of the imbibition-induced strain effects. To determine the Young moduli of the porous matrix, the empty, periodic pore matrix was strained by deforming the simulation box. Subsequently, the average induced stress was determined from the strained pore matrix. To quantify the induced stress, the pore matrix atoms were simulated as a NVT ensemble at 300 K over a timespan of 100 ps with a time step size of 1 fs. The initial 10 ps of the simulation trajectory were not included in the calculation of the induced stress to allow for sufficient system equilibration. For the remaining 90 ps the stress in the pore material was averaged with a sample rate of one sample per 10 fs.

To quantify the stress induced within the material, the diagonal components of the symmetric pressure tensor $\mathbf{p}$ were used. The diagonal components of the symmetric pressure tensor were calculated by⁴⁸

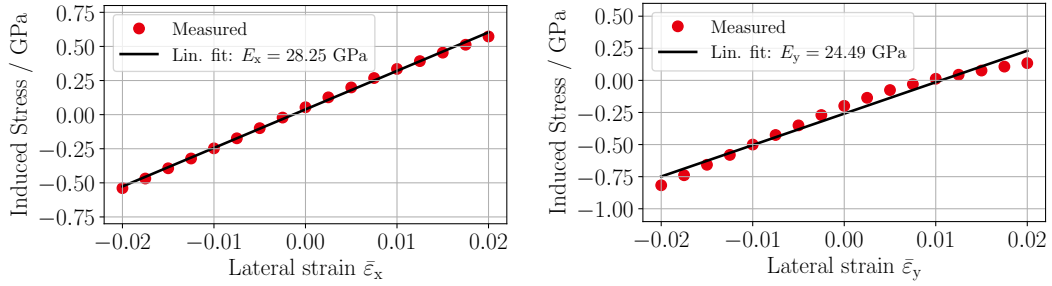
$$\text{diag}(\mathbf{p}) = \frac{1}{V_{\text{total}}} \left(\sum_{i=1}^N \frac{\mathbf{P}_i \odot \mathbf{P}_i}{m_i} + \sum_{i=1}^{N'} \mathbf{r}_i \odot \mathbf{F}_i \right), \quad (3.2)$$

where $\odot$ defines the Hadamard product, N are the atoms in the system, N' the atoms in the system including the ghost atoms of the periodic images and V_{total} the volume of the system, i.e., of the simulation box. The diagonal components of the stress tensor $\boldsymbol{\sigma}$, can be

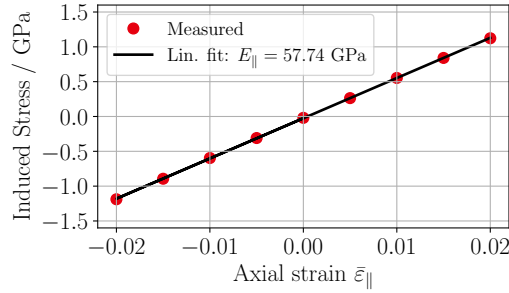
determined from the diagonal of the symmetric pressure tensor through

$$\text{diag}(\boldsymbol{\sigma}) = -\frac{1}{1-\phi} \text{diag}(\mathbf{p}) . \quad (3.3)$$

The values of the symmetric pressure tensor have to be weighted by the inverse solid–volume–fraction $\frac{1}{1-\phi} = \frac{V_{\text{total}}}{V_{\text{solid}}}$, since the pressure of the system can only be balanced by the solid of the pore matrix, which covers a volume, V_{solid} , and not the total volume of the simulation box, V_{total} . Due to the anisotropic nature of the porous matrix, the Young moduli were measured separately along the axial and the lateral directions. The corresponding results are depicted in Fig. 3.5.



(a) Strain-stress relationship along the x-axis, i.e., one lateral pore direction. The resulting Young modulus was $E_x = E_{\perp} = 28.25$ GPa. **(b)** Strain-stress relationship along the y-axis, i.e., one lateral pore direction. The resulting Young modulus was $E_y = 24.49$ GPa. E_y was not used in further analysis.



(c) Strain-stress relationship along the z-axis, i.e., the axial pore direction. The resulting Young modulus was $E_{\parallel} = 57.74$ GPa.

Figure 3.5: Strain-stress relationship measurements (red) of the pore matrix to determine the directional Young moduli $E_x = E_{\perp}$, E_y and $E_z = E_{\parallel}$ with a linear fit (black).

In the axial direction, the Young modulus $E_{\parallel}$ was determined by subjecting the simulation box to strains ranging from -2% to 2% in 0.5% increments and calculating the on average induced stress. Due to the substantial axial length of the pore, it is reasonable to treat the material as a bulk material along the axial direction. As shown in Fig. 3.5c, the

strain-stress relationship exhibits a clear linear behavior. The determined Young modulus of $E_{\parallel} = 57.74$ GPa is on the order of the experimentally determined Young modulus of bulk silica at 298.15 K of $E = 73.06$ GPa determined by Munro⁴⁹.

With approximately 1 nm, the thickness of the pore walls is relatively thin compared to the axial extension of the porous materials. Therefore, it is reasonable to expect the Young modulus in the lateral direction to differ from that of the bulk material. To determine the Young modulus in the lateral pore direction $E_{\perp}$, the porous material was subjected to simultaneous strains, E_x and E_y , in both lateral axes. The induced stress was calculated for induced strains ranging from -2% to 2% , with an increment of 0.2% . The resulting strain-stress relationships are presented in Fig. 3.5a and Fig. 3.5b for the x-axis and for the y-axis, respectively. Both strain-stress relationships in the lateral direction are not entirely linear. However, the relation for the x-axis exhibits only minor deviations from linearity, while the relation for the y-axis displays a clear curvature. Additionally, the strain-stress relationship along the y-axis exhibited induced stress in the absence of strain. The nonlinear behavior of the strain-stress relationship, together with the presence of stress at zero strain, violates the assumption of elastic deformations, as defined in Sec. 2.2. Additionally, the symmetry constraint of the compliance matrix, defined in Eq. (2.16), is not satisfied when the obtained values for the Poisson ratio and Young modulus are substituted. Specifically, a discrepancy of factor two is observed in both terms of the equation. The non-elastic behavior of the pore matrix likely arises from the coupling of the x and y axes of the simulation box. Consequently, the pore matrix did not fully equilibrate to the stresses. This simulation artifact introduces uncertainty in the interpretability of the subsequent quantitative analysis of the imbibition-induced deformation dynamics in Ch. 5. However, note that the coupling of simulation box axes was necessary to stabilize the pore structure.

Because the strain-stress curve along the y-axis showed strong nonlinearity and a large initial stress, only the Young's modulus measured along the x-axis is used in subsequent analyses. This decision is supported by the expectation that the stress and strain will be induced radially into the pore material during the imbibition process, as discussed in Sec. 5.2.3. Therefore, any of the two lateral axes should be fit to determine the lateral Young modulus. The Young modulus in the x direction was determined to be $E_x = E_{\perp} = 28.25$ GPa. It is important to note that the lateral Young modulus, $E_{\perp}$, was only half the magnitude of the axial Young modulus, $E_{\parallel}$. This finding aligns with the hypothesis that the pore material cannot be regarded as a bulk material across the thin pore wall.⁵⁰ Therefore, an identical magnitude of stress should manifest in double the strain in the lateral direction than in the axial direction.

3.3.3 The pore matrix porosity

The porosity, or void fraction, $\phi = \frac{V_{\text{void}}}{V_{\text{total}}}$ of a pore matrix is defined as the ratio of the void volume of the pores, V_{void} , to the total volume, V_{total} , the porous medium covers. In this thesis it is assumed that the porosity remains constant throughout the entire imbibition process due to the fact that the imbibition-induced strains are small. The complement of the porosity, $1 - \phi = \frac{V_{\text{solid}}}{V_{\text{total}}}$, determines the fraction of the volume covered by the solid material, V_{solid} , relative to the total volume V_{total} . Finally, $\frac{\phi}{1 - \phi} = \frac{V_{\text{void}}}{V_{\text{solid}}}$ is interpreted as the void volume to solid volume fraction.

The total volume V_{total} of the porous medium containing a single pore can be determined from the lateral simulation box extensions L_x and L_y and the axial length of the unfilled pore space H as

$$V_{\text{total}} = \frac{1}{2} L_x^0 L_y^0 H = 136.70 \text{ nm}^3. \quad (3.4)$$

The factor of $\frac{1}{2}$ was introduced because the simulation box contained two pore voids. The distance H is also the maximal length the water can imbibe into the pore space. It was determined as the minimal distance of oxygen atoms at the two ends of the pore matrix. To this end, each reservoir at the end of the pore matrix was considered as a group of water molecules. Let $\mathcal{Z}_1 = \{r_z^1, \dots, r_z^{N_1}\}$ be the set of all N_1 axial coordinates of the oxygen atoms in the one reservoir and $\mathcal{Z}_2 = \{r_z^1, \dots, r_z^{N_2}\}$ the set of all N_2 axial coordinates of the oxygen atoms in the other reservoir. Then the axial length H of the empty pore space can be determined from the minimal axial distance of the oxygen atoms in the distinct water reservoirs, i.e., $H = \min(|\mathcal{Z}_1 - \mathcal{Z}_2|) = 11.29 \text{ nm}$. Fig. 3.6 shows a sketch of the method to determine the axial length of the unfilled pore space H .

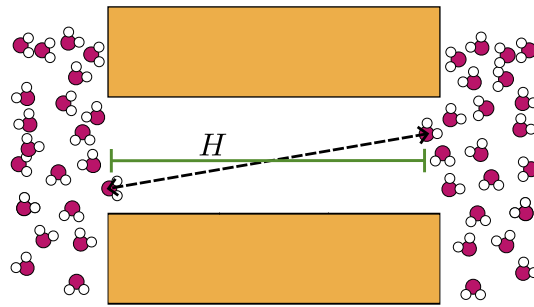


Figure 3.6: Sketch of the approach to determine the maximal imbibition length H . Before the imbibition simulation began, the maximal imbibition length H was determined by the minimal axial distance (green bar) between two oxygen atoms in opposing reservoir sides (dashed black arrow).

The volume of the pore void of a single pore was determined through the volume of the water that entered the pore void during the imbibition process. Hence, the void volume was

calculated by

$$V_{\text{void}} = \frac{1}{2} L_x^0 L_y^0 \Delta L_{\parallel}^{\text{imb}} = 96.44 \text{ nm}^3, \quad (3.5)$$

where $\Delta L_{\parallel}^{\text{imb}} = L_{\parallel}^0 - L_{\parallel}^{\text{final}} = 7.96 \text{ nm}$ is the change in the length of the simulation box extension in the axial direction over the course of the total imbibition process, starting with an axial simulation box extension $L_{\parallel}^0$ and ending with a final axial simulation box extension of $L_{\parallel}^{\text{final}}$. The resulting porosity was calculated as

$$\phi = \frac{V_{\text{void}}}{V_{\text{total}}} = \frac{\Delta L_{\parallel}^{\text{imb}}}{H} = 0.706 \quad (3.6)$$

resulting in a solid volume fraction of

$$1 - \phi = 0.294 \quad (3.7)$$

and the volume of solid confining a single pore of $V_{\text{solid}} = 40.25 \text{ nm}^3$. Tab. 3.3 lists experimentally measured porosities of comparable MCM-41 structures, assuming a density of amorphous silica of 2.2 g cm^{-3} ⁵¹. Consequently, the determined porosity is likely situated at the upper end of the porosities observed in MCM-41 samples.

Table 3.3: Experimentally measured porosities of comparable MCM-41 structures.

Source	Porosity ϕ
Kruk et al. ⁷	0.61
Morsi and Mohamed ⁵²	0.67
Liu et al. ⁵³	0.69

3.3.4 The pore radius

The pore radius r was determined from the void volume $V_{\text{void}} = 96.44 \text{ nm}^3$ and the pore length $H = 11.29 \text{ nm}$ under the assumption of a cylindrical pore as

$$r = \sqrt{\frac{V_{\text{void}}}{H\pi}} = 1.649 \text{ nm}. \quad (3.8)$$

CAPILLARY FLOW DYNAMICS OF WATER IN ORDERED, CYLINDRICAL MESOPORES

This chapter presents a detailed analysis of the capillary flow dynamics during the capillary rise process in ordered, cylindrical mesopores. An overview of research on capillary flow dynamics in cylindrical tubes is presented in Sec. 4.1. The subsequent Sec. 4.2 outlines the method to determine capillary flow dynamics from the conducted imbibition simulations. The results of the imbibition simulations are discussed in Sec. 4.3. Subsequently, Sec. 4.4 and Sec. 4.5 evaluate the agreement between the measured capillary flow dynamics and the theoretical models for the viscosity-dominated regime and the inertia-dominated regime, respectively.

4.1 Capillary flow dynamics of liquids in cylindrical tubes

The contact of a matrix of cylindrical pores, such as MCM-41, with a wetting liquid results in the phenomenon of capillary rise, as discussed in Sec. 2.3.2. According to Jurin's law, if capillary rise occurs under the influence of gravity, the liquid rises until the driving Laplace pressure p_L is balanced by the hydrodynamic pressure p_{hydro} in the imbibing liquid column. The time dynamics of this capillary flow phenomenon, i.e., the penetration length of the liquid column $h(t)$ in dependence of time t , have been subject to scientific investigations for over a century. However, the phenomenon remains an important scientific topic, especially in nanofluidics since the precise understanding of capillary flow in nanosystems offers potential for many novel applications. For instance, the project "Energy harvesting via wetting/drying cycles with nanoporous electrodes" (EHAWEDRY) investigated the generation of electric energy through wetting and drying cycles in porous materials.⁵⁴ For successful industrial translation of this approach, precise knowledge of electrolyte movement during wetting cycles is essential. Switchable imbibition, desalination, and chemical separation represent

additional potential technologies based on capillary flow.^{6,55–57}

The dynamics of the capillary flow process can be modeled by considering the pressure balance in the liquid during capillary rise. Several effects influence the capillary flow dynamics and must therefore be considered in the pressure balance.⁵⁸ The capillary flow is driven by the Laplace pressure $p_L = -\frac{2\gamma \cos \theta}{r}$ and counteracted by multiple contributions in the pressure balance. The hydrostatic pressure $p_{\text{hydro}} = \rho gh$ is the determining factor in the maximum rise height of the liquid. Additionally, two effects depending on the dynamics of the capillary flow process must be considered. First, the acceleration of the liquid column is countered by the inertia of the liquid, which is expressed as $p_{\text{inertia}} = \frac{1}{\pi r^2} \frac{dP}{dt}$ with $\frac{dP}{dt} = \frac{d(\pi r^2 \rho h \frac{dh}{dt})}{dt}$. Second, the Laplace pressure is countered by viscous drag within the fluid, expressed by $p_{\text{visc}} = \frac{8\eta h}{r^2} \frac{dh}{dt}$. During capillary flow these contributions are balanced, i.e., they satisfy

$$-p_L = p_{\text{hydro}} + p_{\text{inertia}} + p_{\text{visc}}. \quad (4.1)$$

As outlined in Sec. 2.3.2, the Laplace pressure exceeds the hydrostatic pressure in capillary flows at short length scales in mesoporous materials. As a result, the equilibrium height in mesoporous materials is on the order of meters to kilometers. Fries and Dreyer⁵⁹ investigated the influence of gravitational effects on capillary rise and found that neglecting hydrostatic pressure introduces an error to the modeled capillary flow dynamics of 3.7 % at an equilibrium rise height of $\frac{h_{\text{equil}}}{10}$. This implies that the influence of the hydrostatic pressure on the dynamics of the imbibition process can be neglected in good approximation for mesoporous materials with spatial dimensions significantly smaller than meters. Since imbibition lengths of nanometers are considered in this thesis, the effect of hydrostatics is neglected in the further discussions about capillary flow dynamics. As a result, Eq. (4.1) condenses to

$$-p_L = p_{\text{inertia}} + p_{\text{visc}}. \quad (4.2)$$

Eq. (4.2) can be written as

$$b = ah \frac{dh}{dt} + \frac{d(h \frac{dh}{dt})}{dt} \quad (4.3)$$

with

$$a = \frac{8\eta}{r^2 \rho} \quad (4.4)$$

and

$$b = \frac{2\gamma \cos \theta}{r \rho}. \quad (4.5)$$

In 1923 Bosanquet⁶⁰ found the solution

$$h_{\text{Bos}}(t) = \sqrt{\frac{2b}{a} \left[t - \frac{1}{a} (1 - e^{-at}) \right]} \quad (4.6)$$

to Eq. (4.3). The capillary flow dynamics, as described by Eq. (4.6), can be categorized into two distinct imbibition regimes. For short times, $t \approx 0$, the capillary flow model is dominated by the inertia of the liquid column, while for extended periods of time, $t \rightarrow \infty$, viscous drag dominates.

The inertia dominated imbibition dynamics during initial imbibition times was investigated by Quéré⁶¹. If $t \approx 0$, it follows that $ah(t) \frac{dh(t)}{dt} \approx 0$. Therefore, the viscous contribution p_{visc} can be neglected in Eq. (4.6) for small imbibition times. Solving

$$-p_L = p_{\text{inertia}} \implies b = \frac{d(h \frac{dh}{dt})}{dt} \quad (4.7)$$

leads to the linear relation

$$h_{\text{Quéré}}(t) = \sqrt{bt} = \sqrt{\frac{2\gamma \cos \theta}{r \varrho}} t = v_{\text{Quéré}} t, \quad (4.8)$$

where $v_{\text{Quéré}}$ denotes the imbibition velocity in the inertia dominated regime. Note that Eq. (4.8) can also be obtained from the first order Taylor series approximation of Eq. (4.6) at $t = 0$. This underlines the fact that Eq. (4.8) describes the inertia dominated time regime for short imbibition times t .

For long imbibition times $t \rightarrow \infty$, Eq. (4.6) converges to

$$h_{\text{LW}}(t) = \sqrt{\frac{2b}{a}} \sqrt{t} = \sqrt{\frac{\gamma r \cos \theta}{2\eta}} \sqrt{t} = c_{\text{LW}} \sqrt{t} \quad (4.9)$$

where c_{LW} is the imbibition coefficient. This is the solution Lucas⁶² and Washburn⁶³ found by considering only the balance of viscous drag and Laplace pressure while neglecting the contribution of inertia. Before Lucas and Washburn, Bell and Cameron⁶⁴ had already reported a square-root dependence of the imbibition length on time. The pressure balance assumed by Lucas and Washburn is written as

$$-p_L = p_{\text{visc}} \implies b = ah \frac{dh}{dt}. \quad (4.10)$$

If Eq. (4.10) is multiplied by the $2\pi r^2$, one arrives at the so called Hagen-Poiseuille-equation⁶⁵

$$\frac{dV(t)}{dt} = -\frac{\pi r^4}{8\eta h} p_L. \quad (4.11)$$

The Hagen-Poiseuille-equation relates the volumetric flow rate $\frac{dV(t)}{dt}$ of a laminar flow of an incompressible liquid through a cylinder with the pressure difference in the liquid. The corresponding velocity flow profile $v_{\text{Pois}}(\rho_{\text{cyl}}, h)$ that satisfies Eq. (4.11) is⁶⁶

$$v_{\text{Pois}}(\rho_{\text{cyl}}, h) = -\frac{p_L}{4\eta h} (r^2 - \rho_{\text{cyl}}^2). \quad (4.12)$$

Thus, the flow profile follows a parabolic distribution as a function of the radial distance ρ_{cyl} from the center of the cylinder. Note that the Hagen-Poiseuille flow relies on the so called no-slip condition, meaning that the velocity of the imbibing liquid is zero at the cylinder walls. For smooth surfaces this does not have to be the case and Washburn⁶³ included the case of a non-zero imbibition velocity at the pore walls by adding a slip coefficient ϵ to Eq. (4.11) to arrive at

$$\frac{dV(t)}{dt} = -\frac{\pi}{8\eta h} p_L (r^4 + 4\epsilon r^3). \quad (4.13)$$

However, for hydrophilic materials, as considered in this thesis, the velocity of the liquid can be assumed to be zero at the cylinder walls. Instead a negative slip length is commonly assumed, caused by layers of immobile adsorbed molecules at the cylinder walls, which effectively reduce the pore radius.^{65,67,68}

Until this point, the capillary flow models considered in this section have assumed that the contact angle θ remains constant throughout the imbibition process and is equivalent to the equilibrium contact angle. However, particularly during the initial stages this condition is not satisfied. Instead the contact angle is assumed to undergo dynamic changes during the process of capillary flow. In light of this limitation in the existing capillary flow models, Bracke et al.⁶⁹ suggested to connect the equilibrium contact angle θ to the dynamic contact angle θ_{dyn} through

$$\cos \theta_{\text{dyn}} = \cos \theta - 2(1 + \cos \theta) \text{Ca}^{1/2}. \quad (4.14)$$

Ca is the so called capillary number that is defined as

$$\text{Ca} = \frac{\eta v}{\gamma}, \quad (4.15)$$

where v is the velocity of the imbibition front. In a subsequent publication, Joos et al.⁷⁰ demonstrated that the incorporation of relation Eq. (4.14) into imbibition dynamics models

lead to a better agreement to experimental observed capillary flow dynamics. However, in the study only systems with an equilibrium contact angle of $\theta = 0^\circ$ were considered. Martic et al.⁷¹ advanced the capillary flow model for a wide range of systems. This was achieved by modeling the velocity dependence of θ_{dyn} with the molecular-kinetic theory of wetting.⁷² The molecular-kinetic theory of wetting explicitly considers the statistical displacements of individual molecules at the three-phase wetting line to model the dynamics of the wetting line. To this end, an additional driving force of the imbibition process, originating from a non-equilibrium surface tension force $\gamma(\cos \theta - \cos \theta_{\text{dyn}})$, was assumed. The non-equilibrium surface tension force and the imbibition front velocity $v = \frac{dh}{dt}$ are related through

$$v = 2K\Lambda \sinh \left[\frac{\gamma(\cos \theta - \cos \theta_{\text{dyn}})}{2nk_B T} \right], \quad (4.16)$$

where K is the frequency of molecular displacement, Λ the average displacement length, and n the number of adsorption sites per unit area. By solving for the dynamic contact angle $\cos \theta_{\text{dyn}}$ and substituting this value into $-p_L$ of Eq. (4.2), one obtains

$$\frac{2}{r} \gamma \left[\cos \theta - \frac{2nk_B T}{\gamma} \operatorname{arcsinh} \left(\frac{1}{2K\Lambda} \frac{dh}{dt} \right) \right] = p_{\text{inertia}} + p_{\text{visc}}. \quad (4.17)$$

Eq. (4.17) can be solved numerically. For small arguments of the arcsinh function, that is for low imbibition velocities v , Eq. (4.16) can be approximated to be linear.⁷³ Under this assumption, the relation

$$v = \frac{\gamma K \Lambda}{nk_B T} (\cos \theta - \cos \theta_{\text{dyn}}) = \frac{1}{c_1} - \frac{\gamma r}{4\eta} \frac{c_2}{c_1} \cos \theta_{\text{dyn}} \quad (4.18)$$

is obtained with $c_1 = \frac{nk_B T}{\gamma K \Lambda \cos \theta}$ and $c_2 = \frac{4\eta}{\gamma r \cos \theta}$. Updating Eq. (4.17) accordingly and solving the differential equation results in

$$h_{\text{MLW}}(t) = -\frac{c_1}{c_2} + \sqrt{\frac{2t}{c_2} + \left(h_0 + \frac{c_1}{c_2} \right)^2}, \quad (4.19)$$

where h_0 determines an initial offset of the imbibition length. Note that Eq. (4.19) reduces to the original Lucas-Washburn equation if $\frac{c_1}{c_2} = 0$. Therefore, the term $\frac{c_1}{c_2}$ is a measure of importance of energy dissipation at the wetting line. The capillary flow dynamics model defined by Eq. (4.19) is referred to as the modified Lucas-Washburn model in the remainder of this thesis.

4.2 Measuring the simulated imbibition length

In order to investigate the capillary flow dynamics in the MD simulations, it was necessary to develop a method for extracting the dynamics of the water column $h(t)$ during imbibition into the porous matrix. Since water, that penetrated the pore space during the imbibition process, originated from the water reservoir, the axial size of the reservoir decreased. The decrease in the size of the water reservoir resulted in a shrinkage of the simulation box extension in the axial direction, $L_{\parallel}(t)$, as the imbibition process progressed. Therefore, the extension of the simulation box along the axial pore direction was used as a proxy to determine $h(t)$. Specifically, the imbibition dynamics of a single water column was calculated by reweighting the changes of the simulation box extension through

$$h(t) = \frac{1}{2} \frac{\left[L_{\parallel}^{\text{final}} - L_{\parallel}(t) \right] H}{L_{\parallel}^{\text{final}} - L_{\parallel}^0}. \quad (4.20)$$

In this equation, the initial simulation box extension is denoted as $L_{\parallel}^0$ and the extension at the end of the imbibition process is denoted as $L_{\parallel}^{\text{final}}$. H represents the maximum possible imbibition length of the water column, as determined in Sec. 3.3.3. The factor of $\frac{1}{2}$ accounts for the simultaneous advancement of two water columns into the pore space from opposite ends. Note that this method of measuring the imbibition dynamics assumes a constant pore void volume, V_{void} . This is due to the fact that changes in the pore void volume would also lead to a shrinking or expansion of the water reservoir and, consequently, to a change in the extension of the simulation box in the axial direction. Given the observation of small deformations of the pore matrix during the imbibition process, the assumption of a constant pore void volume is expected to be accurate within a reasonable margin of error.

4.3 Analyzing the capillary flow process

The capillary flow process was investigated by conducting 20 independent imbibition simulations. During the simulations, water imbibed from the water reservoirs at the axial ends into the pore matrix. At the top of Fig. 4.1, snapshots of slices through one nanopore at 0 ps, 360 ps, 560 ps, 660 ps, and 780 ps, illustrate the imbibition process in an exemplary simulation. The snapshots depict the imbibing water as a continuous blue liquid, though it should be noted that the trajectories of individual water molecules were calculated in the MD simulations. This is demonstrated in the zoom of the third snapshot. During the imbibition process, two water menisci were observed to develop at the front of each water column. As

the imbibition process continued, these menisci became more pronounced, as can be seen in the snapshots of Fig. 4.1 at 360 ps and 560 ps. After approximately 600 ps of the simulation, the menisci merged at the pore wall and formed a small cavity, that is visible in the snapshot at 660 ps. After 780 ps of the simulation, the pore matrix was completely filled with water.

The time dependence of the average penetration depth $h(t)$ of the imbibing water columns was determined for the 20 simulations using the method described in Sec. 4.2. The observed imbibition dynamics demonstrated a linear increase in imbibition length immediately following the commencement of the simulation, as shown by the blue curve in Fig. 4.4. In the figure, the standard deviation of the 20 simulations is indicated by the lighter blue area. The linear trend of imbibition dynamics persisted until approximately 3.3 ps into the simulation. The imbibition dynamics at the first 3.3 ps are expected to be inertia-dominated, as discussed in Sec. 4.5. After the initial linear imbibition dynamics, the imbibition velocity consistently decreased until the pore matrix was completely filled with water from the water reservoir. The corresponding imbibition dynamics are shown in Fig. 4.1 as the blue curve. During the imbibition process, the 20 individual simulations exhibited imbibition dynamics with a very strong consistency, as evidenced by the fact that the standard deviation of the imbibition dynamics (light blue) is barely discernible in Fig. 4.1. During this period, ranging from 3.3 ps to approximately 780 ps, the imbibition dynamics are expected to be dominated by the viscous drag of water. In the subsequent section Sec. 4.4 the implications of the viscosity-dominated imbibition dynamics are discussed in more detail.

After a duration of 780 ps, the pore matrix was completely filled with water. However, the measured imbibition length $h(t)$ continued to increase even after this point in time. This effect is explained by a systematic error in the method of measuring the imbibition length. As outlined in Sec. 4.2, the measurement method of the imbibition length assumes a constant pore space volume V_{void} during the imbibition process. However, once the pore was completely filled by water, a relatively strong lateral expansion of the pore matrix of around 1 % was observed. This expansion lead to an increase in pore volume and, in turn, an additional inflow of water from the water reservoirs into the pore matrix. This additional inflow of water was measured as an increase in imbibition length, despite the water columns already filling the entire pore space, because the axial simulation box extension changed. The pore matrix also exhibited strain during the imbibition process, altering the pore space volume and introducing an error in the measured imbibition dynamics. Due to the pore space volume expansion that occurred during imbibition, the measured imbibition dynamics are assumed to be slightly faster than the actual dynamics of the liquid column. However, the induced strain during active imbibition is expected to be small enough to lead only to a negligible systematic error. The expansive deformations of the pore matrix during the

imbibition process are thoroughly discussed in Ch. 5.

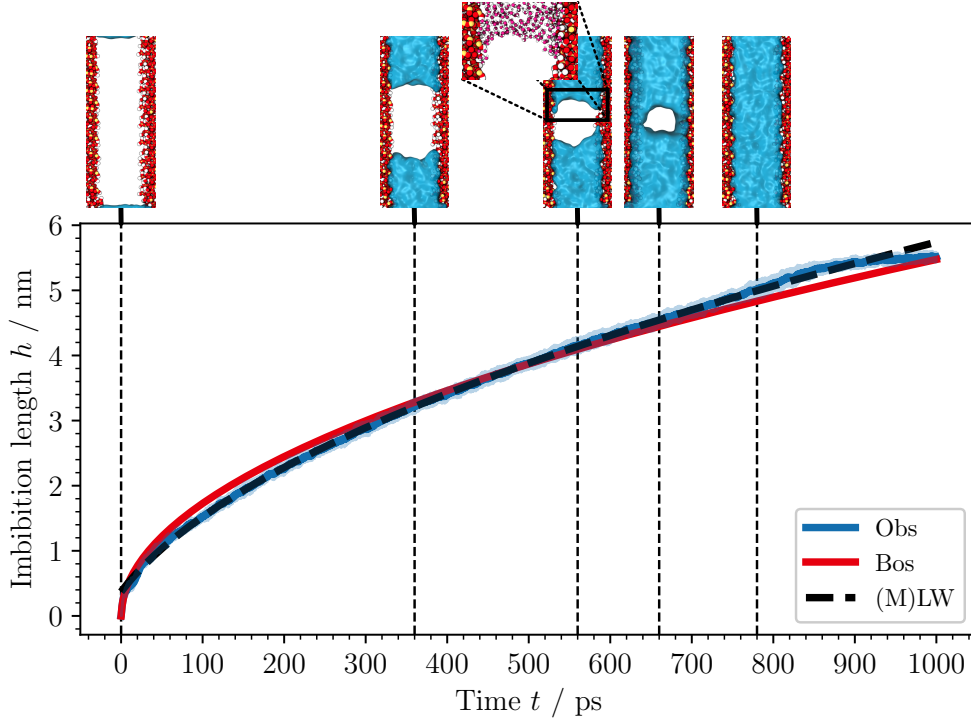


Figure 4.1: Average observed imbibition dynamics over the course of the entire imbibition process. At the top of the figure, exemplary snapshots of one simulation are depicted, showing slices through one nanopore at 0 ps, 360 ps, 560 ps, and 780 ps during the imbibition process. The water molecules are represented as a continuous blue liquid in the snapshots, although in the simulation, the water molecules are calculated as individual molecules, as illustrated in the zoom of the third snapshot. The blue curve indicates the observed imbibition length h of the water column averaged over the 20 simulations (Obs). The standard deviation of the observed imbibition length is shown as the lighter blue area. The red curve represents a fit of the Bosanquet imbibition model (Bos) to the observed imbibition dynamics, and the dashed black curve represents a fit of the (modified) Lucas-Washburn model ((M)LW) to the observed imbibition dynamics.

4.4 Viscosity-dominated imbibition dynamics

In this section, the viscosity-dominated simulated imbibition process, ranging from 3.3 ps to around 780 ps, is investigated. To this end, three imbibition models, namely the Bosanquet model, the Lucas-Washburn model, and the modified Lucas-Washburn model were compared to the results of the observed imbibition dynamics.

Since the Bosanquet imbibition model $h_{\text{Bos}}(t)$ encompasses both the inertia-dominated and viscosity-dominated imbibition regimes, it is supposed to describe the imbibition

process in its entirety. When the Bosanquet model was fitted to the entire time range of the imbibition processes, the model demonstrated strong agreement with the viscous-dominated imbibition dynamics. However, the fit showed significant disagreement with the observed data from the inertia-dominated imbibition regime at imbibition times < 3.3 ps. Additionally, $a = 0.036 \text{ ps}^{-1}$ as determined by the fit, was significantly lower than the value predicted for water by Eq. (4.4). The disagreement of the fit in the inertia-dominated regime originated from the underrepresentation of data from this regime compared to that from the viscosity-dominated regime. As a result, the fitting algorithm optimized the fit with respect to the viscosity-dominated imbibition regime. To address this imbalance, the model's fitting capacity was constrained by predetermining the parameter $a = 2.45 \text{ ps}^{-1}$ using the values in Tab. 3.1 and the pore radius of $r = 1.649 \text{ nm}$. Hence, the utilized fit function was defined as

$$h_{\text{Bos}}(t; b, t_0, h_0) = \sqrt{\frac{2b}{a} \left[(t - t_0) - \frac{1}{a} (1 - e^{-a(t-t_0)}) \right]} + h_0 \quad (4.21)$$

where the parameter $b = \frac{2\gamma \cos \theta}{r\phi} = 3.67 \times 10^{-2} \text{ nm}^2 \text{ ps}^{-1}$, the initial time offset $t_0 = -1.98 \times 10^{-8} \text{ ps} \approx 0.0 \text{ ps}$, and the initial imbibition length offset $h_0 = 9.12 \times 10^{-13} \text{ nm} \approx 0.0 \text{ nm}$ were free fit parameters determined through the fit. The resulting fit of the Bosanquet model is indicated by the red curve in Fig. 4.1. In general, the Bosanquet model demonstrated a satisfactory fit to the observed imbibition dynamics. However, discrepancies between the data and the model were identified. Specifically, during the first 500 ps of the imbibition process, the Bosanquet model slightly overpredicted the imbibition length of the water column, whereas at later times, it slightly underpredicted it. From the model parameters a and b the imbibition coefficient was determined from Eq. (4.9) as $c_{\text{Bos}} = \sqrt{\frac{2b}{a}} = 0.173 \text{ nm}/\sqrt{\text{ps}}$. Subsequently, a static contact angle of $\theta_{\text{Bos}} = 64.19^\circ$ was determined from the imbibition coefficient.

In contrast to the Bosanquet model, the Lucas-Washburn model is only valid for the viscosity-dominated imbibition regime. Therefore, it was only fitted to the observed imbibition dynamics in the viscosity dominated regime after the initial time of 3.3 ps. The fit function of the the Lucas-Washburn model $h_{\text{LW}}(t)$ can be expressed as

$$h_{\text{LW}}(t; c_{\text{LW}}, t_0, h_0) = c_{\text{LW}} \sqrt{t - t_0} + h_0. \quad (4.22)$$

The imbibition coefficient $c_{\text{LW}} = 0.206 \text{ nm}/\sqrt{\text{ps}}$, the initial time offset $t_0 = -37.74 \text{ ps}$, and the initial imbibition length offset $h_0 = -0.89 \text{ nm}$ were determined as free fit parameters. The fitted Lucas-Washburn model is indicated by the dashed black curve in Fig. 4.1. The

Lucas-Washburn model demonstrated strong agreement with the observed data and did not exhibit any of the deviations observed in the Bosanquet model. However, the long initial time t_0 of approximately 40 ps assumed by the model to align the model to the data is noteworthy. As expected, the Lucas-Washburn model was inadequate in representing the initial inertia-dominated imbibition dynamics of the imbibition process. Therefore, a significant deviation between the model and the observed imbibition dynamics during the initial capillary flow times existed. However, this discrepancy is only evident in the first few picoseconds of the imbibition process, and subsequently, the Lucas-Washburn model provides a highly accurate fit to the observed capillary flow dynamics in the viscosity-dominated imbibition regime. The strong agreement of the Lucas-Washburn model with the observed imbibition length suggests that the velocity profile of the imbibing water columns should exhibit a Hagen-Poiseuille flow profile, as described by Eq. (4.12). This hypothesis is supported by Fig. 4.2, which illustrates the mean velocity of oxygen atoms during the entire imbibition process from 0 ps to 780 ps in a 2D histogram across the lateral space of the MCM-41 pore. Despite significant variations in the oxygen atom velocities of the water molecules, the velocity profile shows a clear decrease in velocity with increasing distance from the pore center. This trend matches the velocity profile expected for a parabolic distribution characteristic to a laminar Hagen-Poiseuille flow. A static contact angle of $\theta_{\text{LW}} = 51.96^\circ$ was determined from the imbibition coefficient c_{LW} with Eq. (4.9). Both considered models, the Bosanquet and the Lucas-Washburn model, assume a static contact angle during the imbibition process. However, the snapshots in Fig. 4.1 reveal that the contact angle was not static but underwent changes during the imbibition process. Since the contact angle is a determining factor for the capillary flow dynamics, it is of interest to model the imbibition process considering a dynamic contact angle $\theta_{\text{dyn}}(t)$, which changes in dependence of the imbibition time t .

To incorporate the dynamic contact angle into the analysis of the capillary flow dynamics, the modified Lucas-Washburn model was utilized. Note that this model only holds approximately for slow imbibition velocities. Consequently, erroneous predictions are to be expected, especially during the initial stages of the imbibition process. The modified Lucas-Washburn model was fitted to the observed imbibition data in the form of

$$h_{\text{MLW}}(t; c_1, c_2, h_0) = -\frac{c_1}{c_2} + \sqrt{\frac{2t}{c_2} + \left(h_0 + \frac{c_1}{c_2}\right)^2} \quad (4.23)$$

The resulting fit parameters were $c_1 = 42.184 \text{ ps nm}^{-2}$, $c_2 = 47.146 \text{ ps nm}^{-1}$, and $h_0 = 0.371 \text{ nm}$. Eq. (4.23) fitted the observed data very well, indicating that the velocity of the imbibition front was slow enough to justify the linear approximation employed in Eq. (4.18).

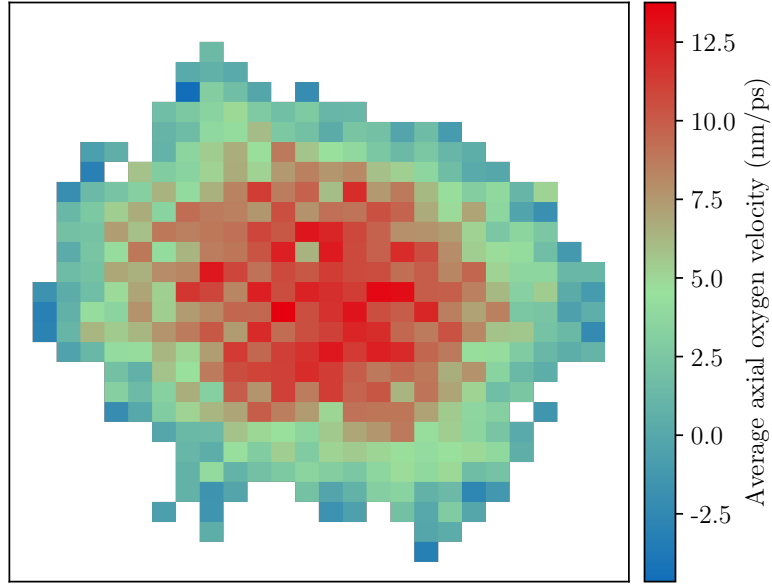


Figure 4.2: Simulated axial velocity component of the oxygen atoms bound in water molecules averaged over the entire axial length and the entire imbibition process, ranging over 780 ps. The decrease in velocity with increasing distance from the pore center is consistent with the parabolic profile characteristic to a laminar Hagen–Poiseuille flow.

In fact, the fit of the modified Lucas-Washburn model aligns with the data equally well as the fit of the original Lucas-Washburn model. This is because both models exhibit the same fit capacity, i.e., with the right choice of fit parameters the functions

$$h_{MLW}(t; c_1, c_2, h_0) \equiv h_{LW}(t; c_{LW}, t_0, h_0) \quad (4.24)$$

are identical. This is noteworthy, since the pressure balance Eq. (4.17) explicitly includes the inertia dominated contribution to derive the modified Lucas-Washburn model, while the original Lucas-Washburn model neglects this contribution. Consequently, by introducing a free fit parameter for the initial time t_0 , the original Lucas–Washburn model, which was derived for static contact angles, gains the ability to account for dynamic contact angles in imbibition processes with slow imbibition velocities. This fact explains the large obtained initial time offset of $t_0 = -37.74$ ps, when the original Lucas-Washburn model was fit to the capillary flow data. In general, this effect might contribute to the success of the original Lucas-Washburn model in reliably modeling imbibition dynamics. Concurrently, these findings underscore the necessity of accurately interpreting the obtained fit parameters as originating from the modified Lucas-Washburn model to derive precise properties of the capillary flow process. Similarly, the equivalence in Eq. (4.24) implies that the modified

Lucas-Washburn model is not applicable to the inertia-dominated regime since the original Lucas-Washburn model entirely neglects this contribution to the imbibition dynamics. Thus, these two models are not suitable for describing the inertia-dominated imbibition regime.

Assuming that the dynamic contact angle evolves as predicted by the modified Lucas-Washburn model, the fit can be used to investigate the temporal evolution of contact angle during imbibition. From the obtained imbibition velocity

$$v(t) = \frac{dh_{MLW}(t)}{dt} = \frac{1}{\sqrt{(c_1 + c_2 h_0)^2 + 2c_2 t}}, \quad (4.25)$$

Eq. (4.18) was solved for $\theta_{dyn}(t)$ to yield

$$\theta_{dyn}(t) = \arccos \left(-\frac{4\eta[c_1 v(t) - 1]}{c_2 \gamma_{lv} r} \right). \quad (4.26)$$

The predicted evolution of the dynamic contact angle as a function of time is depicted in Fig. 4.3. As mentioned, during the initial stages of imbibition, these results should be treated

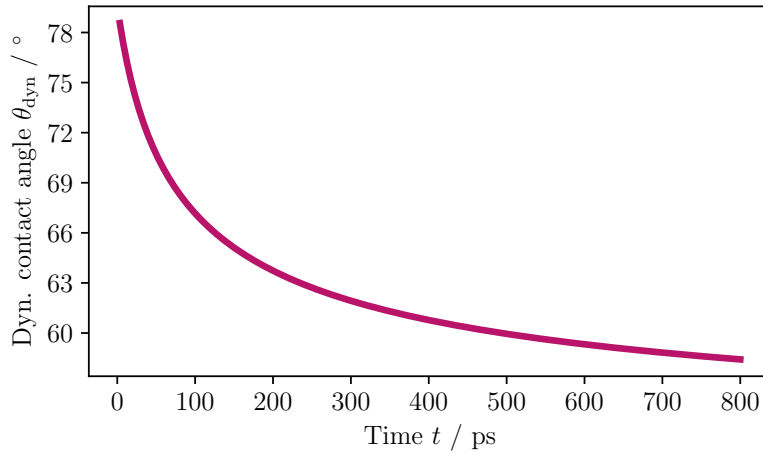


Figure 4.3: Temporal evolution of the dynamic contact angle θ_{dyn} as predicted by the modified Lucas-Washburn model.

with caution because the model's linear approximation does not accurately describe the contact angle evolution in this regime. For infinite imbibition times $t \rightarrow \infty$, the dynamic contact angle model converges to the static contact angle of $\theta_{dyn}^{LW} = 51.96^\circ$ determined by the unmodified Lucas-Washburn model. Note that the determined equilibrium contact angle for water on a silica surface expected from experiment⁷⁴ or other MD simulation studies⁷⁵ is $\theta = 0^\circ$. As a result, the question arises, if the the final equilibrium angle was reached during the imbibition simulation. In particular, the visual inspection of the snapshots in Fig. 4.1

suggests that the evolution of the dynamic contact angle might not have concluded at this stage of the imbibition process.

4.5 Inertia-dominated imbibition dynamics

In this section, the inertia-dominated simulated imbibition dynamics, ranging from 0 ps to 3.3 ps, are investigated. The results of the simulation are compared to the inertia-viscous Bosanquet model and to the inertia-dominated imbibition model proposed by Quéré⁶¹, which is also referenced as linear model in this section.

The inertia-dominated regime of the imbibition dynamics was observed during the initial phase of the imbibition process. The initial imbibition dynamics from 0 ps to 7 ps are depicted in Fig. 4.4. The blue curve represents the average imbibition dynamics observed in the 20 conducted imbibition simulations. The lighter blue area around the imbibition dynamics indicates the standard deviation between the simulations. In the observed imbibition dynamics a linear trend is visible during the first 3.3 ps of the imbibition process. Subsequently, the imbibition dynamics transition to the viscous-dominated imbibition dynamics, which are discussed in Sec. 4.4. Note that the linear imbibition trend is separated from the viscosity-dominated imbibition dynamics by a reduced standard deviation of the ensemble of the 20 imbibition simulations.

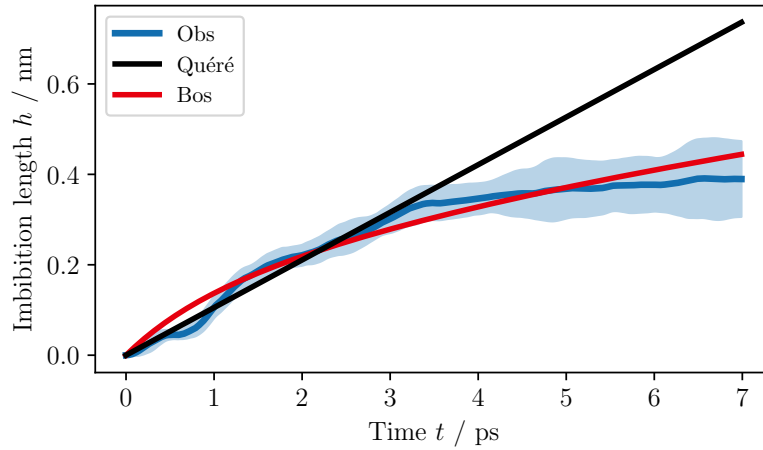


Figure 4.4: Initial average observed imbibition dynamics over the course of the first 7 ps. The blue curve (Obs) indicates the average observed imbibition length h of the water column. The standard deviation of the 20 simulations is indicated by the lighter blue area. The black curve (Quéré) illustrates the fit of the linear Quéré model to the first 3.3 ps of the imbibition process. The red curve (Bos) illustrates a segment of the Bosanquet model that was fitted to the complete imbibition dynamics.

The predictions of the Bosanquet model for the initial imbibition dynamics is depicted in

Fig. 4.4 as the red curve. The Bosanquet model aligns closely with the observed imbibition data. The imbibition velocity of the inertia-dominated regime was determined from the Bosanquet model as $v_{\text{Bos}} = \sqrt{b} = 0.192 \text{ nm ps}^{-1}$. The static equilibrium contact angle θ_{Bos} derived from the imbibition velocity is $\theta_{\text{Bos}} = 64.19^\circ$.

The linear model from Quéré⁶¹ is represented by the black curve in Fig. 4.4. The imbibition velocity was determined as a free fit parameter to $v_{\text{Quéré}} = 0.105 \text{ nm ps}^{-1}$. Thus, the imbibition velocity determined with the linear model is only approximately half the imbibition velocity $v_{\text{Bos}} = 0.192 \text{ nm ps}^{-1}$, that was determined from the Bosanquet model. Using Eq. (4.8), the contact angle in the linear model was determined as $\theta_{\text{Quéré}} = 82.44^\circ$. The value of the contact angle is significantly larger than the $\theta_{\text{Bos}} = 64.19^\circ$ determined from the Bosanquet model. This discrepancy is likely explained by the assumption of a static equilibrium contact angle in the Bosanquet model. Therefore, the model predicted a static contact angle that is smaller than the actual contact angle during the initial imbibition process, but larger than the contact angle observed in the simulations during the final moments of the capillary flow process. Note that the linear model also assumes a static contact angle. Consequently, this problem also transfers to the linear model. However, the linear model was used to predict the imbibition dynamics for a significantly shorter time range than the Bosanquet model. Therefore, the impact of the dynamic contact angle on the modeled imbibition dynamics is expected to be considerably smaller compared to the Bosanquet model.

The time scale of the transition from the linear inertia-dominated regime to the viscosity-dominated regime was investigated by Fries and Dreyer⁵⁸. The authors proposed various methods to quantify the transition times between the different regimes. Important defined points in time were:

- t_1 : The relative deviation of 3 % between the inertia-dominated dynamics $h_{\text{Quéré}}(t)$ of Eq. (4.8) and the inertia-viscous dynamics $h_{\text{Bos}}(t)$ of Eq. (4.6). This point in time is calculated as

$$0.03 = \frac{h_{\text{Quéré}}(t_1) - h_{\text{Bos}}(t_1)}{h_{\text{Quéré}}(t_1)} \implies t_1 = \frac{0.1856}{a} = \frac{0.0232r^2\rho}{\eta}. \quad (4.27)$$

- t_2 : The equivalence of imbibition lengths of $h_{\text{Quéré}}(t)$ and $h_{\text{LW}}(t)$. This point in time is calculated as

$$h_{\text{Quéré}}(t_2) = h_{\text{LW}}(t_2) \implies t_2 = \frac{2}{a} = \frac{r^2\rho}{4\eta}. \quad (4.28)$$

- t_3 : The relative deviation of 3 % between the viscous dynamics $h_{\text{LW}}(t)$ of Eq. (4.9)

and the inertia-viscous dynamics $h_{\text{Bos}}(t)$ of Eq. (4.6). This point in time is calculated as

$$\frac{h_{\text{LW}}(t_3) - h_{\text{Bos}}(t_3)}{h_{\text{LW}}(t_3)} \implies t_3 = \frac{16.921}{a} = \frac{2.1151r^2\varrho}{\eta}. \quad (4.29)$$

Consequently, the transition from inertia to viscosity-dominated capillary flow dynamics lies between Eqs. (4.27) and (4.29), according to Fries and Dreyer⁵⁸. For a value of $a = 2.45 \text{ ps}^{-1}$, the transition is predicted to occur between $\frac{0.2}{a} \approx 0.08 \text{ ps}$ and $\frac{17}{a} \approx 7 \text{ ps}$. From visible inspection, it is evident that the linear regime extends to around 3.3 ps. Therefore, the observed time scale aligns with the expected time frame for the inertia-driven imbibition process. However, it is important to note that the linear imbibition dynamics observed in the MD simulations were strongly dependent on the preparation of the initial simulation configuration. Therefore, the results for the linear imbibition dynamics are prone to systematic errors from simulation artifacts and should be treated with caution.

Chapter 5

IMBIBITION-INDUCED ELASTOCAPILLARITY IN ORDERED, CYLINDRICAL MESOPORES

The subsequent chapter is devoted to an in-depth discussion of the imbibition-induced elastocapillarity in ordered, cylindrical mesopores. To this end, Sec. 5.1 provides an overview about research on elastocapillarity in mesoporous materials. The section is followed by the presentation of a theory to predict the imbibition-induced deformation dynamics in ordered, cylindrical mesopores in Sec. 5.2. Sec. 5.3 presents a methodology to measure imbibition-induced deformation dynamics in MD simulations. In Sec. 5.4, the developed imbibition-induced elastocapillarity model is tested against the deformation dynamics observed in MD simulations of water imbibition into MCM-41. Parts of the work and figures presented hereafter, in particular in Sec. 5.4, have already been published in

[68] J. Sanchez, **L. Dammann**, L. Gallardo, Z. Li, M. Fröba, R.H. Meißner, H.A. Stone & P. Huber, Deformation dynamics of nanopores upon water imbibition, *Proceedings of the National Academy of Sciences*, 121(38):e2318386121, 2024.

5.1 Elastocapillarity in mesoporous materials

Elastocapillarity denotes the elastic deformation of a solid induced by capillary forces.^{76,77} Since capillarity effects originate from interfaces, and mesoporous materials exhibit a high surface-to-volume ratio, elastocapillarity effects significantly affect mesoporous materials. As a result, to mitigate undesired elastocapillarity in mesopores or to exploit the effect for novel approaches in actuation or sensing^{78–81}, a precise understanding of elastocapillarity is essential. The effect of elastocapillarity in porous media was first described by Meehan⁸² as well as Bangham and Fakhoury¹¹, in the form of gas-induced expansion of charcoal.

Since then, numerous studies investigated elastocapillarity effects in porous materials during adsorption and desorption processes.^{50,83–91}

Two effects govern sorption-induced elastocapillarity in mesoporous materials. These are the Laplace pressure effect and the Bangham effect^{88,92}, that were introduced before in Sec. 2.3. Subsequent investigations have analyzed the linkage between capillary forces and elastic deformation, concentrating on isotropic mesoporous solids. For isotropic materials, a so-called pore-load modulus can be defined. The pore-load modulus establishes a linear relation of capillary effects and the macroscopic deformation of the material.^{68,84,87,88} However, this approach applies only to isotropic materials.

Weissmüller et al.¹⁴ demonstrated that explicit consideration of the microscopic geometry of the porous matrix is essential to model elastocapillarity in anisotropic, microscopic structures. These findings led to models that describe adsorption-induced deformation of ordered, cylindrical nanopores, like MCM-41 and AAO.^{93,94} Research indicates that elastocapillarity processes in mesoporous materials occur not only during adsorption but also during capillary rise.^{95,96} The phenomenon of imbibition-induced elastocapillarity exerts a significant impact on porous materials, particularly those that are soft solids.^{97–99} However, studies on imbibition-induced elastocapillarity remain less numerous than those on adsorption-induced elastocapillarity. Recently Sanchez et al.⁶⁸ investigated imbibition-induced elastocapillarity in isotropic mesoporous materials. The results of this study are extended in the next section by the development of a theoretical framework that models imbibition-induced elastocapillarity within matrices of ordered, cylindrical mesopores. To the best of the author's knowledge, this work introduces the first quantitative model that predicts imbibition-induced elastocapillarity dynamics in ordered, cylindrical mesoporous matrices.

5.2 Modeling imbibition-induced elastocapillarity

5.2.1 Imbibition-induced stresses and strains in matrices of ordered, cylindrical pores

The objective of this section is to develop a model that describes the macroscopic imbibition-induced deformation dynamics observed during liquid imbibition into a mesoporous matrix of ordered, cylindrical pores, such as MCM-41, by applying elastic deformation theory. Previous studies have developed models of sorption-induced elastocapillarity for these porous systems.^{14,93,94} As Weissmüller et al.¹⁴ pointed out, the periodicity of the porous matrix allows the deformation behavior of the entire structure to be deduced from that of a

representative volume element (RVE). This approach is also used here to develop a model that describes imbibition-induced elastocapillarity.

■ The representative volume element (RVE) of a matrix of ordered, cylindrical pores

To work with the RVE, pores within the pore matrix are assumed to be cylindrical, with radius r . The length H of these cylindrical pores is assumed to be considerably longer than their radius, i.e., $r \ll H$. From the periodic pores, a primitive cell is constructed that contains precisely one cylindrical pore, which is surrounded by solid material. Note that due to the balance of traction forces, the mean traction forces at the faces of the primitive cell vanish.¹⁴ Consequently, stress-free boundary conditions apply at the edges of the cell.

To obtain an analytical solution for the elastic deformations, the primitive cell must be further simplified. Consequently, the primitive cell is approximated as a RVE of a hollow cylinder. The RVE can be described using cylindrical coordinates, where z is the axial coordinate, ρ is the radial coordinate from the center of the cylindrical pore void, and φ is the azimuthal coordinate. The axial extent of the RVE matches that of the pore matrix from $z = 0$ to $z = H$. The inner radius $\rho = r$ of the RVE corresponds to the radial extent of the pore in the pore matrix. The outer radius $\rho = R$ is chosen so that the porosity ϕ of the RVE matches that of the pore matrix, i.e., $\phi = \frac{V_{\text{void}}}{V_{\text{total}}} = \frac{r^2}{R^2}$.

■ Imbibition-induced stresses

The RVE is considered to be in equilibrium and stress-free as long as the solid surface remains in contact with a surrounding vapor phase. If the pore matrix is put into contact with a liquid reservoir, capillary-flow is triggered. In the RVE, this process is modeled as a column of liquid that penetrates the interior of the RVE and wets the internal surface. The capillary-flow follows the imbibition dynamics $h(t)$ discussed in Ch. 4. The inner surface of the RVE is in contact with the liquid when $z \leq h(t)$, and in contact with the vapor phase when $h(t) < z \leq H$. Note that no partial wetting of the surface is considered in this model. Hence, the liquid–vapor interface is defined as a line that either wets or does not wet the surface. Fig. 5.1 shows a 2D slice of the RVE with the pore solid (s) colored in yellow. The liquid phase (l) is shown in blue, and the vapor phase (v) forms the white background.

The surface of the RVE that is **not** wetted by the liquid remains stress free. Therefore, the boundary conditions

1. $\sigma_\rho|_{h(t) < z \leq H} = 0$

2. $\sigma_\varphi|_{h(t) < z \leq H} = 0$

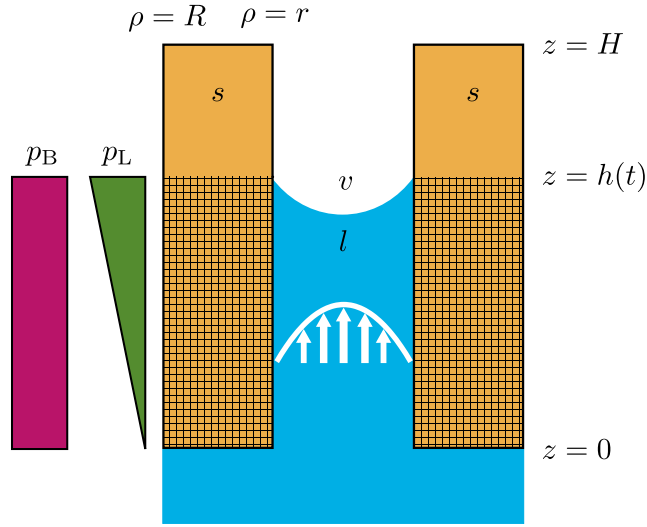


Figure 5.1: Schematic illustration of the imbibition process into a representative volume element (RVE). The radius from the pore center is denoted as ρ and the axial position as z . The inner RVE surface is situated at radius $\rho = r$ and the outer RVE surface at $\rho = R$. The axial extent of the pore is defined from $z = 0$ to $z = H$. The liquid (l) imbibes into a cylindrical pore space filled by the vapor phase (v). The imbibition length of the liquid is denoted as $z = h(t)$. The parabolic flow profile of the liquid is indicated in white. Stress that is induced into the wetted regions of the solid (s) is marked by the grid. The strength of the effective Bangham pressure p_B and the Laplace pressure p_L acting on the surface of the wetted solid are indicated in purple and green, respectively.

$$3. \sigma_z|_{h(t) < z \leq H} = 0$$

are satisfied. In this context, the notation $|_{h(t) < z \leq H}$ is employed to underscore the fact that the stress applies only within the specified limits. Because pore geometries are assumed in which the pore length greatly exceeds the radius, $r \ll H$, local solid stresses at the three-phase contact line, such as line tension⁹⁶, are neglected in the model. In any portion of the solid RVE material that is wetted by the liquid, stress is induced from capillary effects. Two effects must be considered when determining the induced stress. These are the Laplace pressure effect and the Bangham effect.

As outlined in Sec. 2.3.2, the Laplace pressure effect originates from the curvature of the meniscus at the liquid–vapor interface. This curvature induces a pressure drop across the interface, that is calculated by Eq. (2.28). As discussed in Ch. 4, during the initial imbibition process, the contact angle of the imbibing meniscus changes dynamically. Consequently, the Laplace pressure is defined with the dynamic contact angle as

$$p_L = -\frac{2\gamma \cos \theta_{\text{dyn}}}{r}. \quad (5.1)$$

The material is typically subject to an atmospheric pressure of approximately $p_0 = 1$ bar. The

Laplace pressure in mesoporous materials significantly exceeds the atmospheric pressures in magnitude, i.e., $|p_0| \ll |p_L|$. Since the presented model is only valid for elastic deformations, the considered mesoporous materials need to be stiff enough to exhibit only small elastic deformations in reaction to pressure differences as large as the Laplace pressure. Therefore, small pressures, like the atmospheric pressure, can be neglected in the deformation process and $p_0 = 0$ bar holds in good approximation. In consequence, the pressure in the imbibing liquid at the liquid–vapor interface at the axial position is

$$p_1(z = h(t)) = p_L + p_0 \approx p_L . \quad (5.2)$$

The pressure in the liquid is linearly related to the distance from the liquid–vapor interface. Consequently, the pressure in the liquid column can be described in dependence of the axial coordinate as

$$p_1(z) = p_L \frac{z}{h(t)} . \quad (5.3)$$

At passage to the reservoir the pressure in the liquid is

$$p_1(z = 0) = P_0 \approx 0 \text{ bar} . \quad (5.4)$$

The negative pressure in the liquid exerts a force on the inner surface of the RVE, thereby inducing stress in the pore solid σ_p along the radial direction of the pore solid. The influence of the Laplace pressure effect on the inner surface of the RVE is indicated in Fig. 5.1 by the green shape.

In addition to the Laplace pressure effect, the Bangham effect induces stress in the solid material. This stress arises from the release of surface stress when the inner surface of the RVE becomes wet, as discussed in Sec. 2.3.3. Since the RVE is modeled as a perfectly smooth, hollow cylinder, the effective Bangham pressure is given by Eq. (2.33), i.e.,

$$p_B = \frac{\Delta f}{r} . \quad (5.5)$$

The influence of the Bangham pressure on the inner surface of the RVE is indicated in Fig. 5.1 by the purple shape.

The induced stress in the solid directly beneath the liquid–solid interface, measured along the direction of the surface normal of the solid, can be determined using the local balance law defined in Eq. (2.31).^{14,15} In the cylindrical RVE the surface normal aligns with the radial direction. As a result, the radially induced stress at the inner surface of the RVE is

determined by

$$\sigma_\rho|_{\rho=r} = p_B - p_l(z). \quad (5.6)$$

According to Eq. (5.6), the two boundary conditions for the stresses are derived as

$$4. \quad \sigma_\rho|_{\rho=r, z=h(t)} = p_B - p_L$$

$$5. \quad \sigma_\rho|_{\rho=r, z=0} = p_B.$$

As discussed above, the mean traction forces at the cell edges of a primitive cell containing a single pore must vanish because of traction force balance. Approximately, this condition also holds when a cylindrical RVE replaces the primitive cell.¹⁴ Therefore, the radially induced stress can be assumed to vanish at the outer edge, $\rho = R$, of the RVE and the additional boundary condition of

$$6. \quad \sigma_\rho|_{\rho=R, z} = 0.$$

is obtained.

Until now, only the radially induced stress was considered. However, in contrast to the pressure in the liquid that acts only normal to the cylinder surface of the RVE, the surface stress associated with the Bingham effect also acts tangentially to the inner surface of the RVE. The total wetted inner surface area of the RVE is defined as A_{wetted} , and the volume of the solid beneath this wetted area is V_{wetted} . Because for cylindrical pores no porous voids exist along the axial direction of the pore matrix, the axial stress averaged over the wetted volume V_{wetted} suffices to determine the axial strain, i.e., $\sigma_z = \langle \mathbf{a} \mathbf{S} \mathbf{a} \rangle_{V_{\text{wetted}}}$. Here, $\langle \cdot \rangle_{V_{\text{wetted}}}$ denotes the volume average over V_{wetted} , i.e.,

$$\langle \cdot \rangle_{V_{\text{wetted}}} = \frac{1}{V_{\text{wetted}}} \int \cdot dV_{\text{wetted}}. \quad (5.7)$$

As a result, the axially induced strain can be determined using the generalized capillary equation^{94,100} as

$$\sigma_z = -\frac{A_{\text{wetted}}}{V_{\text{wetted}}} \Delta f = -\zeta_{\text{wetted}} \Delta f, \quad (5.8)$$

where $\zeta_{\text{wetted}} = \frac{A_{\text{wetted}}}{V_{\text{wetted}}}$ is the surface-to-volume ratio of the wetted portion of the RVE. The surface-to-volume ratio can be determined from the imbibition length $h(t)$ as

$$\zeta_{\text{wetted}} = \frac{A_{\text{wetted}}}{V_{\text{wetted}}} = \frac{2\pi r h(t)}{\pi(R^2 - r^2)h(t)} = \frac{\frac{r^2}{R^2}}{1 - \frac{r^2}{R^2}} \frac{2}{r} = \frac{\phi}{1 - \phi} \frac{2}{r}, \quad (5.9)$$

where the last equality arises because, by definition, the RVE reflects the porosity of the considered pore matrix. Substitution of Eq. (5.9) into Eq. (5.8) leads to an additional boundary condition for the axially induced stress in the wetted part of the RVE of

$$7. \sigma_z|_{z \leq h(t)} = -\frac{\phi}{1-\phi} 2p_B .$$

Together with an assumption regarding the form of the stress functions, the obtained boundary conditions (1-7) can be applied to determine the induced stresses within the RVE. For the imbibition-induced radial and circumferential stresses, σ_ρ and σ_φ , the approach from Balzer et al.⁹³ is adapted to account for the axial dependence of the pressure in the liquid column $p_1(z)$. The resulting functions for the induced stresses are

$$\sigma_\rho(\rho, z) = \begin{cases} A + \frac{B}{\rho^2} + \frac{z}{h(t)} \left(C + \frac{D}{\rho^2} \right), & \text{if } 0 < z \leq h(t) \\ 0, & \text{if } h(t) < z \leq H \end{cases} \quad (5.10)$$

and

$$\sigma_\varphi(\rho, z) = \begin{cases} A - \frac{B}{\rho^2} + \frac{z}{h(t)} \left(C - \frac{D}{\rho^2} \right), & \text{if } 0 < z \leq h(t) \\ 0, & \text{if } h(t) < z \leq H \end{cases}, \quad (5.11)$$

respectively. The axial strain is assumed to be constant in the solid under the wetted surface, i.e.,

$$\sigma_z(\rho, z) = \begin{cases} F, & \text{if } 0 < z \leq h(t) \\ 0, & \text{if } h(t) < z \leq H \end{cases}. \quad (5.12)$$

The parameters A , B , C , D , and F are determined with the boundary conditions (1-7) as

$$A = -\frac{r^2}{R^2 - r^2} p_B = -\frac{\phi}{1-\phi} p_B \quad (5.13)$$

$$B = \frac{r^2}{R^2 - r^2} R^2 p_B = \frac{\phi}{1-\phi} R^2 p_B \quad (5.14)$$

$$C = \frac{r^2}{R^2 - r^2} p_L = \frac{\phi}{1-\phi} p_L \quad (5.15)$$

$$D = -\frac{r^2}{R^2 - r^2} R^2 p_L = -\frac{\phi}{1-\phi} R^2 p_L \quad (5.16)$$

$$F = -\frac{\phi}{1-\phi} 2p_B . \quad (5.17)$$

Subsequently, the induced stresses are

$$\sigma_\rho(\rho, z) = \begin{cases} \frac{\phi}{1-\phi} \left[-p_B \left(1 - \frac{R^2}{\rho^2} \right) + p_L \frac{z}{h(t)} \left(1 - \frac{R^2}{\rho^2} \right) \right], & \text{if } 0 < z \leq h(t) \\ 0, & \text{if } h(t) < z \leq H \end{cases} \quad (5.18)$$

$$\sigma_\varphi(\rho, z) = \begin{cases} \frac{\phi}{1-\phi} \left[-p_B \left(1 + \frac{R^2}{\rho^2} \right) + p_L \frac{z}{h(t)} \left(1 + \frac{R^2}{\rho^2} \right) \right], & \text{if } 0 < z \leq h(t) \\ 0, & \text{if } h(t) < z \leq H \end{cases} \quad (5.19)$$

$$\sigma_z = \begin{cases} -\frac{\phi}{1-\phi} 2p_B, & \text{if } 0 < z \leq h(t) \\ 0, & \text{if } h(t) < z \leq H \end{cases}. \quad (5.20)$$

Due to the cylindrical symmetry of the RVE, the induced stresses are independent of the azimuthal coordinate φ .

■ Imbibition-induced elastic deformations

The stress induced in the solid causes elastic deformations. The presented model of elastic deformations assumes that the velocity of the imbibition front is sufficiently slow, allowing the wetted pore solid to remain in equilibrium with the induced stresses throughout the imbibition process. Previous studies^{50,92} and the results presented in Ch. 3 indicate that Young's modulus of the porous matrix is smaller in the lateral direction than in the axial direction of the pores. Consequently, the RVE can be modeled as a transversely isotropic material. In this scenario, the induced normal deformations in cylindrical coordinates can be calculated using Hooke's law, defined in Eq. (2.12) with the compliance tensor defined by Eq. (2.15). The resulting normal elastic deformations are

$$\varepsilon_\rho = \frac{1}{E_\perp} [\sigma_\rho - \nu_\perp \sigma_\varphi] - \frac{\nu_{\parallel\perp}}{E_\parallel} \sigma_z = \frac{du_\rho}{d\rho}, \quad (5.21)$$

$$\varepsilon_\varphi = \frac{1}{E_\perp} [\sigma_\varphi - \nu_\perp \sigma_\rho] - \frac{\nu_{\parallel\perp}}{E_\parallel} \sigma_z = \frac{u_\rho}{\rho}, \quad (5.22)$$

$$\varepsilon_z = \frac{1}{E_\parallel} \sigma_z - \frac{\nu_{\perp\parallel}}{E_\perp} [\sigma_\rho + \sigma_\varphi] = \frac{du_z}{dz}. \quad (5.23)$$

By substituting Eqs. (5.18), (5.19), and (5.20) into Eqs. (5.21), (5.22), and (5.23) the imbibition-induced strains of the wetted pore matrix are calculated as

$$\begin{aligned} \varepsilon_\rho^{\text{wetted}} = & \frac{\phi}{1-\phi} p_B \left(\frac{2\nu_{\parallel\perp}}{E_{\parallel}} + \frac{1}{E_{\perp}} \left[(\nu_{\perp} - 1) + (\nu_{\perp} + 1) \frac{R^2}{\rho^2} \right] \right) \\ & - \frac{\phi}{1-\phi} p_L \frac{z}{h(t)} \frac{1}{E_{\perp}} \left((\nu_{\perp} - 1) + (\nu_{\perp} + 1) \frac{R^2}{\rho^2} \right), \end{aligned} \quad (5.24)$$

$$\begin{aligned} \varepsilon_\varphi^{\text{wetted}} = & \frac{\phi}{1-\phi} p_B \left(\frac{2\nu_{\parallel\perp}}{E_{\parallel}} - \frac{1}{E_{\perp}} \left[(1 - \nu_{\perp}) + (\nu_{\perp} + 1) \frac{R^2}{\rho^2} \right] \right) \\ & + \frac{\phi}{1-\phi} p_L \frac{z}{h(t)} \frac{1}{E_{\perp}} \left((1 - \nu_{\perp}) + (\nu_{\perp} + 1) \frac{R^2}{\rho^2} \right), \end{aligned} \quad (5.25)$$

and

$$\varepsilon_z^{\text{wetted}} = 2 \frac{\phi}{1-\phi} \left[p_B \left(\frac{\nu_{\perp\parallel}}{E_{\perp}} - \frac{1}{E_{\parallel}} \right) - p_L \frac{\nu_{\perp\parallel}}{E_{\perp}} \frac{z}{h(t)} \right]. \quad (5.26)$$

Hence, the resulting deformation dynamics for the pore matrix during the imbibition process are obtained as

$$\varepsilon_\rho = \frac{du_\rho}{d\rho} = \begin{cases} \varepsilon_\rho^{\text{wetted}} & \text{if } 0 < z \leq h(t) \\ 0, & \text{if } h(t) < z \leq H \end{cases}, \quad (5.27)$$

$$\varepsilon_\varphi = \frac{u_\rho}{\rho} = \begin{cases} \varepsilon_\varphi^{\text{wetted}} & \text{if } 0 < z \leq h(t) \\ 0, & \text{if } h(t) < z \leq H \end{cases}, \quad (5.28)$$

$$\varepsilon_z = \frac{du_z}{dz} = \begin{cases} \varepsilon_z^{\text{wetted}} & \text{if } 0 < z \leq h(t) \\ 0, & \text{if } h(t) < z \leq H \end{cases}. \quad (5.29)$$

Typically, experiments and simulations determine the lateral and axial macroscopic engineering strains of the pore matrix. This thesis therefore concentrates on these macroscopic strains. In the following section, predictions for the macroscopic strains in a scenario where the pore matrix contacts a liquid reservoir at one end are derived. As depicted in Fig. 5.1, in this scenario, the liquid penetrates the pore matrix from a single direction. Therefore, the imbibition-induced deformation dynamics in this scenario correspond to the imbibition-induced elastocapillarity observed in a monolithic pore matrix of ordered, cylindrical pores during a dilatometry experiment.

5.2.2 Imbibition-induced macroscopic deformation dynamics

■ Laterally induced engineering strain

The laterally induced engineering strain $\varepsilon_{\perp}$ can be determined from the induced circumferential strain at the position of the outer radius $\rho = R$ of the RVE, i.e., as $\varepsilon_{\perp} = \varepsilon_{\varphi}|_{\rho=R} = \frac{u_{\rho}}{\rho}|_{\rho=R}$. Setting $\rho = R$ in Eq. (5.28) leads to

$$\varepsilon_{\perp} = \begin{cases} 2 \frac{\phi}{1-\phi} \left[p_B \left(\frac{\nu_{\parallel\perp}}{E_{\parallel}} - \frac{1}{E_{\perp}} \right) + p_L \frac{1}{E_{\perp}} \frac{z}{h(t)} \right], & \text{if } 0 < z \leq h(t) \\ 0, & \text{if } h(t) < z \leq H \end{cases}. \quad (5.30)$$

Under consideration of the symmetry constraints for elastic deformations defined by Eq. (2.16), Eq. (5.30) simplifies to

$$\varepsilon_{\perp} = \begin{cases} \frac{2}{E_{\perp}} \frac{\phi}{1-\phi} \left[-(1 - \nu_{\perp\parallel}) p_B + p_L \frac{z}{h(t)} \right], & \text{if } 0 < z \leq h(t) \\ 0, & \text{if } h(t) < z \leq H \end{cases}. \quad (5.31)$$

Note that the magnitude of the lateral strain varies along the axial direction of the cylindrical pore, as indicated by the z dependence of Eq. (5.31). Because surface stress release Δf is typically negative¹³, the effective Bangham pressure p_B induces an expansive strain in the pore matrix, which counteracts the contractive strain caused by the Laplace pressure effect.

Depending on the relative magnitude of the Laplace pressure and the effective Bangham pressure, two deformation behaviors are possible during the imbibition. If the effective Bangham pressure effect dominates the Laplace pressure effect, i.e., $|(1 - \nu_{\perp\parallel}) p_B| > |p_L|$, the wetted region of the pore matrix experiences exclusively expansive strain. However, if $|(1 - \nu_{\perp\parallel}) p_B| < |p_L|$, then a point of strain inversion exists along the axial dimension in the region of the wetted pore surface. Specifically, from the liquid reservoir toward the liquid–vapor interface, at the point of inversion, the deformation changes from expansive to contractile. The point of inversion is situated at

$$\frac{z}{h(t)} = (1 - \nu_{\perp\parallel}) \frac{p_B}{p_L}. \quad (5.32)$$

The following derivation establishes a theoretical lower bound for the axial position of the point of inversion $\frac{z^*}{h(t)}$. In other words, under conditions that favor the Laplace pressure effect within the pore matrix, the axial position of the point of inversion that is farthest away from the liquid–vapor interface is determined. To this end, the definitions of the effective

Bangham pressure and Laplace pressure are substituted into Eq. (5.32), to arrive at

$$\frac{z^*}{h(t)} = -(1 - \nu_{\perp\parallel}) \frac{\Delta f}{2\gamma \cos \theta_{\text{dyn}}} . \quad (5.33)$$

The influence of the Bangham effect on the pore solid was derived from the local balance law in Eq. (2.31) for a perfectly smooth cylindrical RVE. In any real pore matrix, the expansive contribution to the observed deformations from the Bangham effect is likely larger than that determined from a perfectly smooth cylindrical material, because surface roughness of the pore leads to larger local curvature, and hence a stronger Bangham effect. However, since a **lower** bound for the position of the point of inversion is to be calculated, the substitution is warranted. In the subsequent step, the dynamic contact angle is assumed to equal the equilibrium contact angle, thus attaining its minimum value, as expected for sufficiently long imbibition times. As a result, $\theta_{\text{dyn}} = \theta$ and the maximal Laplace pressure is assumed. Spontaneous imbibition occurs only when the equilibrium contact angle is $\theta < 90^\circ$. To further evaluate Eq. (5.33), two different wetting scenarios have to be distinguished. Specifically, either partial wetting, i.e., $0^\circ < \theta < 90^\circ$, or complete wetting, i.e., $\theta = 0^\circ$, is considered. In the case of complete wetting, $\gamma_{\text{sv}} - \gamma_{\text{sl}} > \gamma$ holds, while for the case of partial wetting the Young relation defined in Eq. (2.24) is satisfied, i.e., $\gamma_{\text{sv}} - \gamma_{\text{sl}} = \gamma \cos(\theta)$. From Eq. (2.30) it is evident, that the surface stress release and the magnitude of Bangham effect scale with an increased difference of surface energies $\gamma_{\text{sv}} - \gamma_{\text{sl}}$. Given the goal to derive a lower bound for the position of the point of inversion, the Bangham effect is assumed to be minimal. Therefore, the complete wetting scenario is excluded and partial wetting is assumed. Substituting the definition of surface stress release Δf , as given by Eq. (2.30), and applying Young's relation, one arrives at

$$\frac{z^*}{h(t)} = \frac{1}{2}(1 - \nu_{\perp\parallel}) \left(1 - \frac{\frac{d\Delta\gamma}{d\epsilon}}{\gamma \cos \theta} \right) . \quad (5.34)$$

It is noteworthy that the lower bound for the point of inversion depends on the ratio between the change of surface energy under strain, $\frac{d\Delta\gamma}{d\epsilon}$, and the weighted surface energy, $\gamma \cos \theta$. For substantial surface energies and small equilibrium contact angles, this term can be neglected in good approximation. In this case, the theoretically possible lower bound for the point of inversion is derived as

$$\frac{z^*}{h(t)} = \frac{1}{2}(1 - \nu_{\perp\parallel}) \quad (5.35)$$

and therefore dependent on the Poisson ratio of the porous matrix. By selecting the largest possible Poisson ratio typically exhibited by standard materials of $\nu_{\perp\parallel} = 0.5$, one concludes

that, if a point of inversion exists, it must theoretically occur between the liquid–vapor interface of the imbibing liquid column and $\frac{z^*}{h(t)} = 0.25$ of the imbibition length of the liquid column.

When the imbibing liquid column fills the entire pore space at the end of the imbibition process, i.e., $h(t) = H$, the meniscus of the advancing column disappears and the induced Laplace pressure vanishes. The disappearance of the Laplace pressure effect causes a sudden lateral expansion $\varepsilon_{\perp}^{\text{jump}}$ of the pore solid. This lateral expansion is referred to as *Laplace jump* in this work. In the pore matrix, the Laplace jump exhibits a magnitude of

$$\varepsilon_{\perp}^{\text{jump}}(z) = -\frac{2}{E_{\perp}} \frac{\phi}{1-\phi} p_L \frac{z}{H}. \quad (5.36)$$

Therefore, the Laplace jump is strongest at the disappearing liquid–vapor interface and decreases linearly toward the liquid reservoir. After the Laplace pressure effect disappeared, only the expansive Bangham effect acts on the wetted surface of the pore matrix. Consequently, the resulting strain originates exclusively from the constant surface stress release Δf over the entire axial pore length. The final strain is thus

$$\varepsilon_{\perp}^{\text{final}} = -\frac{2}{E_{\perp}} \frac{\phi}{1-\phi} (1 - \nu_{\perp\parallel}) p_B. \quad (5.37)$$

■ Axially induced engineering strain

The macroscopic engineering strain $\varepsilon_{\parallel}$, that would be measured in a dilatometry experiment, can be derived from the infinitesimal strain ε_z obtained by Eq. (5.29). Following Eq. (2.18), the macroscopic axial engineering strain is determined by integration of Eq. (5.29) to obtain

$$\begin{aligned} \varepsilon_{\parallel} &= \frac{u_z(H) - u_z(0)}{H} = \frac{1}{H} \int_0^H \frac{du_z}{dz} dz = \frac{1}{H} \int_0^H \varepsilon_z dz = \frac{1}{H} \int_0^{h(t)} \varepsilon_z dz \\ &= \frac{\phi}{1-\phi} \left[2p_B \left(\frac{\nu_{\perp\parallel}}{E_{\perp}} - \frac{1}{E_{\parallel}} \right) - \frac{\nu_{\perp\parallel}}{E_{\perp}} p_L \right] \frac{h(t)}{H}. \end{aligned} \quad (5.38)$$

In light of the symmetry constraints in the compliance matrix defined in Eq. (2.16), Eq. (5.38) can be simplified to

$$\varepsilon_{\parallel} = -\frac{1}{E_{\parallel}} \frac{\phi}{1-\phi} [2(1 - \nu_{\parallel\perp}) p_B + \nu_{\parallel\perp} p_L] \frac{h(t)}{H}. \quad (5.39)$$

Note that the effective Bangham pressure and the Laplace pressure effect, transmitted through the Poisson effect, lead to an expansion of the pore matrix. Hence, in contrast to the laterally

induced deformations, the axial deformations are always expansive during the imbibition process. Once the pore space is completely filled, the disappearance of the Laplace pressure effect causes a contraction of the pore matrix. The magnitude of the contraction is determined by

$$\varepsilon_{\parallel}^{\text{jump}} = \frac{\nu_{\parallel\perp}}{E_{\parallel}} \frac{\phi}{1-\phi} p_L. \quad (5.40)$$

As can be seen in Eq. (5.40), the contraction is expected to occur due to the Poisson effect. Consequently, the magnitude of the deformation is significantly smaller compared to the Laplace jump in the lateral pore matrix direction, since it is scaled by the Poisson ratio $\nu_{\parallel\perp}$. The final axial engineering strain for the equilibrated pore matrix is determined exclusively by the Bangham effect and equates to

$$\varepsilon_{\parallel}^{\text{final}} = -\frac{2}{E_{\parallel}} \frac{\phi}{1-\phi} (1-\nu_{\parallel\perp}) p_B. \quad (5.41)$$

It should be noted that in the case of identical axial and lateral Young moduli, i.e., $E_{\parallel} = E_{\perp}$, Eq. (5.41) has the same magnitude as the final exhibited lateral strain Eq. (5.37). However, since the lateral Young modulus is expected to be smaller than the axial Young modulus for matrices of ordered, cylindrical pores with thin walls, the final lateral expansion exceeds the final axial expansion.

5.2.3 Imbibition-induced macroscopic deformation dynamics in MD simulations

The conducted MD simulations, that simulate capillary-flow of water into MCM-41 discussed in Ch. 3 and Ch. 4, differ in two aspects from the prerequisites assumed in the previous Sec. 5.2.2. Therefore, the imbibition-induced elastocapillarity model has to be augmented to predict the elastocapillarity dynamics observed in the MD simulations.

First, in the simulations, the liquid imbibes simultaneously from both ends of the pore matrix. In the model, the penetration depths of the individual liquid columns into the pore matrix $h(t)$ are assumed to be equal, implying identical imbibition velocities for both liquid columns. The augmented imbibition geometry is depicted in Fig. 5.2.

Second, the simulated pore matrix is confined within a rectangular simulation box with periodic boundary conditions, that implicitly represent an infinite periodic matrix. Hence, to accurately represent the axial dependence of the lateral deformation dynamics, the simulation box must be flexed. However, the simulation software does not support flexed boxes, and implementing them with periodic boundary conditions is challenging. Therefore, the lateral deformation of a freely deformable pore matrix cannot be represented in the MD simulations. Instead, the induced lateral stresses are averaged over the entire axial length of the simulated

pore matrix H to determine the lateral induced strain observed in the simulations. In this thesis, the engineering strain measured in the MD simulations is distinguished by the $\bar{\epsilon}$ notation from the strain of a freely deformable pore matrix, i.e., a model for $\bar{\epsilon}$ is considered instead of ϵ .

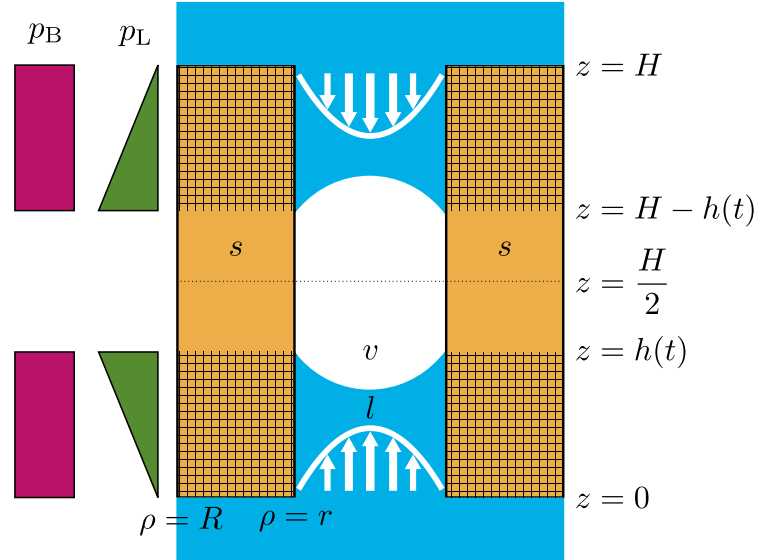


Figure 5.2: Schematic illustration of the imbibition processes into a representative volume element (RVE) during the MD simulations. The radius from the pore center is denoted as ρ and the axial position as z . The inner RVE surface is situated at radius $\rho = r$ and the outer RVE surface at $\rho = R$. The axial extent of the pore is defined from $z = 0$ to $z = H$. The liquid (l) imbibes into the cylindrical pore space filled by the vapor phase (v) from two directions. The imbibition length of the two liquid columns is denoted as $z = h(t)$ and $z = H - h(t)$. The parabolic flow profile of the liquid columns is indicated in white. Stress that is induced into the wetted regions of the solid (s) is marked by the grid. The strength of the effective Bingham pressure p_B and the Laplace pressure p_L acting on the surface of the wetted solid are indicated in purple and green, respectively.

■ Laterally induced engineering strain

For a freely deformable simulated pore matrix, the deformation dynamics observed in the simulations could be directly adapted from Sec. 5.2.2 to include two imbibition fronts from opposite directions. In this case the resulting observed deformations are

$$\epsilon_{\perp}^{\text{sim}}(z) = \begin{cases} \frac{2}{E_{\perp}} \frac{\phi}{1-\phi} \left[-(1 - \nu_{\perp\parallel}) p_B + p_L \frac{z}{h(t)} \right], & \text{if } 0 < z \leq h(t) \\ \frac{2}{E_{\perp}} \frac{\phi}{1-\phi} \left[-(1 - \nu_{\perp\parallel}) p_B + p_L \frac{H-z}{h(t)} \right], & \text{if } H - h(t) < z \leq H \\ 0, & \text{if } h(t) < z \leq H - h(t) \end{cases}, \quad (5.42)$$

where the superscript *sim* denotes the the imbibition geometry of the imbibition simulations with a freely deformable pore matrix. To determine the lateral deformation of the pore matrix confined by the simulation box $\bar{\varepsilon}_\perp$, Eq. (5.42) has to be averaged over the axial pore matrix length, leading to

$$\begin{aligned}\bar{\varepsilon}_\perp &= \frac{1}{H} \int_0^H \varepsilon_\perp^{\text{sim}}(z) dz = \frac{1}{H} \left(\int_0^{h(t)} \varepsilon_\perp^{\text{sim}}(z) dz + \int_{H-h(t)}^H \varepsilon_\perp^{\text{sim}}(z) dz \right) \\ &= \frac{2}{E_\perp} \frac{\phi}{1-\phi} \left[-2(1-\nu_{\perp\parallel})p_B + p_L \right] \frac{h(t)}{H}.\end{aligned}\quad (5.43)$$

As with the predicted lateral strain for the freely deformable pore matrix, the effective Bangham pressure and the Laplace pressure effect constitute counteracting contributions in Eq. (5.43). The Bangham effect introduces an expansive contribution of the pore matrix in the lateral direction, whereas the Laplace pressure effect causes a contractile contribution to the deformation. However, in contrast to the freely deformable pore matrix, the lateral deformation does not depend on the axial coordinate. Therefore, no point of inversion exists in the MD simulations, and the average lateral deformation is either contractile or expansive. By substituting the definitions for the effective Bangham pressure, Laplace pressure and surface stress release, the theoretical maximum contractile deformation observable in MD simulations during the imbibition process can be estimated. The necessary assumptions are equivalent to those used to calculate the lower bound for the point of inversion. Specifically, the following assumptions are made: The pore surface is perfectly smooth, the dynamic contact angle is equal to the equilibrium contact angle, i.e., $\theta_{\text{dyn}} = \theta$, and the case of partial wetting is considered. Subsequently, the maximally induced lateral contraction $\bar{\varepsilon}_\perp^*$ can be determined from Eq. (5.43) to be

$$\bar{\varepsilon}_\perp^* = \frac{2}{E_\perp} \frac{\phi}{1-\phi} \left[-2(1-\nu_{\perp\parallel})p_B + p_L \right] \frac{h(t)}{H} \quad (5.44)$$

$$\Rightarrow \bar{\varepsilon}_\perp^* = \frac{2}{E_\perp} \frac{\phi}{1-\phi} \left[-2(1-\nu_{\perp\parallel}) \frac{\Delta f}{r} + \frac{2\gamma \cos \theta_{\text{dyn}}}{r} \right] \frac{h(t)}{H} \quad (5.45)$$

$$\Rightarrow \bar{\varepsilon}_\perp^* = \frac{4}{E_\perp} \frac{1}{r} \frac{\phi}{1-\phi} \left[-(1-\nu_{\perp\parallel}) \left(\gamma \cos \theta + \frac{d\Delta\gamma}{d\epsilon} \right) + \gamma \cos \theta \right] \frac{h(t)}{H} \quad (5.46)$$

$$\Rightarrow \bar{\varepsilon}_\perp^* = -\frac{4}{E_\perp} \frac{1}{r} \frac{\phi}{1-\phi} \left[\nu_{\perp\parallel} \gamma \cos \theta + (1-\nu_{\perp\parallel}) \frac{d\Delta\gamma}{d\epsilon} \right] \frac{h(t)}{H}. \quad (5.47)$$

Note that the maximally induced contraction depends on the sum of two terms. Assuming the Bangham approximation, the second term $\frac{d\Delta\gamma}{d\epsilon}$ is expected to be of small magnitude in comparison to the first term. Since the first term is scaled by the Poisson ratio $\nu_{\perp\parallel}$,

the theoretically maximal observable contractile lateral deformation remains limited in magnitude even when conditions favor the contractile Laplace pressure. Therefore, for simulations that model realistic pore matrices, the observed lateral deformation during the imbibition process is expected to be predominantly expansive.

Once the imbibition length of the two imbibing liquid columns covers half of the pore matrix length each, i.e., $h(t) = \frac{H}{2}$, the pore matrix is completely filled with the liquid. Consequently, the Laplace pressure vanishes and a Laplace jump occurs. The magnitude of the Laplace jump observed in the MD simulations is

$$\bar{\varepsilon}_{\perp}^{\text{jump}} = -\frac{1}{E_{\perp}} \frac{\phi}{1-\phi} p_L. \quad (5.48)$$

After the Laplace jump, the final observed lateral pore matrix deformation attributed to the Bangham effect, is of the magnitude

$$\bar{\varepsilon}_{\perp}^{\text{final}} = -\frac{2}{E_{\perp}} \frac{\phi}{1-\phi} (1 - \nu_{\perp\parallel}) p_B. \quad (5.49)$$

As a result, once the pore is entirely filled by the liquid, the final lateral macroscopic strain is identical to the lateral strain obtained for the freely deformable pore matrix considered in Sec. 5.2.2, i.e., $\bar{\varepsilon}_{\perp}^{\text{final}} = \varepsilon_{\perp}^{\text{final}}$.

■ Axially induced engineering strain

To determine the induced macroscopic axial strain observed in the MD simulations, the infinitesimal axial strain described by Eq. (5.29) has to be adapted to account for the two simultaneous imbibing liquid columns. The adapted infinitesimal induced axial strain reads as

$$\varepsilon_z^{\text{sim}} = \begin{cases} -\frac{2}{E_{\parallel}} \frac{\phi}{1-\phi} \left[(1 - \nu_{\parallel\perp}) p_B + \nu_{\parallel\perp} p_L \frac{z}{h(t)} \right], & \text{if } 0 < z \leq h(t) \\ -\frac{2}{E_{\parallel}} \frac{\phi}{1-\phi} \left[(1 - \nu_{\parallel\perp}) p_B + \nu_{\parallel\perp} p_L \frac{H-z}{h(t)} \right], & \text{if } H - h(t) < z \leq H \\ 0, & \text{if } h(t) < z \leq H - h(t) \end{cases}. \quad (5.50)$$

The macroscopic axial strain is determined from Eq. (2.18) as

$$\begin{aligned}
 \bar{\varepsilon}_{\parallel} &= \frac{u_z^{\text{sim}}(H) - u_z^{\text{sim}}(0)}{H} = \frac{1}{H} \int_0^H \frac{du_z^{\text{sim}}}{dz} dz = \frac{1}{H} \int_0^H \varepsilon_z^{\text{sim}} dz \\
 &= \frac{1}{H} \left(\int_0^{h(t)} \varepsilon_z^{\text{sim}}(z) dz + \int_{H-h(t)}^H \varepsilon_z^{\text{sim}}(z) dz \right) \\
 &= -\frac{2}{E_{\parallel}} \frac{\phi}{1-\phi} [2(1-\nu_{\parallel\perp})p_B + \nu_{\parallel\perp}p_L] \frac{h(t)}{H}.
 \end{aligned} \tag{5.51}$$

Once the imbibition length of the two imbibing liquid columns covers half of the pore matrix length each, i.e., $h(t) = \frac{H}{2}$, the pore matrix is completely filled by liquid. As a result, the Laplace pressure vanishes, and the pore matrix contracts with a magnitude of

$$\bar{\varepsilon}_{\parallel}^{\text{jump}} = \frac{\nu_{\parallel\perp}}{E_{\parallel}} \frac{\phi}{1-\phi} p_L. \tag{5.52}$$

Given the proportionality between the contractive strain and the Poisson ratio, the anticipated effect is small. The final axial strain upon complete filling of the pore matrix is

$$\bar{\varepsilon}_{\parallel}^{\text{final}} = -\frac{2}{E_{\parallel}} \frac{\phi}{1-\phi} (1-\nu_{\parallel\perp}) p_B, \tag{5.53}$$

which is identical to the final axial strain in Sec. 5.2.2. Furthermore, the observed strain equals the final lateral strain $\bar{\varepsilon}_{\perp}^{\text{final}}$ if the lateral and axial Young moduli would be identical, i.e., $E_{\parallel} = E_{\perp}$.

5.3 Measuring the induced pore matrix strain in the MD simulations

This section outlines the methodology for determining the laterally and axially induced deformation dynamics in the conducted imbibition simulations.

To measure the dynamics of laterally induced deformation $\bar{\varepsilon}_{\perp}(t)$, the simulation box extension lateral to the cylindrical nanopores $L_{\perp}(t)$ offers a convenient way to determine the average lateral engineering strain through

$$\bar{\varepsilon}_{\perp}(t) = \frac{L_{\perp}(t) - L_{\perp}^0}{L_{\perp}^0}, \tag{5.54}$$

where $L_{\perp}^0$ denotes the initial lateral simulations box extension. Note that due to the coupling of L_x and L_y each of the two simulation box extensions can be chosen to be $L_{\perp}$.

In comparison, measuring the axially induced deformation dynamics $\bar{\varepsilon}_{\parallel}(t)$, is a more

complex process. The complexity arises because the axial extension of the pore matrix is not precisely defined and is subject to thermal fluctuations of the constituent atoms. Therefore, the axial engineering strain $\bar{\varepsilon}_{\parallel}(t)$ was estimated based on the axial strain between two groups of atoms within the pore solid at the end of the pore matrix. The atom groups consisted of $n_1 = 228$ and $n_2 = 217$ silicon and oxygen atoms situated at the last 5 Å of the axial pore matrix endings. This region of the pore matrix surface had already been in contact with water molecules prior to the initiation of the imbibition process. Therefore, any change in the separation between the two atomic groups must arise from induced strain caused by the wetting of other atoms. Absolute differences in the axial position components $z_{ij} = |z_i - z_j|$ for each atom pair were calculated from two atom groups, yielding a total of $n = n_1 n_2 = 49476$ axial difference components. From these n differences, a value for the axial strain, $\bar{\varepsilon}_{\parallel}(t)$, was estimated for each time step. The value was determined by taking the average of the axial atom distance components through

$$\bar{\varepsilon}_{\parallel}(t) \approx \frac{1}{n} \sum_{ij}^n \frac{z_{ij}(t) - z_{ij}^0}{z_{ij}^0}, \quad (5.55)$$

where z_{ij}^0 are the initial axial differences between the atom groups. Fig. 5.3 depicts a sketch of the method to determine the axial strain.

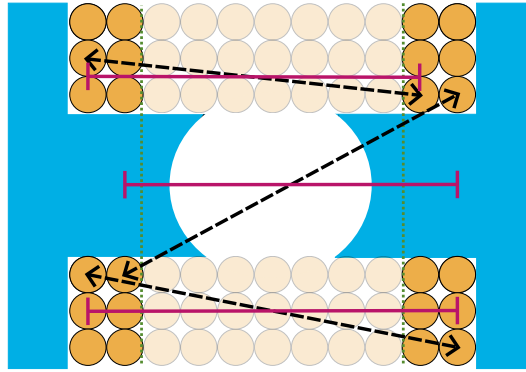


Figure 5.3: Sketch of the method to determine the axial engineering strain. The silicon and oxygen atoms contained in the solid are represented as yellow circles. The solid atoms within the last 5 Å of the pore matrix are separated from the rest of the solid atoms by the dotted green line. The axial distance components from all possible $n = 12 \times 12 = 144$ atom pairs would be utilized for the calculation of the induced axial strain. Here, three of the possible 144 atom pairs are marked by the dashed black arrows. The axial distance components, i.e., the values for the $z_{ij}(t)$, are marked by the purple bars. Finally, the axial strain would be determined as the average strain in each of the 144 axial distance components with respect to the initial atom configuration.

5.4 Dynamics of the imbibition-induced elastocapillarity: Theory vs. simulations

To test the developed theory of imbibition-induced elastocapillarity, the theoretical predictions were compared to the pore matrix deformations observed in the MD simulations during the imbibition of water into MCM-41. As discussed in Ch. 3, the coupling of the lateral simulation box axes caused the simulated pore matrix to deviate from elastic deformation properties in the lateral direction. Specifically, the porous system exhibited in one direction stress in a strain-free equilibrium state. However, as demonstrated below, numerous qualitative predictions of the elastic model concerning imbibition-induced deformation dynamics agree with observations from the imbibition simulations. Therefore, the observed deviations from elastic deformation theory are hypothesized to have a negligible effect on the qualitative outcomes of the simulated imbibition-induced elastocapillarity. However, the effect on the quantitative simulation outcomes remains unclear.

To obtain the dynamics of the laterally observed macroscopic strain, $\epsilon_{\perp}(t)$, and axially observed macroscopic strain, $\epsilon_{\parallel}(t)$, of the pore matrix during the imbibition process, the observed simulation data was analyzed following the method described in Sec. 5.3. The measured strains are depicted in Fig. 5.4 (c) for the lateral and in Fig. 5.4 (d) for the axial strain, respectively. The error bars indicate the standard deviations of the observed strain between the individual simulations. The different methods to determine the strain explain the different magnitudes of the error bars for the measurements. Specifically, the axial strain, determined through the positions of individual atoms, was influenced by the thermal motion of the atoms, resulting in a larger standard deviation. In contrast, the lateral strain, measured through the extension of the simulation box, was less susceptible to fluctuations, resulting in smaller deviations between simulations.

The observed results of the strain dynamics in the lateral and axial pore matrix directions were divided into three distinct regimes, as illustrated with the background coloration in Fig. 5.4. The induced strain during the active imbibition process was observed from 0 ps to 780 ps during the simulation. The active imbibition process is marked as regime I (yellow). Regime II (blue) marks the time following the termination of the imbibition process and the subsequent equilibration of the porous matrix to its final strain state. For the laterally observed strain, the equilibration occurred over a period of 620 ps, starting from 780 ps until 1400 ps. The equilibration of the pore matrix in the axial direction was observed to occur more rapidly, over a time span of 320 ps, from 780 ps to around 1100 ps. In the red regime III, the pore matrix was fully equilibrated. With the exception of thermal fluctuations in this

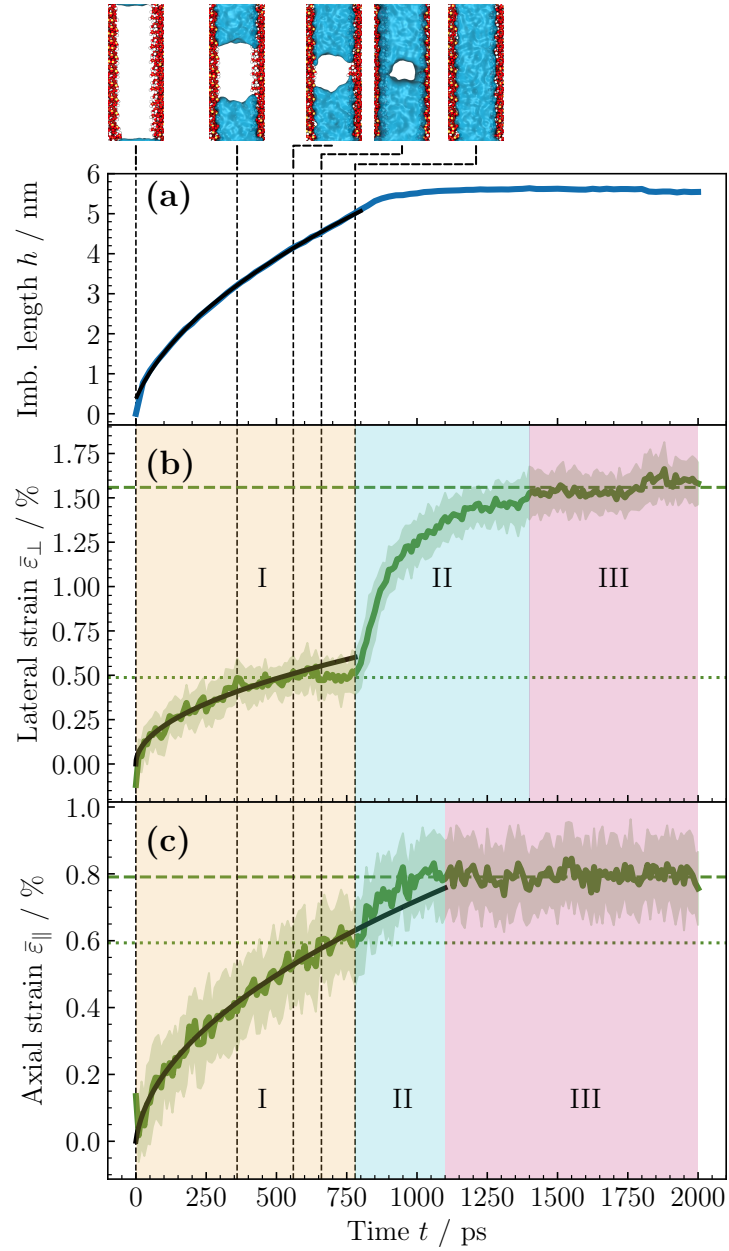


Figure 5.4: Imbibition induced strain in dependence of the imbibition dynamics. (a) Imbibition length of the water column $h(t)$ into the pore space in dependence of the time t (blue) with a fit of the modified Lucas-Washburn model (black). The five snapshots above (a) depict slices through the MCM-41 pore during the imbibition process from left to right at 0 ps, 360 ps, 560 ps, 660 ps and 780 ps. Observed lateral (b) and axial (c) strain of the pore matrix in dependence of the time t (green) with fits of Eq. (5.59) (black). The final induced strain at complete pore filling before and after equilibration is marked by the horizontal dotted and dashed green line, respectively. The background coloration distinguishes the different strain regimes, i.e., the strain during the active imbibition process I (yellow), the strain during the equilibration phase II (blue), and the final strain after equilibration III (red).

phase of the simulation, no additional strain dynamics were discernible until the end of the simulation at 2000 ps.

The deformation of the porous matrix was dominated by expansive behavior during the simulations. However, the precise nature of the expansion differed along the lateral and axial directions of the pore matrix. The subsequent sections provide a thorough examination of the induced strain dynamics. To provide a more concise explanation of the physical effects of the deformation dynamics, the observed strains are not discussed in the chronological order. Instead, they are discussed starting with the final time regime III, followed by the regimes I and II.

■ Regime III: Final strain of pore matrix in equilibrium

In this section, the observed strain of the completely water-filled and fully equilibrated pore matrix is discussed. Once the pore matrix was completely filled and equilibrated, it exhibited a final static expansive strain in the lateral and axial directions. This is depicted in regime III of Fig. 5.4 (b) and (c). The dashed horizontal green lines indicate the final observed static strain in the pore matrix. The final strain in the lateral direction was measured at $\bar{\epsilon}_{\perp}^{\text{final}} = 1.56\%$, and the final strain in the axial direction was measured at $\bar{\epsilon}_{\parallel}^{\text{final}} = 0.79\%$.

Previous studies examined the complete filling of ordered, cylindrical pores by adsorption and predicted that the final lateral and axial strain of ordered, cylindrical mesopores would be equal in magnitude.^{14,93,94} The results of the presented simulations contradict this assessment. The final laterally observed pore matrix strain was approximately twice the axially observed pore matrix strain, i.e., $\frac{\bar{\epsilon}_{\perp}^{\text{final}}}{\bar{\epsilon}_{\parallel}^{\text{final}}} = 1.97$. It is important to note that, in contrast to the theory presented in this thesis, the prior studies assumed Young's modulus to be isotropic. In this thesis, Young's modulus is assumed to be anisotropic. As a result, theoretical predictions for the final strains, as determined by Eq. (5.49) and Eq. (5.53), do not predict equal strains, but equal induced stresses

$$\sigma_{\perp}^{\text{final}} = \frac{\bar{\epsilon}_{\perp}^{\text{final}} E_{\perp}}{1 - \nu_{\perp\parallel}} = -2 \frac{\phi}{1 - \phi} p_B \quad (5.56)$$

and

$$\sigma_{\parallel}^{\text{final}} = \frac{\bar{\epsilon}_{\parallel}^{\text{final}} E_{\parallel}}{1 - \nu_{\parallel\perp}} = -2 \frac{\phi}{1 - \phi} p_B. \quad (5.57)$$

From Eq. (5.56) and Eq. (5.57) the final stresses in the simulations were determined to be $\sigma_{\perp}^{\text{final}} = 0.59$ GPa and $\sigma_{\parallel}^{\text{final}} = 0.64$ GPa. Since the induced stresses were found to be nearly equal in magnitude, the simulations support the theoretical prediction of equal stresses in the lateral and axial direction of the completely filled pore matrix. The total evolution of the

stress induced into the pore matrix during the imbibition simulation is depicted in Fig. 5.5 in the lateral (dark green) and the axial (light green) directions.

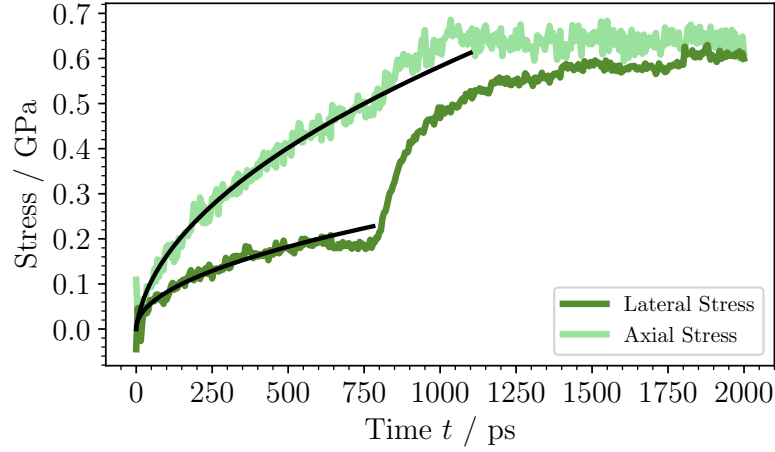


Figure 5.5: Imbibition-induced stress in lateral (dark green) and axial (light green) direction of the pore matrix in dependence of the imbibition time.

From Eq. (5.56) and Eq. (5.57) the effective Bangham pressure and, subsequently, the release of surface stress was determined as $p_B^{\text{final},\perp} = -1233$ bar in the lateral pore matrix direction and $p_B^{\text{final},\parallel} = -1334$ bar in the axial pore matrix direction. The superscripts indicate that the effective Bangham pressure was determined from the final observed strains. According to Eq. (2.33), the surface stress release values were calculated as $\Delta f^{\text{final},\perp} = -203 \text{ mJ m}^{-2}$ and $\Delta f^{\text{final},\parallel} = -220 \text{ mJ m}^{-2}$. Consequently, the determined values exhibited good mutual agreement. However, independent verification of the obtained values is challenging.

An approach to obtain an independent estimate of surface stress release is to estimate the surface energy release $\Delta\gamma$ from Young's relation Eq. (2.24) and then compare that quantity to surface stress release under the assumption of the Bangham approximation $\Delta f \approx \Delta\gamma$. To calculate the surface energy release, the asymptotic dynamic contact angle $\theta_{\text{LW}} = 51.96^\circ$, determined from the modified Lucas-Washburn imbibition model for infinite times, was substituted into the Young relation to obtain a surface energy release of

$$\Delta\gamma = -\gamma \cos \theta = -43 \text{ mJ m}^{-2}. \quad (5.58)$$

The surface energy release value determined was significantly lower than the surface stress release determined with the elastic strain model. However, this discrepancy may also arise from an inadequate application of the Young relation to determine the surface energy release. As discussed in Ch. 4, the snapshots of simulation in Fig. 5.4 and other MD simulation

studies⁷⁵ as well as experimental results⁷⁴ support the theory that the comparatively brief simulated imbibition time prevented the dynamic contact angle from converging to the equilibrium contact angle of $\theta = 0^\circ$. For Young's relation to correctly predict the surface energy release, the dynamic contact angle must equal the equilibrium contact angle, and the equilibrium contact angle must be greater than $> 0^\circ$. Therefore, the significant difference between the two values indicates that the equilibrium contact angle was not reached. Hence, Young's relation may not be applicable in this case, and the surface energy release is probably greater than the determined value of $\Delta\gamma = -43 \text{ mJ m}^{-2}$.

Another approach to verify the determined values for the surface stress release is to compare them with reported surface stress release values found in literature. Unfortunately, no reported values for the release of surface stress for silica upon water wetting were found. However, Brunauer et al.⁷⁴ reported a surface energy of $\gamma_{sl} = 130 \text{ mJ m}^{-2}$ for water-wetted amorphous silica and $\gamma_{sv} = 260 \text{ mJ m}^{-2}$ for the silica vapor interface. Assuming the Bangham approximation, the surface stress release is estimated as $\Delta f \approx \Delta\gamma = -130 \text{ mJ m}^{-2}$. In comparison, the estimated surface stress release determined from the induced strain is almost a factor two larger. The cause of this discrepancy is difficult to determine, as several factors could contribute. One potential reason could be inaccuracies in the surface energies reported in the literature and the subsequent estimate of the surface stress release. Another potential explanation could be an inaccurate modeling of the water-silica interactions in the simulations or the above discussed deviations from the properties of elastic deformation. Finally, the assumption of a perfectly smooth cylindrical pore geometry may not be accurate. In particular, due to roughness at the pore solid surface, the surface area of the simulated pores may exceed the surface area assumed by the RVE. Surface roughness would result in larger local curvatures at the inner surface of the pore and a higher surface-to-volume ratio ζ_{wetted} . Both effects would amplify the Bangham effect in the lateral and axial directions. As a result of the significant uncertainties, the surface stress release obtained from the simulations can only be said to approximately coincide with realistic values.

■ Regime I: Dynamically induced strain during the imbibition process

This section discussed the strain dynamics observed during the active imbibition process. The time period of the imbibition process is indicated by the yellow background I in Fig. 5.4. During the imbibition process, both observed strain directions, i.e., the lateral pore matrix direction in Fig. 5.4(b) and the axial pore matrix direction in Fig. 5.4(c), exhibited expansive deformations. After 780 ps the pore space was entirely filled with water and the laterally induced strain reached $\bar{\epsilon}_{\perp}^{\text{filled}} = 0.49\%$ while the axially induced strain reached

$\bar{\varepsilon}_{\parallel}^{\text{filled}} = 0.59\%$. The strain magnitudes are indicated by the horizontal dotted lines in Fig. 5.4.

The strain dynamics during the imbibition process are predicted by Eq. (5.43) in the lateral direction and by Eq. (5.51) in the axial direction. The theoretical predictions indicate that the strain dynamics should be proportional to the imbibition length of the water column and thus to the imbibition dynamics, i.e., $\bar{\varepsilon}_{\perp}(t) \propto \frac{h(t)}{H}$ and $\bar{\varepsilon}_{\parallel}(t) \propto \frac{h(t)}{H}$. As discussed in Sec. 4.4, the viscosity-dominated imbibition dynamics are well described by the Lucas-Washburn and the modified Lucas-Washburn model. If the contact angle is constant during the imbibition process, the Laplace pressure remains constant and the entire time dependence of the induced strain can be explained by the evolution of the imbibition length, i.e., $\bar{\varepsilon}_{\perp}(t) \propto \sqrt{t}$ and $\bar{\varepsilon}_{\parallel}(t) \propto \sqrt{t}$. However, the dynamic contact angle is only constant in the original Lucas-Washburn model. In the modified Lucas-Washburn model, an explicit change in the dynamic contact angle during the imbibition process is assumed. With a dynamic contact angle $\theta_{\text{dyn}}(t)$, the Laplace pressure $p_L \propto -\cos(\theta_{\text{dyn}}(t))$ in the water columns becomes explicitly time-dependent. The evolution of Laplace pressure under the assumption of the modified Lucas-Washburn model is depicted in Fig. 5.6 as purple curve. For comparison, constant Laplace pressures are shown for three cases. The yellow line corresponds to a contact angle of $\theta_{\text{Max}} = 0^\circ$ yielding a Laplace pressure of $p_L^{\text{Max}} = -840$ bar. The black line corresponds to the Laplace pressure $p_L^{\text{LW}} = -518$ bar determined from the contact angle of the original Lucas-Washburn model $\theta_{\text{LW}} = 51.96^\circ$. The cyan line corresponds to a Laplace pressure of $p_L^{\text{Bos}} = -366$ bar determined from the contact angle of the Bosanquet model $\theta_{\text{Bos}} = 64.19^\circ$. Specifically, for the first simulated time period of capillary-flow ranging from 100 ps to 200 ps, the Laplace pressure is predicted to be considerably lower for the modified Lucas-Washburn model compared to any of the other imbibition models assuming a constant contact angle.

However, to describe the temporal dependence of the pore matrix strain, it is crucial to note that the stress is induced exclusively at the inner pore surface that is covered by the imbibing water column. Therefore, the influence of the changing contact angle on the strain dynamics at the beginning of the imbibition process is mitigated by the short imbibition length of the imbibing water column. The Laplace pressure weighted by the normalized imbibition length $\frac{h(t)}{H}$ for the different imbibition models is depicted in Fig. 5.7. It is evident from Fig. 5.7, that the effect of the dynamic contact angle on the induced strain is markedly reduced by the short imbibition length. For the predominant duration of the imbibition process, the weighted Laplace pressure of the modified Lucas-Washburn model was comparable to that of the original Lucas-Washburn and the Bosanquet models. Consequently, the strain observed from the modified Lucas-Washburn model should exhibit a temporal behavior similar to that of models with constant contact angles. Therefore, it can be assumed that the strain

dynamics are in good approximation proportional to $\sqrt{t}$.

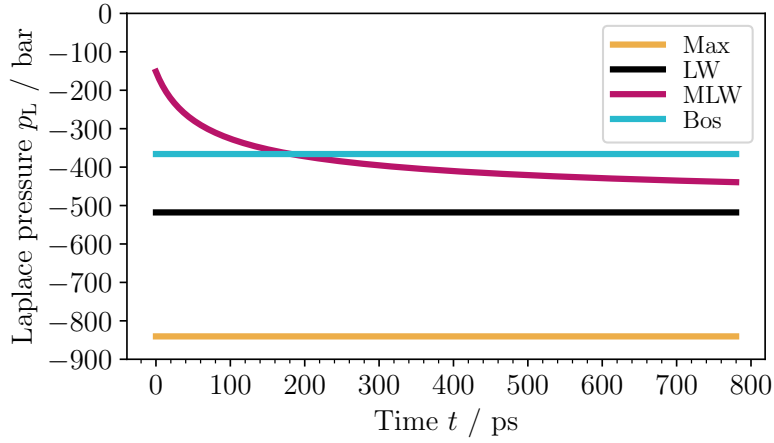


Figure 5.6: Predicted evolution of Laplace pressures for different imbibition models. These are the Lucas-Washburn model $p_L^{\text{LW}} = -518$ bar (black), the modified Lucas-Washburn model p_L^{MLW} (purple), and the Bosanquet model $p_L^{\text{Bos}} = -366$ bar (cyan). The maximally possible Laplace pressures $p_L^{\text{max}} = -840$ bar, assuming a contact angle of 0° , is included for comparison (yellow).

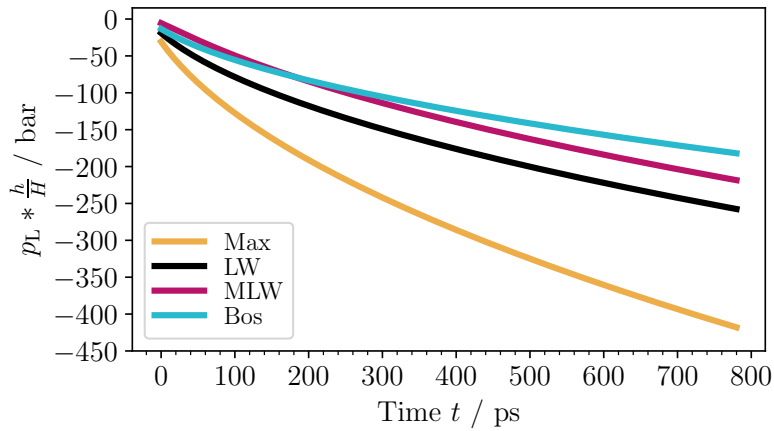


Figure 5.7: Imbibition length weighted Laplace pressures for different imbibition models. These are the Lucas-Washburn model (black), the modified Lucas-Washburn model (purple), and the Bosanquet model (cyan). The weighted pressure for a contact angle of 0° is depicted in yellow.

To test the predicted $\sqrt{t}$ proportionalities of the strain dynamics, a $\sqrt{t}$ dependency was fitted to the observed strain in the form of

$$\bar{\varepsilon}_{\perp/\parallel}(t; c_{\perp/\parallel}, t_0, \varepsilon_0) = c_{\perp/\parallel} \sqrt{t - t_0} + \varepsilon_0, \quad (5.59)$$

where $c_{\perp/\parallel}$, t_0 , and ε_0 were free fit parameters. The two resulting fits to the observed

laterally and axially induced strains are depicted as black curves in Fig. 5.4 (c) and Fig. 5.4 (d), respectively. The resulting fit parameters for the lateral strain dynamics were $c_{\perp} = 2.15 \times 10^{-2} \text{ \%}/\sqrt{\text{ps}}$, $t_0 \approx 0 \text{ ps}$, and $\varepsilon_0 = 0.12 \text{ \%}$, while the fit parameters for the axial strain were $c_{\parallel} = 2.42 \times 10^{-2} \text{ \%}/\sqrt{\text{ps}}$, $t_0 = -3.5 \text{ ps}$, and $\varepsilon_0 = -0.18 \text{ \%}$. Note that the strains depicted in Fig. 5.4(b) and Fig. 5.4(c) were offset by the ε_0 values obtained from the fit, such that the depicted deformations start from $\varepsilon_0 = 0$. As evident from Fig. 5.4 (c) and Fig. 5.4 (d), the induced strain dynamics align with Eq. (5.59), affirming that the dynamically induced strains do in fact evolve proportional to the imbibition dynamics.

By combining Eq. (5.43) and Eq. (5.51) with the Lucas-Washburn imbibition model defined in Eq. (4.9), the strain coefficients $c_{\perp}$ and $c_{\parallel}$ can be represented by

$$c_{\perp} = \frac{2}{E_{\perp}} \frac{\phi}{1-\phi} [-2(1-\nu_{\perp\parallel})p_B + p_L] c_{\text{LW}}^{\text{norm}} \quad (5.60)$$

and

$$c_{\parallel} = -\frac{2}{E_{\parallel}} \frac{\phi}{1-\phi} [2(1-\nu_{\parallel\perp})p_B + \nu_{\parallel\perp}p_L] c_{\text{LW}}^{\text{norm}}, \quad (5.61)$$

respectively. Here, $c_{\text{LW}}^{\text{norm}} = \frac{c_{\text{LW}}}{H} = 2.04 \times 10^{-2} \text{ ps}^{-\frac{1}{2}}$ is defined as the normalized imbibition coefficient. To determine the normalized imbibition coefficient, the imbibition length was normalized to pore filling fractions. That is, the normalized imbibition length was set to one at the time where the pore was entirely filled by the water columns after 780 ps simulation time. Subsequently, the normalized imbibition coefficient was determined by fitting Eq. (4.22) to the normalized imbibition length. This approach eliminated the requirement to determine a precise total imbibition length H in order to obtain $c_{\perp}$ and $c_{\parallel}$.

Solving Eq. (5.60) and Eq. (5.61) for the the effective Bangham pressure p_B^{dyn} and the Laplace pressure p_L^{dyn} leads to

$$p_B^{\text{dyn}} = -\frac{1-\phi}{\phi} \frac{E_{\parallel}c_{\parallel} + E_{\perp}c_{\perp}\nu_{\parallel\perp}}{4(1-\nu_{\perp\parallel}\nu_{\parallel\perp})c_{\text{LW}}^{\text{norm}}} \quad (5.62)$$

and

$$p_L^{\text{dyn}} = \frac{1-\phi}{\phi} \frac{E_{\perp}c_{\perp}(1-\nu_{\parallel\perp}) - E_{\parallel}c_{\parallel}(1-\nu_{\perp\parallel})}{2(1-\nu_{\perp\parallel}\nu_{\parallel\perp})c_{\text{LW}}^{\text{norm}}}, \quad (5.63)$$

where the superscript *dyn* indicates that the two values were determined from the dynamically induced strain.

By using the obtained coefficients $c_{\perp}$ and $c_{\parallel}$ to determine the induced Laplace pressure, a value of $p_L^{\text{dyn}} = -666 \text{ bar}$ was obtained. This value exceeds the Laplace pressure obtained for the imbibition models of $p_L^{\text{Bos}} = -366 \text{ bar}$ and $p_L^{\text{LW}} = -518 \text{ bar}$. At the same time, it is

smaller than the maximum estimated value of $p_L^{\max} = -840$ bar for a constant contact angle of $\theta_{\max} = 0^\circ$. A potential explanation for the discrepancy between the predicted Laplace pressures is the deviation of the pores from the assumed ideal cylindrical geometry. These deviations could have lead to Laplace pressures in the imbibing liquid that were higher than predicted by a cylindrical pore geometry. However, altogether the obtained values for the Laplace pressure were in the right order of magnitude.

From Eq. (5.62) an effective Bangham pressure of $p_B^{\text{dyn}}(r) = -672$ bar was obtained. A surface stress release of $\Delta f^{\text{dyn}} = -111 \text{ mJ m}^{-2}$ was calculated from the effective Bangham pressure. The calculated surface stress release aligns with the estimated surface stress of $\Delta f \approx -130 \text{ mJ m}^{-2}$ derived from the surface energy values reported by Brunauer et al.⁷⁴ However, compared to the surface stress releases determined from the final expansive strain of the equilibrated pore matrix, i.e., $\Delta f^{\text{final},\perp} = -203 \text{ mJ m}^{-2}$ and $\Delta f^{\text{final},\parallel} = -220 \text{ mJ m}^{-2}$, the dynamically determined surface stress release was of significantly lower magnitude. A potential explanation for this discrepancy could be a time delay in the equilibration of the pore matrix to the induced surface stress upon wetting. The delay in pore matrix equilibration to the induced stress would lead to additional expansive deformations after the pore space was completely filled by water. These expansive deformations would be observed in addition to the effect of the Laplace jump. The anticipated additional strain during the equilibration phase, $\bar{\epsilon}_{\perp}^{\text{delayed}}$ and $\bar{\epsilon}_{\parallel}^{\text{delayed}}$, was estimated by rescaling the observed final strain in lateral and axial directions with the difference between the determined effective Bangham pressures

$$\bar{\epsilon}_{\perp}^{\text{delayed}} = \bar{\epsilon}_{\perp}^{\text{final}} \frac{(p_B^{\text{final},\perp} - p_B^{\text{dyn}})}{p_B^{\text{final},\perp}} \quad (5.64)$$

and

$$\bar{\epsilon}_{\parallel}^{\text{delayed}} = \bar{\epsilon}_{\parallel}^{\text{final}} \frac{(p_B^{\text{final},\parallel} - p_B^{\text{dyn}})}{p_B^{\text{final},\parallel}}. \quad (5.65)$$

The expected delayed lateral and axial expansions are calculated with Eq. (5.64) and Eq. (5.65) to $\bar{\epsilon}_{\perp}^{\text{delayed}} = 0.71 \%$ and $\bar{\epsilon}_{\parallel}^{\text{delayed}} = 0.39 \%$, respectively. This additional expansive contribution to the total strain is thus expected to manifest during the equilibration phase of the pore matrix in regime II and is discussed in the next section.

During the imbibition process, two deviations of the observed strain dynamics from the functional form of Eq. (5.59) were observed. One deviation occurred during the initial 20 ps of the imbibition simulation in the lateral and axial direction. During the initial stages of the imbibition process, significant fluctuations in strain were observed in both directions of the pore matrix. Fig. 5.8a and Fig. 5.8b show the induced lateral strain during the first

50 ps of the imbibition process in the lateral and axial pore matrix direction, respectively. The strain dynamics expected from the deformation model are indicated as black curves. In the lateral direction, the strain fluctuated around the deformation predicted from the model with a maximal amplitude of around 0.12 %. In the axial direction, a rapid initial expansion of about 0.15 % was observed. Following this expansion, a more pronounced contraction of about 0.25 % was observed before the strain began to align with the elastic model. The precise origin of the fluctuations remains uncertain. The fluctuations could result from physically sound processes, such as line tension exerted by forming menisci, or they could represent simulation artifacts, for instance, from the initial equilibration of the pore matrix. Although the pore matrix was equilibrated before the imbibition process commenced, the entry of water was artificially prevented. Therefore, the pore matrix may not have been in true equilibrium with the water reservoir. As a result, additional, unphysical equilibration effects during the initial stages of imbibition might have occurred, possibly manifesting as the observed fluctuations. Consequently, the fluctuations are presumed to be simulation artifacts in the remainder of this thesis.

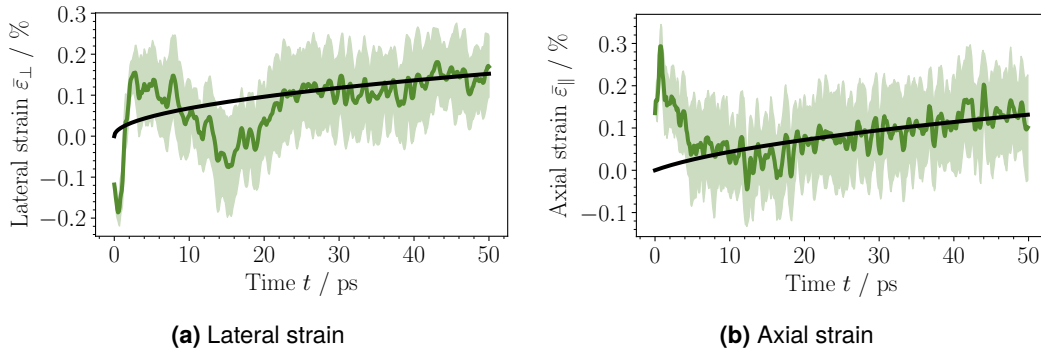


Figure 5.8: Initial observed deformation dynamics during the first 50 ps of the imbibition simulation (green). The black curve represents the fit of Eq. (5.59) to the observed strains (black).

The second observed deviation from the deformation model occurred during the final moments of the imbibition process, from approximately 660 ps to 780 ps in the lateral direction of the pore matrix. During this period, the expansive behavior stagnated. This contradicts the models predictions of continuous expansion. The deviation from the model was likely caused by a change in the dynamic contact angle θ_{dyn} during the final stages of the imbibition process. As illustrated in the second-to-last snapshot in Fig. 5.4 at 660 ps, the two menisci collided at the surface of the pore during that time. The contact of the menisci led to a decrease in the contact angle. This reduction of the contact angle is expected to have led to an increase in Laplace pressure within the imbibing liquid, resulting in an

increased contractile contribution from the Laplace pressure in the liquid. Therefore, the contractile contribution of the increased Laplace pressure counterbalanced the expansive behavior induced by the effective Bingham pressure during the final stages of the active imbibition process, resulting in a stagnation of lateral expansion.

■ **Regime II: Pore matrix equilibration after complete pore filling**

After 780 ps, the active imbibition process concluded. At this point, the pore space was completely filled with water. Subsequently, additional expansive behavior was observed in the lateral and axial directions during the equilibration of the pore matrix. The equilibration period is indicated in Fig. 5.4 (b) and (c) as regime II with a blue background coloration. The expansive deformation during equilibration was more pronounced in the lateral direction than in the axial direction. In addition, the deformation process lasted longer in the lateral than in the axial direction. Specifically, the equilibration process took approximately 620 ps in the lateral direction. During this time, the pore matrix expanded by an additional $\Delta\bar{\varepsilon}_{\perp}^{\text{jump}} = 1.07\%$, until a final strain of around $\bar{\varepsilon}_{\perp}^{\text{final}} = 1.56\%$ was reached. In contrast, in the axial direction the matrix expanded over a period of approximately 320 ps by $\Delta\bar{\varepsilon}_{\parallel}^{\text{jump}} = 0.20\%$, reaching a final strain of approximately $\bar{\varepsilon}_{\parallel}^{\text{final}} = 0.79\%$.

The significant expansive lateral strain observed during the equilibration phase can be attributed to the disappearance of the water menisci upon complete filling of the pore space, which in turn led to a disappearance of the contractive Laplace pressure. The disappearance of the contractile Laplace pressure resulted in a sudden expansive equilibration of the pore matrix in the lateral direction. This phenomenon was predicted by the developed deformation model and called Laplace jump. The Laplace pressure required to produce a Laplace jump of $\Delta\bar{\varepsilon}_{\perp}^{\text{jump}} = 1.07\%$ was calculated from Eq. (5.48) to be $p_L^{\text{jump}} = -1264$ bar. This value is nearly twice that obtained from the imbibition-induced strain dynamics of $p_L^{\text{dyn}} = -666$ bar.

Some of the discrepancy can be attributed to the increase of Laplace pressure in the liquid during the collision of the menisci at the pore surface at the final moments of the imbibition process discussed previously. However, assuming a maximal contact angle of $\theta_{\text{Max}} = 0^\circ$, the Laplace pressure was calculated to be $p_L^{\text{Max}} = -840$ bar. As a result, the change of Laplace pressure in the liquid is not potent enough to explain the entire discrepancy.

In the previous section, a discrepancy was identified between the effective Bingham pressures calculated from the strain dynamics and the pressure derived from the final static strain of the pore matrix at equilibration. A temporal delay in the equilibration of the pore matrix was proposed as a potential explanation for this discrepancy. An additional required expansive lateral strain of 0.71% was estimated from the delayed equilibration of the pore

matrix. Consequently, a delayed Bangham effect that acts expansively, in combination with the Laplace jump, could explain the large expansive deformations observed at the time of the Laplace jump.

By subtracting the suspected additional delayed Bangham pressure from the observed expansive lateral strain during the equilibration period, the strain attributed to the Laplace jump decreases to $\Delta\bar{\varepsilon}_{\perp}^{\text{jump}} - \Delta\bar{\varepsilon}_{\perp}^{\text{delayed}} = 1.07\% - 0.71\% = 0.36\%$. This expansive strain corresponds to the disappearance of a Laplace pressure of $p_L^{\text{jump,delayed}} = -426$ bar. While lower, this value aligns more closely with the Laplace pressure of $p_L^{\text{dyn}} = -666$ bar determined from the strain dynamics. In addition, the value aligns more closely with the final Laplace pressure of $p_L^{\text{LW}} = -518$ bar determined from the modified Lucas-Washburn model at the end of the imbibition process. The improved agreements between the respective Laplace pressures support the theory that additional strain effects from a delayed Bangham effect are observed after the pore space is fully filled by water. Therefore, the assumption of a continuous strain-stress equilibrium of the pore matrix during the imbibition process appears to be invalid.

In the axial pore matrix direction an additional expansive strain of $\Delta\bar{\varepsilon}_{\parallel}^{\text{jump}} = 0.20\%$ was observed. This observed expansive behavior is not explained by the theoretical model presented in Sec. 5.2. In contrast, a contraction of the pore matrix in the axial direction is expected from the Poisson effect. This contraction is expected to be proportional to the Poisson ratio scaled Laplace pressure. Assuming the previously determined value of $p_L^{\text{jump,delayed}} = -426$ bar for the vanishing Laplace pressure, a contraction of approximately -0.05% in the axial direction is anticipated. In accordance with the lateral deformations, this discrepancy may also be explained by a delay in the equilibration of the pore matrix to the surface stress release. In the previous section, an additional expansive contribution of $\bar{\varepsilon}_{\parallel}^{\text{delayed}} = 0.39\%$ to the axial strain in the equilibration phase was calculated from the difference between the effective Bangham pressure determined from the dynamic strain and the final static strain observed in equilibrium. The combination of contractile and expansive effects results in an expected expansive strain of $\Delta\bar{\varepsilon}_{\parallel}^{\text{jump}} - \Delta\bar{\varepsilon}_{\parallel}^{\text{delayed}} = 0.39\% - 0.05\% = 0.34\%$. This value is larger than the actual additional expansive strain of 0.20% . The observed discrepancy may be attributed to inaccuracies in the determined strain and surface stress release values. Conclusively, the assumption that the pore matrix equilibrates with delay could explain the observed expansive strain, which contrasts with the contractile strain predicted by the elastic deformation model.

Chapter 6

LIQUID-TO-SOLID PHASE TRANSITIONS WITH THE PRINCIPLE OF MAXIMUM RELATIVE ENTROPY

As demonstrated in the previous Chs. 3, 4 and 5, MD simulations provide a robust method to examine the behavior of water during capillary flow and the effects of imbibition-induced elastocapillarity within cylindrical, ordered mesopores. The phase transition of water from liquid to solid within these structures also presents a scientifically compelling process for simulation. However, as outlined in the subsequent Sec. 6.1, simulating liquid-to-solid phase transitions in MD simulations poses significant challenges. In Sec. 6.2, an algorithm is presented that combines information from RDFs with MD simulations via the principle of maximum relative entropy. Sec. 6.3 demonstrates that this algorithm can structurally bias liquid systems or mediate liquid-to-solid phase transitions in MD simulations. Parts of the work and figures presented hereafter have already been published in

[101] **L. Dammann**, R. Kohns, P. Huber & R. H. Meißner, Maximum Entropy-Mediated Liquid-to-Solid Nucleation and Transition. *Journal of Chemical Theory and Computation*, 21(4):1997-2011, 2025.

6.1 Liquid-to-solid phase transitions in MD simulations

6.1.1 Relevance of crystallization processes for technology and science

Crystallization processes are of high importance for natural science and technological applications. For example, crystallization processes influence the climate¹⁰², in particular through crystal formation within clouds¹⁰³. Furthermore, they are important in biology^{104,105}, semiconductor manufacturing¹⁰⁶, metal and alloy production¹⁰⁷, and pharmacy¹⁰⁸. Over the past several years there has been a considerable scientific debate regarding the behavior

and atomic structure of ice under confinement in mesoporous systems.^{6,109–120} Additionally, further investigations are necessary to clarify phase-transition-induced elastocapillarity effects, which have been observed in mesoporous materials during liquid-to-solid transitions of water.^{3,121–126} Consequently, the capability to investigate crystallization processes at the atomic level is of broad interest. As demonstrated in Ch. 4 and Ch. 5, MD simulations can be used to investigate the capillary flow of water in mesoporous materials and induced elastocapillarity effects at the atomic scale. Consequently, MD simulations of phase transitions of water within a pore matrix could provide valuable data to enhance the atomic-scale understanding of these transitions in nanoporous confinement and their effects on the porous material. However, as discussed in the following section, the simulation of liquid-to-solid phase transitions in MD simulations is a challenging task.

6.1.2 The problems of crystallization in MD simulations

Classical nucleation theory (CNT), outlined in Sec. 2.5, provides a framework to rationalize the challenges of directly observing liquid-to-solid phase transitions in MD simulations. For a crystallization process to occur in CNT, a critical nucleation seed has to form. To this end, the supercooled liquid system has to overcome the Gibbs free energy maximum depicted in Fig. 2.5. In other words, regions of low sampling probabilities have to be overcome in MD simulations. Depending on the height of the free energy barrier, in real systems with many molecules the stochastic formation of a critical nucleus can occur on time scales of seconds.³² This time range is not feasible to sample in MD simulations with time step sizes on the order of femtoseconds. While stronger cooling of the system lowers the Gibbs free energy barrier, it also reduces the kinetics of the molecules, thus increasing the number of simulated time steps required for the system to reorganize into the critical nucleation seed.

For water in confinement, the challenges become even more severe. Due to the suppression of phase transitions of water in nanoconfinement, significant supercooling of the confined liquid water is required for crystallization to occur. Consequently, the kinetic energy of the water molecules decreases. Furthermore, the system size and complexity cannot be arbitrarily reduced because simulations must include both the pore space and the pore matrix materials. Given the significant challenges associated with modeling crystallization processes in MD simulations, enhanced modeling strategies are required to investigate crystallization in MD simulations. In the subsequent section, some of these strategies are discussed.

6.1.3 Advantages and disadvantages of methods to investigate crystallization processes in MD simulations

Several methods are available to investigate crystallization processes in MD simulations. Each method exhibits a distinct set of advantages and disadvantages. A comprehensive review of these methods would exceed the scope of this work. Therefore, a concise overview of the available methods is provided and their advantages and disadvantages are discussed from a general viewpoint and in the context of crystallization within mesoporous confinement.

A straightforward method to examine crystallization processes in MD simulations involves insertion of crystal seeds into liquid systems.^{127–131} Under appropriate thermodynamic conditions and if the seed exceeds the critical nucleus size, the simulated system crystallizes from the seed. An advantage of the crystal seed insertion method is the simplicity of the approach. However, with crystal seed insertion, MD simulations cannot examine the crystal seed formation process. Additionally, a precise knowledge about the critical nucleus is required in terms of crystal lattice and nucleus form to insert a physically realistic nucleus. This limitation becomes critical when crystallization is investigated in mesopores, because the precise structure of the crystal lattice and the behavior of water with respect to the surface water layer and the crystalline core within the pore space remain uncertain. Additionally, crystallization in mesopores demands extensive simulation times because significant supercooling is required to stabilize the seed, and this supercooling induces slow molecular kinetics.

An alternative to crystal seed insertion is simulated annealing.^{132,133} In simulated annealing, the system temperature is gradually reduced from an initial value above the freezing point to a final value below that point. The procedure aims to drive the system toward the global free-energy minimum. As with crystal seed insertion, this method offers simplicity. However, a key challenge is to determine the optimal cooling rate. Additionally, the quenching process requires considerable computational time, and successful convergence to the appropriate free energy minimum is not guaranteed. As the objective of simulated annealing is to locate a free energy minimum, the approach is structure-agnostic. Consequently, it is infeasible to reproduce metastable crystalline phases. The method is not well-suited for investigating crystallization under strong confinement, as the required supercooling leads to low system kinetics. Crystallization therefore proceeds very slowly, requiring significantly more computational resources for simulations.

More complex methods that generally enable rare event sampling are replica exchange methods.^{134–139} In the default replica exchange method (REM) atomic configurations from independent simulations at different temperatures are exchanged according to the so called

Metropolis-Hastings criterion. The exchange of atomic configurations between systems at different temperatures increases the probability to overcome the free energy barrier. Therefore, REM represents an effective solution to model certain rare events. A key drawback of REM is the requirement for overlapping energy histograms between independent simulations to facilitate configuration exchange. Consequently, multiple parallel simulations may be required. Additionally, like simulated annealing, REM is structure agnostic and cannot target a specific metastable phase. With respect to crystallization studies of water in mesopores, the method is of limited use because the significant required supercooling necessitates a very large set of independent simulations that span the energy interval required to trigger the formation of a critical nucleus.

Finally, certain methods introduce a bias potential into the MD simulation to enhance the probability of forming crystalline atomic structures during the simulation.^{140–147} Two noteworthy methods are umbrella sampling¹⁴⁸ and well-tempered metadynamics¹⁴⁹. The main advantage of these methods lies in their ability to actively steer the system toward the desired configuration. Hence, this configuration may also correspond to a metastable crystalline phase. Furthermore, it is feasible to calculate an estimate of the free energy landscape based on a collective variable (CV). The CV must represent a meaningful degree of freedom that generates a free energy surface distinguishing the liquid and crystalline phases. The requirement of a CV can also be considered a disadvantage, as developing a meaningful CV can be a complex process which requires knowledge about the modeled transition. To obtain an estimate of the free energy surface, it must be explored incrementally. If the free energy barrier is large, the algorithm may require extensive simulation times to mediate a phase transition. In comparison with other approaches, applying a bias potential represents the most effective method to investigate crystallization in mesoporous systems. The method's effectiveness stems from its independence from strong supercooling, which avoids low molecular kinetics. However, developing a single meaningful collective variable remains challenging because of the limited structural information on crystalline water in mesopores. Given these challenges, reliance on MD simulation alone to investigate crystallization in mesopores may not represent the most effective strategy. However, MD simulations are not the sole means of obtaining insights regarding the crystallization of water in mesopores on the atomic scale.

6.1.4 Wide-angle X-ray scattering (WAXS), radial distribution functions (RDF) and MD simulations

WAXS measurements are commonly used to investigate the atomic or molecular structure of matter. Accordingly, in the past, WAXS was also employed to investigate the molecular structure of water in mesoporous confinement.^{109,110,112,115,116,119,150} In the WAXS data, the information about isotropic atomic structures, e.g., unordered atoms or a large number of crystallites with different orientations, is encoded in the so called structure factor function $S(q)$, which is determined by the Debye equation.¹⁵¹ Here, q is the length of the wavevector of the scattered coherent X-rays. The structure factor function $S(q)$ can be directly related to the radial distribution function $g(r)$ of an atomic system by applying a Fourier transform.¹⁵² The RDF of a material provides information about the average radial inter-distances r of atoms within the material. Note that the naming convention for the RDF varies within different scientific communities. Another commonly used name for the RDF is the pair distribution function (PDF). Unfortunately, the RDF is not unambiguously associated with a specific atomic structure. In other words, a single RDF can be created by a variety of atomic structures. Consequently, determining atomic and molecular structures from WAXS measurements and the obtained RDFs poses an ill-posed inversion problem. Nonetheless, the RDF of the atomic system contains a significant amount of information regarding the atomic configurations. Therefore, it is natural to ask whether this information could support the investigation of phase transition processes in MD simulations.

Multiple approaches exist that combine RDFs or structure factor functions with MD simulations or molecular Monte Carlo sampling methods, either to bias the simulations or to reproduce atomic structures. The Henderson uniqueness theorem¹⁵³ proves that for a fluid system with exclusively identical pair interactions, such as a Lennard-Jones system, each RDF uniquely determines the interaction potentials of the constituents. Therefore, the interaction potential can be exclusively defined as a function of the RDF. For systems with more complex interactions, the structure factor function or RDFs, do not uniquely define the interaction potentials. However, they can be integrated into the simulations as a bias V to the original potential energy $U(\mathcal{R})$ of the simulation. Hence, a new potential energy $U^{\text{biased}} = U + V$ is defined, where the bias potential is chosen such that the functional behavior of the structure factor function or RDFs is reproduced in the simulated system.

One of the simplest computational strategies to generate an atomic structure consistent with the structure factor function or RDF is the Reverse Monte Carlo (RMC) method.^{154–156} This method was explicitly developed to produce atomic configurations from M experimentally observed data points $\mathbf{Y}^{\text{obs}} = \{Y_1^{\text{obs}}, \dots, Y_k^{\text{obs}}, \dots, Y_M^{\text{obs}}\}$. The methodology can be classified

as a molecular Monte Carlo simulation. RMC does not take into account any prior potential energy defined through interaction potentials, but simulates the complete interactions of the particles based on a harmonic bias potential derived from the experimental data, defined as

$$U_{\text{RMC}}^{\text{biased}} = V_{\text{RMC}} = \sum_{k=1}^M \lambda_k \left[Y_k^{\text{obs}} - Y_k(\mathcal{R}) \right]^2. \quad (6.1)$$

In this context, $Y_k(\mathcal{R})$ are the values of the observables of interest calculated from the instantaneous positions $\mathcal{R}$ of the system particles. λ_k is set as a free parameters, that quantify the confidence in the k^{th} observed data point. Molecular Monte Carlo simulations sample atomic configurations from the Boltzmann distribution, which in this case is defined by an M-dimensional Gaussian probability distribution

$$P(\mathcal{R}) \propto e^{-V_{\text{RMC}}} = e^{-\sum_{k=1}^M \lambda_k \left[Y_k^{\text{obs}} - Y_k(\mathcal{R}) \right]^2}. \quad (6.2)$$

As mentioned above, the experimentally determined RDF or structure factor function provides insufficient information to define a unique atomic configuration. In consequence, the sampled atomic configurations cannot be confirmed as physically sound.

The Hybrid Reverse Monte Carlo (HRMC) method and an extension that incorporates MD sampling^{157,158} extend the concept of RMC sampling by incorporating experimental data as the bias potential to the potential energy. The methods combine the experimentally derived RMC potential V_{RMC} with the original potential energy U , yielding a biased potential energy $U_{\text{HRMC}}^{\text{biased}} = U + V_{\text{RMC}}$. Compared with RMC, this approach biases the simulation toward sampling configurations that are physically more plausible.

Both methods, RMC and HRMC, require the selection of parameters λ_k to quantify the bias potential strength of the experimental data on the sampled atomic configurations. The bias potential strength must reflect the uncertainty of the experimental values and of the original potential energy of the system, yet these values are difficult to quantify. As a consequence, the parameters λ_k , which exert a significant influence on the generated samples, are typically chosen arbitrarily. Therefore, establishing a clear protocol for selecting the optimal coupling parameters would represent a significant advance.

Additionally, the functional design of the experimentally derived bias potential has a significant impact on the sampled atomic configurations. As the following section will demonstrate, if the experimental data were obtained from the average of many atoms, as is the case for the structure factor function and the RDF, it can be argued that a harmonic bias is not the optimal choice for the bias potential. A more effective strategy for determining the functional form of the bias potential and the magnitude of the coupling parameters can

be obtained through the principle of maximum relative entropy, which is presented in the following section.

6.2 The principle of maximum relative entropy to combine RDFs with MD simulations

6.2.1 The principle of maximum relative entropy

Sometimes a probability distribution of a random variable must be assumed despite limited information about the distribution. In this case, the principle of maximum entropy states that the probability distribution that maximizes the Shannon entropy with respect to the constraints provided by the limited information is the optimal choice. The rationale behind this principle is that the chosen distribution should encode minimal information about the random variable while satisfying the limited existing information. This approach ensures that only a minimal number of realizations of the random variable are excluded by the resulting probability distribution, while the samples obtained from the distribution remain consistent with the limited available information. The principle of maximum entropy was first developed in 1957 by Jaynes^{159,160} and has been successfully applied in MD and molecular Monte Carlo simulations. For instance, Cilloco¹⁶¹ used the principle of maximum entropy to reproduce a target RDF derived from a Lennard-Jones system in a molecular Monte Carlo simulation. Subsequently, Pitera and Chodera¹⁶² presented a method that reproduces target observables in MD simulations.

The principle of maximum entropy can be extended to formulate an approach that does not generate a new probability distribution, but instead biases a given prior probability distribution P_0 to generate a revised distribution P that incorporates new information.¹⁶³ This approach is known as the principle of maximum **relative** entropy. Here, the term *relative* indicates that the entropy of the new probability distribution is measured relative to the original probability distribution. The principle of maximum relative entropy can also be regarded as the principle of minimal information transfer from the prior probability distribution to the new probability distribution. Mathematically, the relative entropy $S[P||P_0]$ between two probability density functions of MD simulations is defined as

$$\begin{aligned} S[P||P_0] &= - \int d\mathcal{R} \int d\mathcal{P} P(\mathcal{R}, \mathcal{P}) \ln \frac{P(\mathcal{R}, \mathcal{P})}{P_0(\mathcal{R}, \mathcal{P})} \\ &= - \int d\mathcal{R} \int d\mathcal{P} P(\mathcal{R}, \mathcal{P}) [\ln P(\mathcal{R}, \mathcal{P}) - \ln P_0(\mathcal{R}, \mathcal{P})] . \end{aligned} \quad (6.3)$$

Eq. (6.3) is also referred to as the Kullback-Leibler divergence. The measure of relative entropy is maximized when on average the probability of sampling a microstate $\{\mathcal{R}, \mathcal{P}\}$ under distribution P is as similar as possible to the probability of sampling the same microstate under the distribution P_0 . Hence, in the absence of new information about the probability distribution P , the relative entropy Eq. (6.3) is maximized $P_{\text{ME}} = \arg \max_P S[P||P_0]$ when $P_{\text{ME}} = P_0$.

As detailed by Cesari et al.¹⁶⁴, the principle of maximum relative entropy can be used to update the probability distributions of microstates in MD simulations with new information obtained from experiments. To this end, consider M experimentally measured quantities $\mathbf{Y}^{\text{obs}} = \{Y_1^{\text{obs}}, \dots, Y_k^{\text{obs}}, \dots, Y_M^{\text{obs}}\}$ of a thermodynamic system. In MD simulations, the same observable can be modeled by determining the observed quantity as an average over all microstates $\{\mathcal{R}, \mathcal{P}\}$, i.e.,

$$\langle Y_k \rangle = \int d\mathcal{R} \int d\mathcal{P} Y_k(\mathcal{R}) P(\mathcal{R}, \mathcal{P}). \quad (6.4)$$

Therefore, for the simulation to reproduce the measured data points, the M constraints

$$\{\langle Y_1 \rangle = Y_1^{\text{obs}}, \dots, \langle Y_k \rangle = Y_k^{\text{obs}}, \dots, \langle Y_M \rangle = Y_M^{\text{obs}}\} \quad (6.5)$$

have to be satisfied.

According to the principle of maximum relative entropy, the updated ensemble probability distribution P_{ME} should be the distribution P that maximizes the relative entropy $S[P||P_0]$ relative to the prior probability distribution P_0 , i.e.,

$$\begin{aligned} P_{\text{ME}} &= \arg \max_P S[P||P_0] \\ \text{subject to } &\{\langle Y_1 \rangle = Y_1^{\text{obs}}, \dots, \langle Y_k \rangle = Y_k^{\text{obs}}, \dots, \langle Y_M \rangle = Y_M^{\text{obs}}\}. \end{aligned} \quad (6.6)$$

P_{ME} can be determined using the method of Lagrange multipliers, resulting in the functional

$$\begin{aligned} \mathcal{L} &= S[P||P_0] - \lambda_0 (\langle Y_0 \rangle - 1) - \sum_{k=1}^M \lambda_k (\langle Y_k \rangle - Y_k^{\text{obs}}) \\ &= - \int d\mathcal{R} \int d\mathcal{P} P(\mathcal{R}, \mathcal{P}) \ln \frac{P(\mathcal{R}, \mathcal{P})}{P_0(\mathcal{R}, \mathcal{P})} - \lambda_0 \left(\int d\mathcal{R} \int d\mathcal{P} P(\mathcal{R}, \mathcal{P}) - 1 \right) \\ &\quad - \sum_{k=1}^M \lambda_k \left(\int d\mathcal{R} \int d\mathcal{P} Y_k(\mathcal{R}) P(\mathcal{R}, \mathcal{P}) - Y_k^{\text{obs}} \right). \end{aligned} \quad (6.7)$$

Note that an additional constraint

$$\langle Y_0 \rangle = \langle 1 \rangle = \int d\mathcal{R} \int d\mathcal{P} P(\mathcal{R}, \mathcal{P}) = 1 \quad (6.8)$$

was added to Eq. (6.7) to ensure the normalization of the biased probability distribution P . The probability distribution that maximizes Eq. (6.7) is determined with variational calculus to

$$\frac{\delta \mathcal{L}(P)}{\delta P} = -\ln \frac{P(\mathcal{R}, \mathcal{P})}{P_0(\mathcal{R}, \mathcal{P})} - 1 - \lambda_0 - \sum_{k=1}^M \lambda_k Y_k(\mathcal{R}) = 0. \quad (6.9)$$

By solving for $P(\mathcal{R}, \mathcal{P})$ the biased probability distribution is obtained as

$$P_{\text{ME}}(\mathcal{R}, \mathcal{P}) = P_0(\mathcal{R}, \mathcal{P}) e^{-1-\lambda_0} e^{-\sum_{k=1}^M \lambda_k Y_k(\mathcal{R})}. \quad (6.10)$$

Here, $e^{-1-\lambda_0}$ is identified as a constant that ensures the normalization of the biased probability distribution. By substituting the Boltzmann distribution defined Eq. (2.38) as $P_0(\mathcal{R}, \mathcal{P})$ into Eq. (6.10), the influence of the applied bias on the original potential energy can be presented by

$$\begin{aligned} P_{\text{ME}} &\propto e^{-\beta U(\mathcal{R}) - \sum_{k=1}^M \lambda_k Y_k(\mathcal{R})} = e^{-\beta(U(\mathcal{R}) + \sum_{k=1}^M \tilde{\lambda}_k Y_k(\mathcal{R}))} \\ &= e^{-\beta(U(\mathcal{R}) + V_{\text{ME}}(\mathcal{R}))} = e^{-\beta U_{\text{ME}}(\mathcal{R})}. \end{aligned} \quad (6.11)$$

Thus,

$$V_{\text{ME}}(\mathcal{R}) = \sum_{k=1}^M \tilde{\lambda}_k Y_k(\mathcal{R}) \quad (6.12)$$

is the bias potential determined from the principle of maximum relative entropy. In combination with the original potential of the unbiased system $U(\mathcal{R})$, a new maximum relative entropy potential is defined by

$$U_{\text{ME}}(\mathcal{R}) = U(\mathcal{R}) + V_{\text{ME}}(\mathcal{R}). \quad (6.13)$$

The strength of the bias potential V_{ME} relative to the original potential U is determined by the coupling parameters

$$\tilde{\lambda}_k = \frac{\lambda_k}{\beta}. \quad (6.14)$$

In Sec. 6.2.3, a methodology is presented to determine the Lagrange parameters $\tilde{\lambda}_k$. The availability of a methodology to determine the Lagrange parameters represents a significant advantage over RMC and HRMC, since it ensures that the relative strength between the original and bias potential is established on objective criteria.

The principle of maximum relative entropy provides a compelling rationale for avoiding the introduction of a harmonic potential to bias MD simulations toward reproduction of experimental measurements, as done in RMC and HRMC. To follow this argument, one considers M constraints that constrain a simulated system to reproduce M particular variances $\text{Var}(Y(\mathcal{R})) = \Sigma_k$ centered around M measured Y_k^{obs} data points. Hence, there are M constraints of the form

$$\int d\mathcal{R} \int d\mathcal{P} [Y_k(\mathcal{R}) - Y_k^{\text{obs}}]^2 P(\mathcal{R}, \mathcal{P}) = \langle [Y_k(\mathcal{R}) - Y_k^{\text{obs}}]^2 \rangle = \Sigma_k. \quad (6.15)$$

By determining the biased probability distribution with the constraints defined in Eq. (6.15) following Eq. (6.7), one arrives at the sum of harmonic bias potentials

$$V_{\text{RMC}} = \sum_{k=1}^M \lambda_k [Y_k(\mathcal{R}) - Y_k^{\text{obs}}]^2. \quad (6.16)$$

Note that this is the bias potential used by RMC and HRMC described in Sec. 6.1.4. Consequently, according to the principle of maximum relative entropy, the harmonic bias potential represents the optimal choice for biasing a system to reproduce an observable determined through the thermodynamic average and, **simultaneously**, the variance of this observable in the atomic system. While the thermodynamic average of the observable is measured by experiment, the variance of the observable with respect to the atomic configurations is typically undetermined from the obtained data. Therefore, the harmonic bias potential constrains the system with arbitrary information about the variance of the atomic configuration, which is not contained in the experimental data.

In the context of MD simulations, the principle of relative maximum entropy was employed in the past in the coarse-graining of interaction potentials^{165–167}, the design of free energy surfaces in combination with metadynamics¹⁶⁸, and the update of existing force fields to better fit observables^{169,170}. White and Voth¹⁷¹ described a method that enables indirect reproduction of target RDFs in MD simulations by utilizing the moments of a target RDF to bias the modeled system. This thesis also focuses on reproducing target RDFs in MD simulations via the principle of maximum relative entropy. To this end, an algorithm is presented in the next section that reproduces target RDFs by biasing MD simulations on the basis of individual bins of the target RDF. This approach offers several advantages over the method of White and Voth¹⁷¹, which relies on moment matching of the RDF. For instance, a bin-wise partition of the RDF offers greater flexibility to adapt the bias to features of interest in the target RDF. This approach also enables the reproduction of RDFs that are composed of a superposition of partial RDFs of individual atom types. This capability is essential when

utilizing RDFs derived from WAXS data. Finally, bin-wise bias offers precise control over the induced virial and thus facilitates accurate pressure regulation in the MD simulations.

6.2.2 An algorithm to combine RDFs with MD simulations

A RDF of an atomic system derived via Fourier transformation of a WAXS measurement is mathematically defined as¹⁵²

$$g(r) = \frac{1}{2\pi^2 r} \frac{\tilde{V}}{\langle f \rangle^2 \tilde{N}(\tilde{N} - 1)} \sum_{i=1}^{\tilde{N}} \sum_{j \neq i}^{\tilde{N}-1} f_i f_j \delta(r - r_{ij}). \quad (6.17)$$

Here, $\tilde{N}$ is the number of atoms, $\tilde{V}$ is the volume of thermodynamic system, and $\delta(\cdot)$ is the delta distribution. The factors f_i and f_j are the atom type specific form factors of atom i or j . In WAXS measurements, the atomic form factors describe the scattering intensities of different atom types in the WAXS signal. When RDFs are derived from WAXS data, these form factors must be retained, otherwise they may be set to one. In general, the values of the atomic form factors depend on the scattering wave vector q . However, in this thesis, the Morningstar-Warren approximation¹⁷² is employed, resulting in q -independent atomic form factors. $\langle f \rangle$ defines the average of the atomic form factor, calculated according to the relative proportion of atom types in the considered system.

As evident from Eq. (6.17), the RDF of a thermodynamic system is represented as a weighted series of delta distributions. In practice however, RDFs obtained from experiments or simulations cannot be described using delta distributions. Therefore, the RDF is typically calculated and represented as a histogram $\tilde{g}_b$ with bins b ranging from 1 to B . Each bin extends over a range of $\pm\Delta/2$ around its radial center position r_b . To approximate the RDF, the bin size is usually chosen to be small, offering higher resolution. Mathematically, the binning into a histogram can be represented as an integration over all delta distributions $\delta(\rho_b - r_{ij})$ that lie within the bin boundaries from $(r_b - \frac{\Delta}{2})$ to $(r_b + \frac{\Delta}{2})$. Here, ρ_b denotes the position in bin b and is defined on the interval $[r_b - \frac{\Delta}{2}, r_b + \frac{\Delta}{2}]$. Thus, the value of the RDF at bin b is described by

$$\tilde{g}_b = \frac{\tilde{V}}{\langle f \rangle^2 \tilde{N}(\tilde{N} - 1) \delta V_b} \sum_{i=1}^{\tilde{N}} \sum_{j \neq i}^{\tilde{N}-1} f_i f_j \int_{(r_b - \frac{\Delta}{2})}^{(r_b + \frac{\Delta}{2})} d\rho_b \delta(\rho_b - r_{ij}). \quad (6.18)$$

Here, δV_b describes the volume of the spherical bin and is defined as

$$\delta V_b = \frac{4}{3}\pi \left[\left(r_b + \frac{\Delta}{2} \right)^3 - \left(r_b - \frac{\Delta}{2} \right)^3 \right]. \quad (6.19)$$

In MD simulations only instantaneous RDFs g_b can be calculated, containing the information of a much smaller number of atoms $N \ll \tilde{N}$ and smaller volumes $V \ll \tilde{V}$. However, under the assumption of ergodicity, the thermodynamic RDF $\tilde{g}_b$ can be estimated from the ensemble average $\langle \cdot \rangle$ of the instantaneous RDFs obtained in MD simulations via

$$\tilde{g}_b \approx \langle g_b \rangle = \left\langle \frac{V}{\langle f \rangle^2 N(N-1) \delta V_b} \sum_{i=1}^N \sum_{j \neq i}^{N-1} f_i f_j \int_{(r_b - \frac{\Delta}{2})}^{(r_b + \frac{\Delta}{2})} d\rho_b \delta(\rho_b - r_{ij}) \right\rangle \quad (6.20)$$

for sufficiently many time steps.

Assuming a target RDF $\tilde{g}_b^{\text{target}}$ is obtained, e.g., through WAXS measurements of a real system that is not reproduced in the MD simulations, i.e., $\tilde{g}_b^{\text{target}} \neq \langle g_b \rangle$, the principle of maximum relative entropy can be employed to bias the MD simulation so that the target RDF is reproduced in the simulation. Since the RDF is represented as a sequence of bins, to match the average RDF determined from the MD simulations with the target RDF, the bin values are constrained by the B constraints

$$\{\langle g_1 \rangle = \tilde{g}_1^{\text{target}}, \dots, \langle g_b \rangle = \tilde{g}_b^{\text{target}}, \dots, \langle g_B \rangle = \tilde{g}_B^{\text{target}}\}. \quad (6.21)$$

Solving for the maximum relative entropy as detailed in Sec. 6.2.1 results in a biased probability distribution of

$$P_{\text{ME}} \propto e^{-\beta(U(\mathcal{R}) + \sum_{b=1}^B \tilde{\lambda}_b g_b(\mathcal{R}))} = e^{-\beta(U(\mathcal{R}) + V_{\text{ME}}(\mathcal{R}))} = e^{-\beta U_{\text{ME}}(\mathcal{R})}. \quad (6.22)$$

The bias potential V_{ME} is thus defined by

$$V_{\text{ME}} = \sum_{b=1}^B \tilde{\lambda}_b g_b. \quad (6.23)$$

For the bias potential to be deployable within the context of MD simulations, it has to be derivable with respect to the positions of individual atoms i to determine the bias forces

$$\mathbf{F}_i^{\text{ME}} = \nabla_i V_{\text{ME}}(\mathcal{R}) = \sum_{b=1}^B \tilde{\lambda}_b \nabla_i g_b(\mathcal{R}). \quad (6.24)$$

However, the definition of the RDF provided in Eq. (6.18) contains non-differentiable delta-distributions. This limitation can be alleviated by replacing the delta-distributions with differentiable kernel functions $\Theta(\rho_b - r_{ij})$ in order to approximate the original RDF. The kernel functions are required to be centered at r_{ij} , to extent over the radial bin range $\pm\Delta/2$, and to integrate to one, i.e.,

$$\int_{-\infty}^{\infty} d\rho_b \Theta(\rho_b - r_{ij}) = 1. \quad (6.25)$$

The simplest kernel function, that does not introduce any kind of variations over the length of the considered bin is a rectangular kernel function

$$\Theta(\rho_b - r_{ij}) = \begin{cases} \frac{1}{\Delta} & \text{if } \left| \frac{\rho_b - r_{ij}}{\Delta} \right| < \frac{1}{2} \\ 0 & \text{otherwise} \end{cases}. \quad (6.26)$$

By replacing the delta distributions in Eq. (6.20) one arrives at

$$\tilde{g}_b \approx \langle g_b \rangle = \left\langle \frac{V}{\langle f \rangle^2 N(N-1) \delta V_b} \sum_{i=1}^N \sum_{j \neq i}^{N-1} f_i f_j \int_{(r_b - \frac{\Delta}{2})}^{(r_b + \frac{\Delta}{2})} d\rho_b \Theta(\rho_b - r_{ij}) \right\rangle. \quad (6.27)$$

Eq. (6.27) approximates the RDF well for sufficiently large sample sizes of the r_{ij} and small enough bin sizes Δ . Due to the extent of Θ , the contribution of the kernel function spreads over to an adjacent bin when the center of the kernel function r_{ij} does not coincide with the bin center r_b . The center position of the kernel function r_{ij} determines the adjacent bin to which the kernel function contributes. If the center of the kernel is positioned at $r_b - \frac{\Delta}{2} < r_{ij} < r_b$ the kernel contributes to the bins $b-1$ and b . If it is positioned at $r_b < r_{ij} < r_b + \frac{\Delta}{2}$ the kernel contributes to b and $b+1$ instead. The effect on the histogram of replacing the delta-distribution with the rectangular kernel distribution is displayed in Figure 6.1.

With the introduction of the kernel function it is possible to calculate

$$\begin{aligned} \nabla_i g_b(\mathcal{R}) &= \frac{f_i V}{\langle f \rangle^2 N(N-1) \delta V_b} \sum_{j \neq i}^{N-1} f_j \nabla_{r_i} \int_{(r_b - \frac{\Delta}{2})}^{(r_b + \frac{\Delta}{2})} d\rho_b \Theta(\rho_b - r_{ij}) \\ &= \frac{f_i V}{\langle f \rangle^2 N(N-1) \delta V_b} \frac{\mathbf{r}_{ij}}{r_{ij}} \sum_{j \neq i}^{N-1} f_j \left[\Theta\left(r_b - \frac{\Delta}{2} - r_{ij}\right) - \Theta\left(r_b + \frac{\Delta}{2} - r_{ij}\right) \right]. \end{aligned} \quad (6.28)$$

By substituting Eq. (6.28) into Eq. (6.24) and rearranging the force on atom i originating

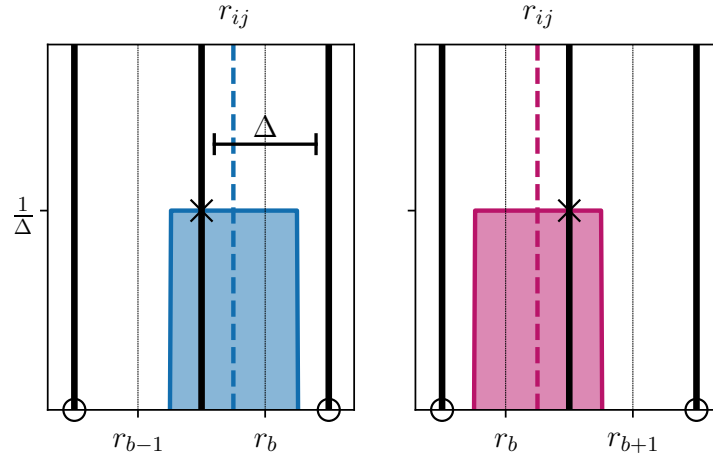


Figure 6.1: Sketch of the contribution of each distance r_{ij} to the RDF g_b . The colored dashed lines represent the original delta distribution $\delta(\rho_b - r_{ij})$ at r_{ij} . The delta distributions are replaced by rectangular kernel functions $\Theta(\rho_b - r_{ij})$ centered around r_{ij} . The contribution of an atom pair i and j at a distance r_{ij} to the bin b is defined by the area under the rectangular function in the bin b (lighter color). Due to the extent of the rectangular kernel function, the distance r_{ij} contributes to the RDF intensity of two adjacent bins. If the center of the kernel function r_{ij} is situated to the left of the center of the bin r_b , the affected bins are $b - 1$ and b (blue). If it is situated to the right of the center of bin r_b , the affected bins are b and $b + 1$ (red). The black cross indicates the only non-zero value of the kernel function $\Theta(r_b - \frac{\Delta}{2} - r_{ij}) = \Theta(r_{b-1} + \frac{\Delta}{2} - r_{ij}) = \frac{1}{\Delta}$ (blue) and $\Theta(r_b + \frac{\Delta}{2} - r_{ij}) = \Theta(r_{b+1} - \frac{\Delta}{2} - r_{ij}) = \frac{1}{\Delta}$ (red) at the bin boundaries. At all other bin boundaries the kernel function is zero (black circle).

from the bias potential is determined as

$$\mathbf{F}_i^{\text{ME}} = \sum_{j \neq i}^{N-1} \mathbf{F}_{ij}^{\text{ME}} = \sum_{j \neq i}^{N-1} \frac{f_i f_j V \hat{F}_{ij}}{\langle f \rangle^2 N(N-1)} \frac{\mathbf{r}_{ij}}{r_{ij}} \quad (6.29)$$

with

$$\hat{F}_{ij} = \sum_{b=1}^B \hat{F}_{ij}^b = \sum_{b=1}^B \frac{\tilde{\lambda}_b}{\delta V_b} \left[\Theta \left(r_b + \frac{\Delta}{2} - r_{ij} \right) - \Theta \left(r_b - \frac{\Delta}{2} - r_{ij} \right) \right]. \quad (6.30)$$

From Eq. (6.30), it is evident that the kernel functions Θ have to be evaluated at the bin boundaries $r_b + \frac{\Delta}{2}$ and $r_b - \frac{\Delta}{2}$ to determine $\hat{F}_{ij}$. Due to the limited extent of the kernel function, the kernel contribution is restricted to a maximum of two adjacent bins. Hence, each kernel function only exhibits a non-zero value at a single bin boundary (marked by the black cross in Fig. 6.1), while all other contributions are zero (marked by black circle in Fig. 6.1). Therefore, the sum over all bins $\sum_{b=1}^B$ for each kernel function in Eq. (6.30) can be condensed to the two adjacent bins to which the kernel function contributes. One of the two bins is always the bin $\hat{b}$ in which the radial distance r_{ij} is situated in. The position of the other relevant bin depends on the position of the radial distance r_{ij} relative to the

center of the bin $r_{\hat{b}}$. If r_{ij} is situated left to the center of bin $\hat{b}$, the kernel contributes to $\hat{b} - 1$ (red kernel function in Fig. 6.1). If it is situated right in the center of bin $\hat{b}$ instead, the kernel contributes to $\hat{b} + 1$ (blue kernel function in Fig. 6.1). Consequently, Eq. (6.30) can be simplified to

$$\hat{F}_{ij} = \begin{cases} \frac{1}{\Delta} \left[\frac{\tilde{\lambda}_{\hat{b}}}{\delta V_{\hat{b}}} - \frac{\tilde{\lambda}_{\hat{b}-1}}{\delta V_{\hat{b}-1}} \right] & \text{if } r_{\hat{b}} - \frac{\Delta}{2} < r_{ij} < r_{\hat{b}} \\ \frac{1}{\Delta} \left[\frac{\tilde{\lambda}_{\hat{b}+1}}{\delta V_{\hat{b}+1}} - \frac{\tilde{\lambda}_{\hat{b}}}{\delta V_{\hat{b}}} \right] & \text{if } r_{\hat{b}} < r_{ij} < r_{\hat{b}} + \frac{\Delta}{2} \end{cases}. \quad (6.31)$$

As detailed in Sec. 2.4, in MD simulations, the pressure of the system is determined from the virial Eq. (2.44). Since the introduction of a bias potential leads to a change in forces acting in the system, the total virial of the system T_{total} is altered to

$$T_{\text{total}} = T_0 + T_{\text{ME}}, \quad (6.32)$$

where T_0 is the original virial of the system and T_{ME} is the virial originating from the bias forces. Adapted from the definition of the virial in Eq. (2.44), the introduced bias virial is

$$T_{\text{ME}} = \frac{1}{3V} \sum_i^N \mathbf{F}_i^{\text{ME}} \mathbf{r}_i = \frac{1}{3V} \sum_i^N \sum_{b=1}^B \tilde{\lambda}_b \nabla_i g_b(\mathcal{R}) = \sum_{b=1}^B T_{\text{ME}}^b. \quad (6.33)$$

In the last term, the summations have been interchanged to define the bin specific bias virial

$$T_{\text{ME}}^b = \frac{1}{3V} \sum_i^N \tilde{\lambda}_b \nabla_i g_b(\mathcal{R}). \quad (6.34)$$

The strength of the added bias potential, and thus of the introduced forces and virial, depend on the bin specific Lagrange parameters $\tilde{\lambda}_b$. Consequently, these parameters define the strength of the introduced bias and are of high importance. The following section describes how the Lagrange parameters can be determined by applying an iterative gradient descent algorithm.

6.2.3 Determining the Lagrange parameters

To determine the Lagrange parameters $\lambda = \{\lambda_1, \dots, \lambda_B\}$, Eq. (6.6) subject to Eq. (6.8) and Eq. (6.21) has to be solved. Mead and Papanicolaou¹⁷³ showed that this constrained optimization problem can be reformulated with a Legendre transformation¹⁷³ to the problem of minimizing

$$\Gamma(\lambda) = \ln \left[\int d\mathcal{R} P_0(\mathcal{R}) e^{-\sum_{b=1}^B \lambda_b g_b(\mathcal{R})} \right] + \sum_{b=1}^B \lambda_b \tilde{g}_b^{\text{target}}. \quad (6.35)$$

As a result, the Lagrange parameters λ_b that maximize the relative entropy are equal to the parameters that minimize Eq. (6.35). To determine the parameters that minimize Γ , the algorithm of gradient descent can be employed. The gradient of Γ with respect to λ_b is

$$\frac{\partial \Gamma}{\partial \lambda_b} = \tilde{g}_b^{\text{target}} - \frac{\int d\mathcal{R} P_0(\mathcal{R}) e^{-\sum_{b=1}^B \lambda_b g_b(\mathcal{R})} g_b(\mathcal{R})}{\int d\mathcal{R} P_0(\mathcal{R}) e^{-\sum_{b=1}^B \lambda_b g_b(\mathcal{R})}} = \tilde{g}_b^{\text{target}} - \langle g_b \rangle. \quad (6.36)$$

Consequently, to determine the gradient of Γ with respect to λ_b , it is sufficient to calculate the difference between the target RDF $\tilde{g}_b^{\text{target}}$ and the average of the simulated RDF $\langle g_b \rangle$ at bin b . As a result, an update step of gradient descent for the Lagrange parameters can be calculated as

$$\lambda'_b = \lambda_b + \xi \frac{\partial \Gamma}{\partial \lambda_b} = \lambda_b + \xi \left(\tilde{g}_b^{\text{target}} - \langle g_b \rangle \right), \quad (6.37)$$

where ξ is a freely chosen parameter in the gradient descent algorithm that determines the update strength of the Lagrange parameter at each iteration.

To guarantee the discovery of a global minimum of $\Gamma(\lambda)$ with the gradient descent algorithm, $\Gamma(\lambda)$ has to be a convex function. This requirement is equivalent to the requirement of a positive-definite Hessian matrix¹⁶² that is calculated as

$$\frac{\partial^2 \Gamma}{\partial \lambda_b \partial \lambda_{b'}} = \langle g_b g_{b'} \rangle - \langle g_b \rangle \langle g_{b'} \rangle, \quad (6.38)$$

where b and b' are two individual bins of the RDFs. From Eq. (6.38) it is evident that the Hessian matrix is positive-definite only when the individual bins of RDF are uncorrelated. However, in typical RDFs, this condition is not satisfied. Specifically, the RDF values for neighboring bins are correlated. Therefore, the method of relative maximum entropy has to be considered as a method to reproduce independent observables of a thermodynamic system, and in the case of reproducing RDFs, no formal guaranty exists that the gradient descent algorithm converges to an optimal solution. Instead, the method may converge to a local minimum of $\Gamma(\lambda)$. From a theoretical perspective, this challenges the use of gradient descent to determine the Lagrange parameters. However, despite the theoretical limitations of gradient descent, the results of Sec. 6.3 demonstrate that an improved method of gradient descent is satisfactory to discover suitable Lagrange parameters for a wide range of applications. Three adaptations were introduced to improve the gradient descent algorithm.

The first adaption pertains the relative updates of the Lagrange parameters. In the standard gradient descent algorithm of Eq. (6.37), each update of the Lagrange parameters is proportional to the difference between the target RDF $\tilde{g}_b^{\text{target}}$ and the average of the simulated RDF $\langle g_b \rangle$ at bin b . However, to determine the minimum of $\Gamma(\lambda)$, only the direction of

the gradient, i.e., the sign of the gradient $\text{sgn}\left(\frac{\partial \Gamma}{\partial \lambda_b}\right) = \text{sgn}\left(\tilde{g}_b^{\text{target}} - \langle g_b \rangle\right)$, is relevant. The method assumes that the Lagrange parameters are statistically independent. Hence, no theoretical basis requires the update of any individual Lagrange parameter to exceed the others. To align the update strength of the parameters, an exponential scaling parameter p with $p \leq 1$ is introduced. With the exponential scaling parameter, the new gradient descent update is defined as

$$\lambda'_b = \lambda_b + \xi \text{sgn}\left(\frac{\partial \Gamma}{\partial \lambda_b}\right) \left|\frac{\partial \Gamma}{\partial \lambda_b}\right|^p = \lambda_b + \xi \text{sgn}\left(\tilde{g}_b^{\text{target}} - \langle g_b \rangle\right) \left|\tilde{g}_b^{\text{target}} - \langle g_b \rangle\right|^p. \quad (6.39)$$

Consequently, adjusting the exponential scaling parameter p in Eq. (6.39) effectively reduces the variation in weighting of the Lagrange parameter updates. This adjustment improves stability for large bin specific differences in $\frac{\partial \Gamma}{\partial \lambda_b}$ and is particularly advantageous for RDFs derived from crystalline structures that exhibit significant intensity disparities.

The second update to the gradient descent algorithm is motivated by the fact that the difference between the target RDF $\tilde{g}_b^{\text{target}}$ and the measured RDF $\langle g_b \rangle$ is progressively reduced with each gradient descent iteration. Consequently, the convergence of the Lagrange parameters slows as the simulated RDF converges to the target RDF during the gradient descent. To mitigate this effect, the gradient of each bin is normalized by the sum of the absolute values of all gradients $\sum_{b=1}^B \left|\frac{\partial \Gamma}{\partial \lambda_b}\right|^p = \sum_{b=1}^B \left|\tilde{g}_b^{\text{target}} - \langle g_b \rangle\right|^p$. This update ensures that the cumulative change of the Lagrange parameter remains constant throughout the entire iterative gradient descent process. The constant updates facilitate the selection of an appropriate update parameter ξ and reduce the required computational time.

The third adaption is motivated by the fact that the introduction of the bias potential leads to a change of total virial in the simulated system due to the introduction of bias virial. The virial change can cause a substantial change in volume when simulating systems as isobaric ensembles. For strong bias potentials, such as those required to induce a liquid-to-solid phase transition, the change in volume can be significant enough to impede the mediation of a phase transition. A problematic excessive contraction or expansion is observed in simulations when the elements of the sum of the individual bin specific virials $\sum_{b=1}^B T_{\text{ME}}^b$, as defined in Eq. (6.34), do not sufficiently cancel out, such that $T_{\text{ME}} \ll 0$ or $T_{\text{ME}} \gg 0$. To mitigate the introduction of large pressures in the system, an additional bin dependent scaling parameter κ_b is introduced in the gradient descent algorithm. The pressure change in the system is adjusted by setting $\kappa_b < 1.0$ for bins b that make a negative contribution during excessive contraction or a positive contribution during excessive expansion. The remaining update rates remain unchanged, i.e., $\kappa_b = 1.0$. The slower increase of magnitude for Lagrange parameters λ_b that introduce a problematic amount of virial pressure in the system, leads to

a lower bias virial $T_{\text{ME}} = \sum_{b=1}^B T_{\text{ME}}^b$. Hence, excessive expansion or contraction is mitigated. This strategy, which aims to mitigate the impact of undesired virial activity, has proven to be effective despite its straightforward design.

Including the discussed adaptations, the resulting updated gradient descent algorithm is defined as

$$\lambda'_b = \lambda_b + \xi \kappa_b \frac{\text{sgn}\left(\frac{\partial \Gamma}{\partial \lambda_b}\right) \left|\frac{\partial \Gamma}{\partial \lambda_b}\right|^p}{\sum_{b=1}^B \left|\frac{\partial \Gamma}{\partial \lambda_b}\right|^p} = \lambda_b + \xi \kappa_b \frac{\text{sgn}\left(\tilde{g}_b^{\text{target}} - \langle g_b \rangle\right) \left|\tilde{g}_b^{\text{target}} - \langle g_b \rangle\right|^p}{\sum_{b=1}^B \left|\tilde{g}_b^{\text{target}} - \langle g_b \rangle\right|^p}. \quad (6.40)$$

To employ the presented algorithm, four parameters must be manually configured. The subsequent section offers guidance on the selection of these parameters.

6.2.4 Choosing the right parameters

To employ the maximum relative entropy algorithm, the update parameter ξ , the virial scaling parameter κ_b , the bin size of the RDF Δ , and the number of bins B have to be set.

The update parameter ξ is instrumental in determining the magnitude of the update to the Lagrange parameters for each update cycle. Therefore, increasing the update parameter reduces the number of cycles required for the average of the instantaneous RDFs $\langle g_b \rangle$ to converge to the target RDF $\tilde{g}_b^{\text{target}}$. As a result, a large update parameter avoids computational overhead. However, the choice of an excessive magnitude of the update parameter should be avoided for two reasons. First, excessively large values for the update parameter can cause abrupt changes in the forces acting within the simulation, which may result in simulation instability. Second, when liquid-to-solid phase transitions are simulated, the formation of the nucleation seed remains a statistical process even in biased simulations, albeit with highly increased probability. Therefore, the system has to be simulated for a sufficient time under the correct applied bias to form a nucleation seed. These two aspects limit the applicable magnitude of the update parameter. Recommendations derived from exemplary simulations suggest values of ξ from 10 to 5 for liquid systems that are biased without inducing a phase transition. To induce a phase transition, the parameter ξ must be reduced to a value between 5 and 1, enabling the statistical process of nucleus formation.

The exponential scaling parameter p is related in its functionality to the update parameter. As the scaling parameter decreases, the magnitude of the update for each bin becomes more uniform. As a result, for very low exponential scaling parameters, the algorithm assigns approximately equal importance to every bin of the RDF. As outlined in Sec. 6.3.2.4, lower values for the exponential scaling parameter improve the crystallization speed of water to ice.

However, at a certain point, no further benefit is gained by decreasing the exponential scaling parameter. For water, exponential scaling parameter values between 1 to 0.01 can be used with better results for lower parameters. It is important to note that only one system was tested with exponential scaling parameters $p < 1$. As a consequence, the suitable values for the exponential scaling parameter could deviate in other systems.

Another parameter that has to be specified is the virial scaling parameter κ_b . Scaling the virial becomes essential for systems undergoing liquid-to-solid transitions that exhibit significant contraction or expansion. As outlined in this thesis, this applies to the crystallization of liquid TiO_2 . In this case, the values were set to

$$\kappa_b = \begin{cases} 0.25 & \text{if } T_{ME} < 0 \\ 1.0 & \text{if } T_{ME} \geq 0 \end{cases}. \quad (6.41)$$

The final two parameters that have to be selected are the number of bins B for the RDF and the bin size Δ . These parameters define the number of Lagrange multipliers that have to be determined. It is not possible to provide a general guideline for the selection of the values for these two parameters. However, two factors should be considered. The bin size should be sufficiently small and the number of bins should be sufficiently large so that the important features of the RDF are well resolved. However, bins should not be excessively small, because smaller bins can result in an insufficient number of statistics, which can, in turn, lead to noisy Lagrange parameters. Consequently, the forces in the simulation may fluctuate, potentially leading to simulation instabilities. Concurrently, the total range of the RDF and thus the number of bins should remain small to avoid computational overhead from the computation of an extensive RDF.

6.2.5 Implementation

To evaluate the presented algorithm, the algorithm was implemented as an extension to the LAMMPS code.¹⁸ The implementation supports the high-performance computing capabilities of LAMMPS with the Message Passing Interface (MPI). The C++ source code is available at <https://collaborating.tuhh.de/m-29/software/maxentrdf>. To appropriately include the influence of the atomic structure factors in the calculations of the RDFs, the implementation builds in part on the code of the DIFFRACTION package developed by Coleman et al.¹⁷⁴ The DIFFRACTION package employs an analytical approximation of the atomic structure factors¹⁷⁵ that was parametrized by Fox et al.¹⁷⁶ After implementation, the method was evaluated in exemplary simulations, described in the next section.

6.3 Exemplary simulations with the maximum relative entropy algorithm

The maximum relative entropy approach is applicable to a wide range of applications. This thesis presents two general use cases to evaluate the usefulness of the developed algorithm. In the first case, the algorithm is used to reproduce a target RDF in a liquid system. Specifically, a liquid water system described by the TIP3P potential¹⁷⁷ is biased to match the target RDF obtained from a system described by the TIP4P/2005 potential³⁹. In the second case, the algorithm is employed to mediate liquid-to-solid phase transitions in liquid systems. Specifically, the phase transition of liquid TiO_2 to the stable and metastable polymorphs of rutile and anatase, as well as the phase transition of liquid water into hexagonal ice I_h are investigated. For convenience in the subsequent discussion, the simulated RDFs $\langle g_b \rangle$ are not presented as a histogram but as a continuous functions of $\{\langle g_1 \rangle, \dots, \langle g_B \rangle\} \approx g(r)$ in dependence of the radial distance $\{r_1, \dots, r_B\} \approx r$. However, during the computation of the results, the histogram representation of the data was utilized and the continuous form is employed solely for presentation purposes.

6.3.1 Biasing liquid systems

Water exhibits multiple properties, that are historically challenging to represent in MD simulations with a single force field. Consequently, a wide variety of molecular models with different levels of complexity that focus on different properties of water have been developed.¹⁷⁸ As a result, the individual water models exhibit deviations in the RDFs. This section illustrates how the maximum relative entropy algorithm can be applied to align RDFs from different water models. For this demonstration, the TIP3P model was biased to reproduce the RDF obtained from liquid water modeled with the TIP4P/2005 model. In comparison to the TIP3P model, the TIP4P/2005 model demonstrates superior capabilities in modeling bulk water properties, including density, viscosity, diffusion coefficient, and local water structure. This enhancement in performance arises from the refined charge distribution originating from the ghost atom in the TIP4P/2005 model. However, the ghost atom increases computational complexity. Therefore, the question arises as to whether the information contained in the RDF of the TIP4P/2005 model can be utilized to improve the TIP3P model and thereby combine the advantages of both models. To investigate this question, the RDF of an equilibrium liquid water system modeled by TIP4P/2005 at a temperature of 300 K and a pressure of 1 atm was computed to act as the target RDF. The resulting target RDF ranged from 0 Å to 8 Å with a bin size of 0.08 Å. Subsequently, the target RDF was used to bias

the liquid TIP3P system, which was modeled at a temperature of 300 K and a pressure of 1 atm. From the biased system, the instantaneous RDF was calculated every ten time steps and averaged over 100 time steps. From the result, the Lagrange multipliers λ_b were updated. The update rate was set to $\xi = 10.0$ and no virial-specific weighting was applied, i.e., $\kappa_b = 1$ for all bins.

Fig. 6.2a presents the result of the applied bias. In the upper part of the plot, the blue curve represents the RDF of the TIP3P model before the bias, whereas the red curve indicates the RDF after applying the bias. The target RDF generated with the TIP4P/2005 model is shown as the black curve. The lower part of the figure illustrates the discrepancy between the TIP4P/2005 target RDF and the unbiased and biased RDFs of the TIP3P model in blue and red, respectively. The mean absolute error (MAE) was calculated to quantify the difference between the unbiased and biased RDFs and the target RDF. The MAE between the unbiased RDF and target RDF was 0.058 while the MAE between the biased RDF and target RDF was 0.016, as depicted in the legend of the lower left graph of Fig. 6.2a. It is evident from Fig. 6.2a, that the bias of the liquid TIP3P model caused the TIP3P RDF to converge toward the target RDF from the liquid TIP4P/2005 model. However, the question arises as to whether the convergence of properties is only limited to the RDF or if other properties are also influenced by the application of the bias. To address this question, the bias's effect on two additional properties of the liquid TIP3P system is examined. These are the angular distribution function $f(\theta)$ (ADF) of the oxygen atoms and the diffusion constant D . The ADF has been selected to provide insight into the impact of the algorithm on properties that are dependent on the structural distribution of atoms, apart from the RDF. The diffusion constant D has been selected to provide insight into the impact of the algorithm on the system's dynamics.

The ADF of the oxygen atoms was calculated at distances from 0 Å to 3.4 Å over an angle θ of 180° in 2° bins for the unbiased and biased liquid system of TIP3P as well as for the target system of liquid TIP4P/2005. The obtained ADFs are depicted in the upper part of Fig. 6.2b. The lower part depicts the deviation between the unbiased and biased TIP3P systems to the TIP4P/2005 system. From Fig. 6.2b it is evident that the bias not only exerted an effect on the RDF of the TIP3P system, but also on the ADF. Specifically, applying the bias promoted the formation of a more pronounced angular distribution among the water molecules. Hence, the ADF of the biased TIP3P system exhibited a substantial decrease in deviation from the TIP4P/2005 reference. This interpretation is corroborated by the decrease in MAE from 0.065 to 0.023. These results indicate that the algorithm may have applications beyond reproducing a specific RDF by aligning the general structural distribution of two systems.

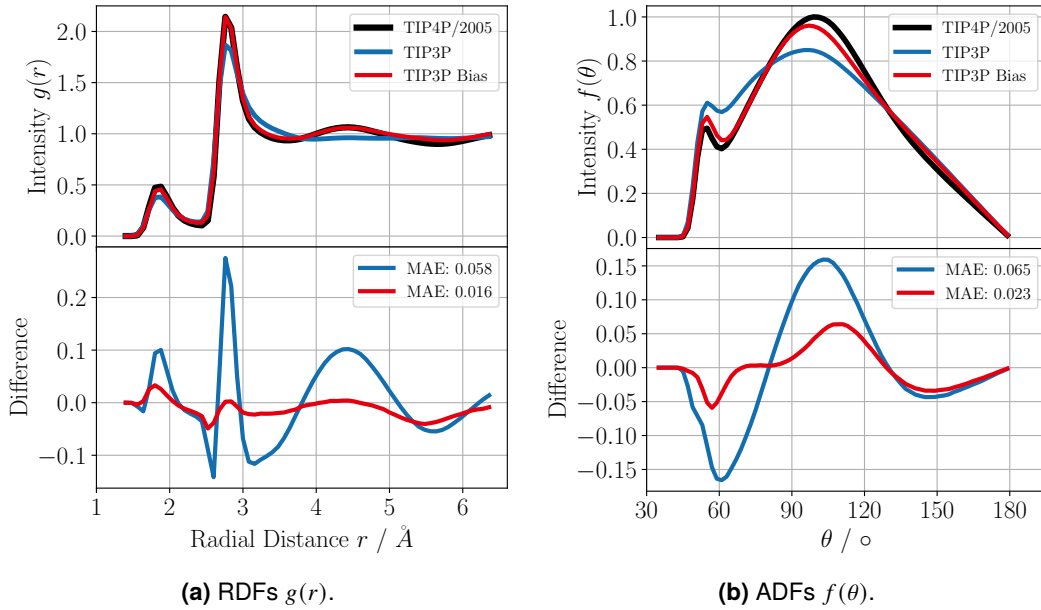


Figure 6.2: Upper panel: RDF (left) and ADF (right) of liquid water systems modeled with different interatomic potentials. The TIP4P/2005 water model from which the target RDF/ADF was extracted is depicted as black curve. The RDF/ADF of the unbiased TIP3P water model is depicted in blue, while the biased TIP3P water model is depicted in red. Bottom panel: Difference in the RDF/ADF between the target TIP4P/2005 water model and the unbiased (blue) and biased (red) TIP3P water model. The two respective mean absolute errors (MAE) between the functions are provided in the legend, with smaller values indicating better alignment.

To assess the bias's effect on the dynamics of the system, the diffusion constant D was calculated for the TIP4P/2005 system and for the unbiased and biased TIP3P systems. The quantity was obtained from the slope of the mean squared displacement $\langle r_{\text{MSD}}^2 \rangle$ of oxygen atoms bound in the water molecules. The diffusion constant can be determined from the time t dependent mean squared displacement through the linear relation

$$6Dt = \langle r_{\text{MSD}}^2 \rangle. \quad (6.42)$$

The mean squared displacements measured at discrete simulation times are depicted in Fig. 6.3. The fit of the linear relations of Eq. (6.42) are shown as the continuous lines. The from the fit resulting diffusion constants are presented in Tab. 6.1. For the TIP4P/2005 model, the diffusion constant showed close agreement with the system size-independent value reported by Tazi et al.⁴² of $D = 2.49 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. It also exhibited close agreement with the experimentally determined value for water $D = 2.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ from Krynicki et al.¹⁷⁹ In contrast, the diffusion constant of the liquid TIP3P system is significantly lower. To align with the TIP4P/2005 value, the diffusivity had to increase when the bias is applied.

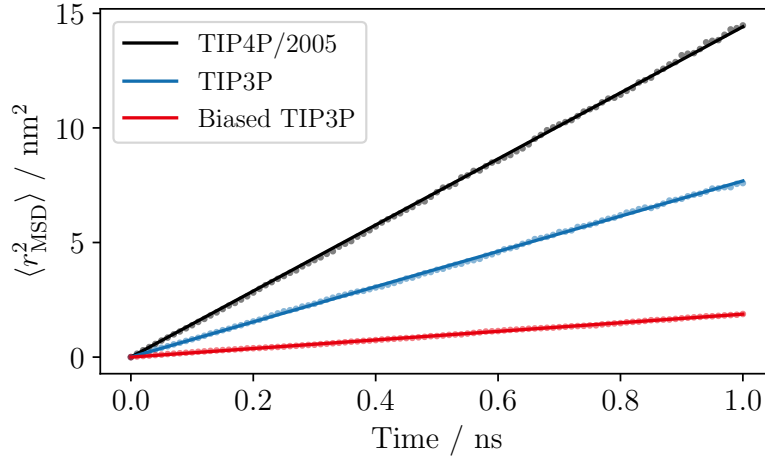


Figure 6.3: Mean squared displacement $\langle r_{\text{MSD}}^2 \rangle$ of the oxygen atoms bound in the water molecules in dependence of simulation time. The mean squared displacements measured at discrete simulation times are depicted as dots. The linear fit as a continuous line. Black represents the TIP4P/2005 water model, blue the unbiased TIP3P model and red the biased TIP3P model, respectively.

Table 6.1: Diffusion coefficients D of oxygen atoms bound in the water molecules for the considered water models at 300 K and 1 atm.

Water model	Diffusion coeff. $D / \text{m}^2 \text{s}^{-1}$
TIP4P/2005	2.40×10^{-9}
TIP3P	1.28×10^{-9}
Biased TIP3P	0.31×10^{-9}

However, the applied bias reduced the diffusion of the system to a point where approximately one-fourth of the original diffusivity remained. This reduction arises from the positional constraints imposed by the bias, as the algorithm biases positional time averages instead of dynamic properties. Note that the incorporation of the bias caused a slight reduction in the simulation's computational speed. In the presented case, the modeling speed decreased from 3.2 simulated nanoseconds per day for the unbiased TIP3P water model to 2.7 simulated nanoseconds per day. This corresponds to a 16 % reduction.

Based on the evaluation of liquid water, the maximum relative entropy algorithm effectively reproduces the structural properties of the liquid. However, applying the bias potential substantially slows the system's dynamics. Therefore, the application of the algorithm is not recommended when dynamic properties are of relevance in the simulation.

6.3.2 Mediation of liquid-to-solid phase transitions

This section evaluates the capacity of the maximum relative entropy algorithm to drive liquid-to-solid phase transitions in MD simulations, demonstrated in two exemplary simulations, i.e., crystallization of TiO_2 and water. Until now, no argument was provided to explain why the maximum relative entropy algorithm should be capable of mediating liquid-to-solid phase transitions in MD simulations. This argument is provided in the subsequent section.

■ 6.3.2.1 Altering the free energy surface to induce phase transitions

The free energy surface, also known as the potential of mean force, of the set of instantaneous RDF bins $\mathbf{g} = \{g_1, \dots, g_B\}$ that are measured in the MD simulation, is calculated by

$$F_0(\mathbf{g}) = -\frac{1}{\beta} \log \int d\mathcal{R} \delta(\mathbf{g}'(\mathcal{R}) - \mathbf{g}) P_0(\mathcal{R}). \quad (6.43)$$

As such, the free energy surface constitutes a hypersurface of B dimensions. Stable phases of atomic systems correspond to local minima of the free energy surface. These local minima are separated by free energy barriers that prevent spontaneous transition of the system from one stable phase to the other. As outlined in Section Sec. 2.5, the classical nucleation theory states that these barriers arise from the energetically unfavorable step of forming a crystallization seed smaller than the stable nucleus. As discussed in Sec. 6.1.2, these free energy barriers are challenging to overcome in MD simulations.

The blue curve in Figure 6.4 represents a hypothetical free energy surface for the one-dimensional case of a single RDF value $g_{b'}$ at bin b' . The free energy surface displays two free energy minima. The resulting Boltzmann probability distribution is indicated by the lighter distributions in the minima. The local free energy minimum at smaller values of $g_{b'} \approx 1.5$ represents the liquid phase, while the local minimum at larger $g_{b'} \approx 6.5$ can be associated with the crystalline state of a system. Both minima are separated by a free energy barrier. The height of the barrier is indicated by the dashed line. The liquid state has a lower free energy than the crystalline state. Thus, the crystalline state is not stable but metastable in the considered unbiased simulation. As demonstrated by Cesari et al.¹⁶⁴, the application

of a linear bias to a MD simulation tilts the free energy hypersurface since

$$\begin{aligned}
 F(\mathbf{g}) &= -\frac{1}{\beta} \log \int d\mathcal{R} \delta(\mathbf{g}'(\mathcal{R}) - \mathbf{g}) P_{\text{ME}}(\mathcal{R}) \\
 &= -\frac{1}{\beta} \log \int d\mathcal{R} \delta(\mathbf{g}'(\mathcal{R}) - \mathbf{g}) P_0(\mathcal{R}) e^{-\lambda \mathbf{g}'(\mathcal{R})} \\
 &= F_0(\mathbf{g}) + \frac{1}{\beta} \lambda \mathbf{g}.
 \end{aligned} \tag{6.44}$$

The magnitude and angle of tilt of the free energy surface depend on the absolute and relative magnitude of the Lagrange parameters λ . Figure 6.4 shows the resulting tilt of the free energy surface induced by a linear bias of the strengths $\lambda_{b'} = -5.0$, $\lambda_{b'} = -15.0$, and $\lambda_{b'} = -25.0$.

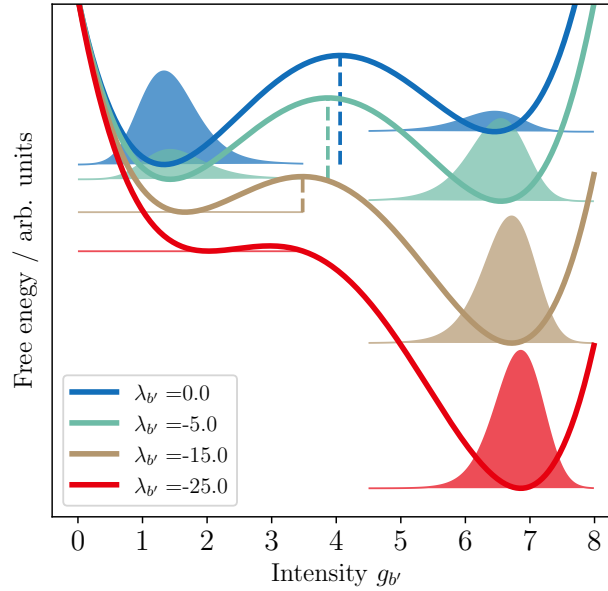


Figure 6.4: Hypothetical free energy surface as a function of the RDF intensity $g_{b'}$ at a specific bin position $r_{b'}$. Two local free energy minima, separated by a free energy barrier, are apparent. The resulting Boltzmann probability distribution is indicated by slightly lighter distributions in the energy minima. The bias increase is expressed in the decrease of the Lagrange multiplier $\lambda_{b'}$ from $\lambda_{b'} = 0.0$ (blue) to $\lambda_{b'} = -25.0$ (red). The height of the free energy barrier is indicated by the vertical dashed lines.

Two important effects on the geometry of the free energy surface originating from the tilt can be distinguished. First, as the bias strength increases, the free energy of the metastable phase decreases until it becomes the global minimum. At that point, the former stable liquid state becomes metastable, and the crystalline state becomes the new stable state of the system. Therefore, the bias can induce stable crystalline states that would not form in absence of the bias. Secondly, the free energy barrier decreases with increasing bias. This trend persists

until the barrier disappears, at which point the system freely transitions from the metastable to the new stable state.

While the one-dimensional example offers clear insight as to why the maximum relative entropy algorithm is capable of mediating liquid-to-solid phase transitions, it is crucial to note that biasing a system to reproduce a RDF tilts a hyperdimensional free-energy surface. Therefore, the tilt angle of the free-energy surface is a key factor in determining the success of the mediation process for the liquid-to-solid phase transition. The algorithm can induce liquid-to-solid phase transitions when the tilt angle of the free energy surface points toward the stable free energy minimum. Consequently, the tilt angle plays an important role in the success of the mediation of the liquid-to-solid phase transition. The evolution of the tilt angle during the iterative execution of the algorithm is determined by the relative strength of the update of the Lagrange parameters λ , which itself is determined by the choice of the update parameter ξ , the exponential scaling parameter p , and the virial scaling parameter κ_b . Therefore, it is essential to set these parameters to values that promote a phase transition.

The following section introduces a robust classification scheme based on average local bond order parameters to assign each atom in the MD simulation to a phase state. This method is required to evaluate the efficacy of the maximum relative entropy algorithm in mediating liquid-to-solid phase transitions.

■ 6.3.2.2 Average local bond order parameters

The average local bond order parameters were first presented by Lechner and Dellago¹⁸⁰ and are in turn based on the so called Steinhardt order parameters¹⁸¹. The Steinhardt order parameters for the atom i is calculated as

$$q_l^i = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^l |q_{lm}^i|^2} \quad (6.45)$$

with

$$q_{lm}^i = \frac{1}{N_n^i} \sum_{j=1}^{N_n^i} Y_{lm}(\mathbf{r}_{ij}). \quad (6.46)$$

Here N_n^i is the number of nearest neighbors to the atom i . Y_{lm} are spherical harmonics with l being the degree and m the order of the spherical harmonic. The average local bond order parameters are calculated through the introduction of an additional averaging over the values

q_{lm}^i resulting in a definition of

$$\bar{q}_l^i = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^l |\bar{q}_{lm}^i|^2}, \quad (6.47)$$

with

$$\bar{q}_{lm}^i = \frac{1}{\hat{N}_n^i} \sum_{k=1}^{\hat{N}_n^i} q_{lm}^k. \quad (6.48)$$

Here, $\hat{N}_n^i$ is defined as the nearest neighbors, including the particle i itself. q_{lm}^k is defined as in Eq. (6.46). The average local bond order parameters constitute a valuable tool for distinguishing different atomic structures. However, to calculate the average local bond order parameters, it is necessary to determine the individual degrees of the average local bond order parameter l and the radial distance cut-off values for the nearest neighbor for the individual atomic structures.

In the subsequent section, the average local bond order parameters are employed in a case study demonstrating the crystallization of TiO_2 induced by the maximum relative entropy method.

■ 6.3.2.3 Polymorphs of TiO_2

TiO_2 is an important material with a wide range of applications, including photocatalytic water splitting^{182,183}, photodynamic therapy for cancer treatment¹⁸⁴, inactivation of antibiotic resistant bacteria¹⁸⁴, and gas sensing¹⁸⁵. At room temperature and atmospheric pressure, crystalline TiO_2 occurs in three polymorphs, namely rutile, anatase and brookite. Of the three polymorphs, rutile is the most stable. With its polymorphs, TiO_2 offers the opportunity to test the maximum relative entropy algorithm to mediate the crystallization of liquids to a specific desired crystal structure. In this section, the biased crystallization of TiO_2 into rutile and anatase is demonstrated.

To this end, two systems, containing a single rutile and anatase crystal, were simulated as an isobaric-isothermal ensemble at a temperature of 300 K and a pressure of 1 atm. As interaction potential, the potential developed by Matsui and Akaogi¹⁸⁶ was employed with the Knowledgebase of Interatomic Models (KIM)¹⁸⁷. From the crystals, the respective atomic form factor weighted RDFs were calculated by averaging the instantaneous RDFs of the crystal every 10 time steps of 1 fs length over a total of 1,000,000 time steps. The RDF was calculated over a range of 0 Å to 8 Å with a bin size of 0.08 Å. The resulting RDFs are depicted in Fig. 6.5. Subsequently, these two RDFs served as target RDFs for the maximum

relative entropy algorithm.

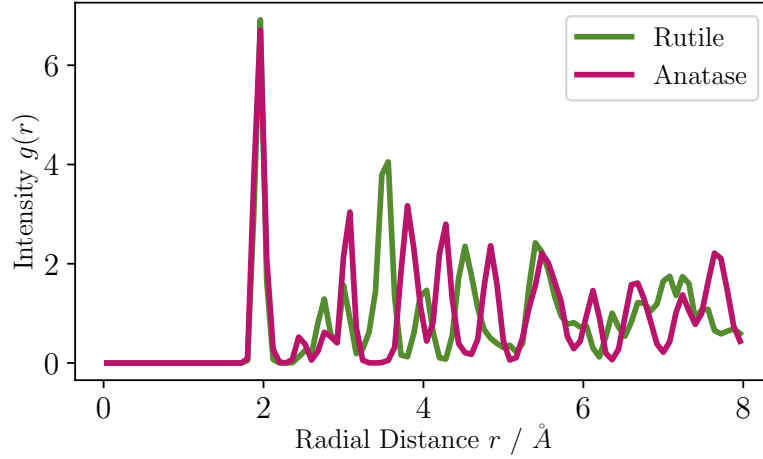


Figure 6.5: Determined RDFs of a single crystal of rutile (green) and anatase (purple).

Two systems of liquid TiO_2 were biased with the target RDFs. The two differently biased systems started with the same initial conditions. Both contained 1250 titanium and 2500 oxygen atoms and were equilibrated to a temperature of 2500 K and 1 atm. Both systems were modeled with a time step length of 1 fs. An equilibrated system was used as initial configuration to simulate the NpT ensemble at 2500 K and 1 atm. Note that the increased temperature of 2500 K did not prevent the phase transition to occur because the free energy of the crystalline phase decreased with the applied bias, as discussed in Sec. 6.3.2.1. The Lagrange parameters of the algorithm were updated according to Eq. (6.40) every 100 time steps with the average of the instantaneous RDF $\langle g_b \rangle$ sampled every ten time steps. The update parameter was set to $\xi = 5.0$ for rutile and $\xi = 1.25$ for anatase. For both systems, the exponential scaling parameter was set to $p = 1.0$. If biased without virial balancing, the system exhibited a pronounced contraction from an increased applied bias. To counteract this effect, the virial scaling factor was set to $\kappa_b = 0.25$.

The effect of the stepwise bias increase is depicted in Fig. 6.6 and Fig. 6.7 for the rutile target RDF and the anatase target RDF, respectively. The plots illustrate the evolution of the MAE between the target RDF and the average RDF $\langle g_b \rangle$ determined in the system. The target RDF is depicted as a black curve in the inset. Qualitatively, the evolution of the MAE was similar for both systems. During the initial simulation phase, the MAE decreased approximately linearly with increasing bias strength. After a certain bias threshold was exceeded, the simulation showed a gradual increase in temperature with further bias increase. The gradual increase in temperature in the system can be attributed to the sharp crystalline

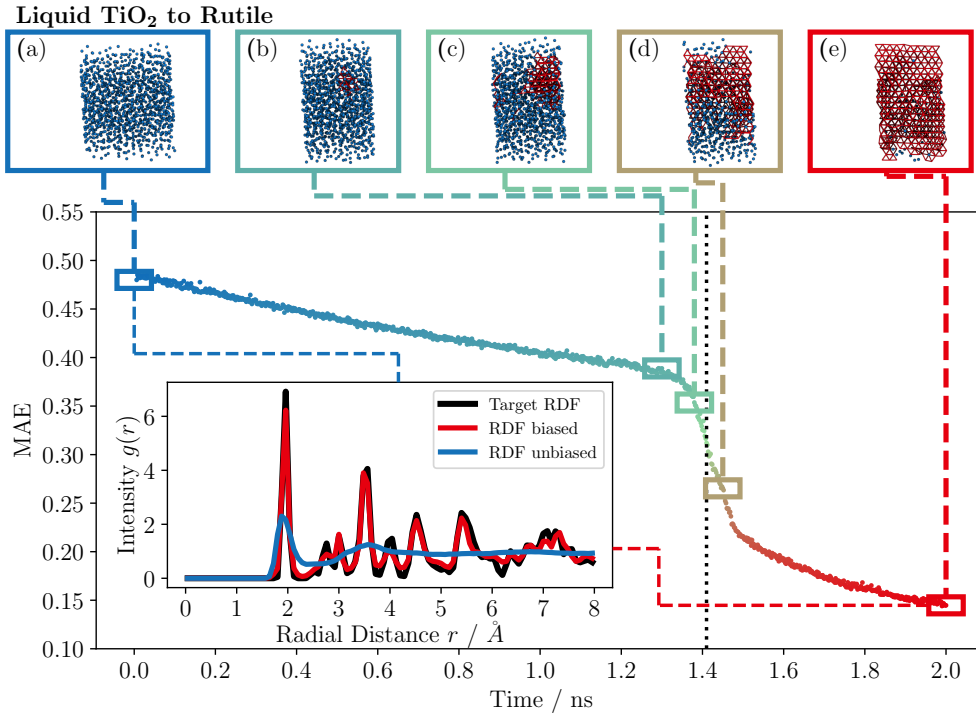


Figure 6.6: Crystallization of liquid TiO_2 to rutile. The mean absolute error (MAE) between the RDF of the biased TiO_2 system and the target RDF is shown in blue for higher values and red for lower values. The dotted vertical black line indicates the moment a stable nucleus was formed. The positions of the titanium atoms are depicted in the above snapshots, from left to right at 0 ns, 1.3 ns, 1.38 ns, 1.45 ns, and 2 ns. The atoms in the liquid and rutile phases, as determined from the average local bond order parameters, are colored blue and red, respectively. The inset illustrates the RDF of the unbiased liquid simulation (blue) and the final state of the system (red) with the target RDF (black).

peaks present in the RDF. The peaks cause significant variations in the Lagrange parameters across neighboring bins. Following Eq. (6.31), a significant disparity in Lagrange parameters results in substantial forces within the system. These forces were not sufficiently mitigated by the thermostat. Consequently, the system temperature increased. It was possible to mitigate this effect by increasing the thermostat damping parameter or by decreasing the time step size. However, mitigating this simulation artifact was not essential, as the target RDF was successfully reproduced anyway. After a certain amount of applied bias, the evolution of MAE changed for both systems from a moderate negative slope to a steep decrease of MAE. For the rutile target, this transition occurred after approximately 1.3 ns of simulation time. For the anatase target, the corresponding time was 10.7 ns. The significant decrease in MAE became less pronounced at approximately 1.5 ns in the system with rutile target RDF, whereas in the anatase target system this transition occurred after approximately 12.0 ns. Until the rutile simulation ended at 2.0 ns, the decrease in MAE remained small compared to

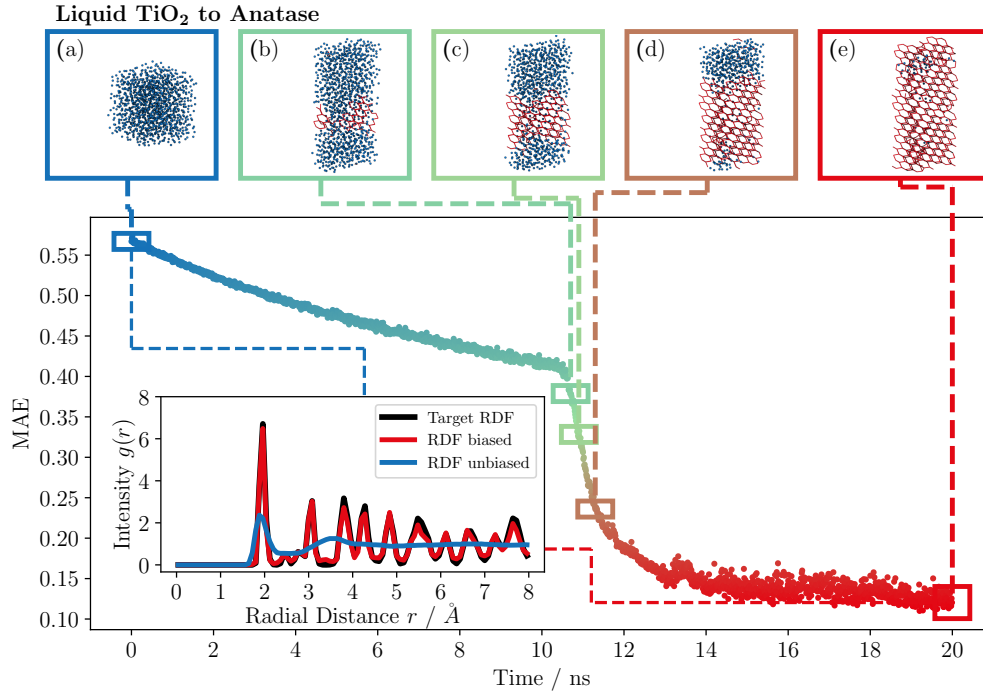


Figure 6.7: Crystallization of liquid TiO_2 to anatase. The mean absolute error (MAE) between the RDF of the biased TiO_2 system and the target RDF is shown in blue for higher values and red for lower values. The positions of the titanium atoms are depicted in the above snapshots, from left to right at 0 ns, 10.7 ns, 10.9 ns, 11.3 ns, 20 ns. The atoms in the liquid and anatase phases, as determined from the average local bond order parameters, are colored blue and red, respectively. The inset illustrates the RDF of the unbiased liquid simulation (blue) and the final state of the system (red) with the target RDF (black).

the earlier substantial change. For the anatase case, the MAE remained relatively constant until the end of the simulation at approximately 20.0 ns. The final RDF at the end of the simulation is represented by a red curve in the inset of Fig. 6.6 for rutile and Fig. 6.7 for anatase, respectively. As evident from the insets, the RDFs closely align with the respective target RDFs of rutile or anatase.

To further investigate the atomic structure of the systems during the biased simulations, average local bond order parameters were calculated for all titanium atoms. Subsequently, the obtained bond order parameters were used to determine the phase of the individual atoms, i.e., liquid or crystalline. To differentiate between the liquid and crystalline phases, a suitable degree of the average local bond order parameters and number of nearest neighbors were determined. To this end, histograms of the bond order parameter values for titanium atoms were constructed at the initial and final simulation times to guide the selection of these parameters. For the rutile system, the average local bond order parameter of the eighth degree

$\bar{q}_8$ was selected. It was calculated with the 12 nearest neighbors of each atom. Fig. 6.8 depicts the distribution of the $\bar{q}_8$ as histograms at the initial and final times of the biased simulation in blue and purple, respectively. The histogram shows minimal overlap. The threshold value to classify the respective titanium atoms was determined to be the dividing line at $\bar{q}_8 = 0.073$. Atoms with a bond order parameter value ≤ 0.073 were assigned to the liquid phase, whereas atoms with values > 0.073 were assigned to the crystalline rutile phase.

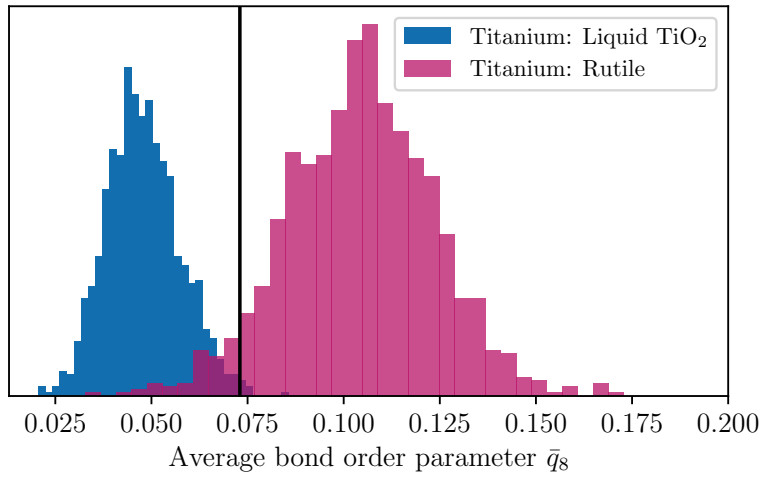


Figure 6.8: Histograms of the average local bond order parameters $\bar{q}_8$ for the rutile system. The histograms are calculated from the titanium atoms of the unbiased liquid TiO_2 system (blue) and the biased crystalline rutile system (purple). The black line marks the threshold value $\bar{q}_8 = 0.073$.

The same procedure was applied to the anatase system. In this case, the average local bond order parameter of degree 10 calculated over the 12 nearest neighbors was employed. The resulting values differentiated between the initial and final structures of the simulation. The corresponding histograms are depicted in Fig. 6.9. The dividing line was set at $\bar{q}_{10} = 0.085$. Therefore, titanium atoms with bond order parameters ≤ 0.085 were classified as liquid TiO_2 , and those with bond order parameters > 0.085 were classified as belonging to the anatase phase.

The threshold values for the average local bond order parameters enabled the classification of every titanium atom during the course of the biased simulations into either the liquid or the crystalline phase. The snapshots at the top of Fig. 6.6 and Fig. 6.7 show the classified titanium atoms at different times during biased simulations. The blue atoms were identified as liquid titanium atoms and the red atoms were classified as belonging to either the rutile or anatase phase. The snapshots are linked to the respective MAE and simulation time through

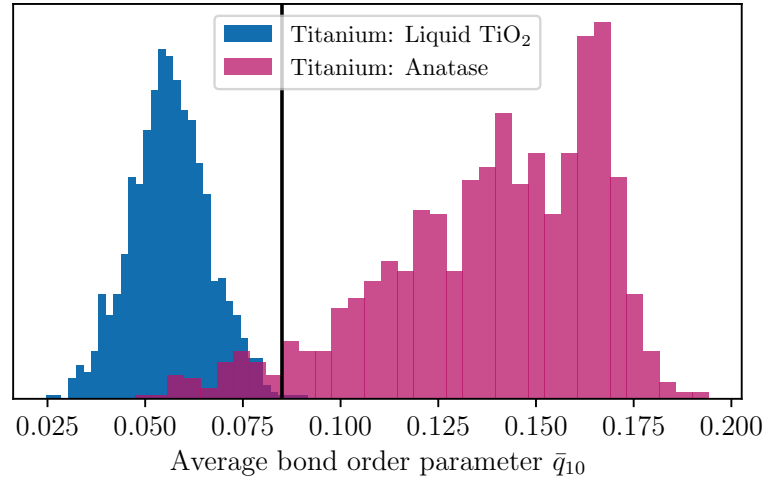


Figure 6.9: Histograms of the average local bond order parameters $\bar{q}_{10}$ for the anatase system. The histograms are calculated from the titanium atoms of the unbiased liquid TiO_2 system (blue) and the biased crystalline anatase system (purple). The black line marks the threshold value $\bar{q}_{10} = 0.085$.

the colored lines. Snapshot (a) shows that the system remained liquid until immediately before the MAE decreased steeply. As shown in snapshot (b), nucleation seeds appeared before the steep MAE decrease in both simulations. The nucleation seed proceeded to grow, and the system transformed into a crystalline phase. This transformation persisted until the system converted to either rutile or anatase, depending on the target RDF of the bias (snapshots (c)-(e)). Both crystalline phases contained only minor defects. Therefore, the steep descent of the MAE indicates a phase transition from liquid to crystalline, as predicted by CNT. The agreement between the average instantaneous RDF $\langle g_b \rangle$ and the target RDF $\tilde{g}_b^{\text{target}}$ at the end of the simulations confirmed the creation of the desired crystalline phase, i.e., rutile or anatase. Note that the application of the bias reduced the computational speed from 8.7 to 6.9 simulated nanoseconds per day. Therefore, This modification reduced the simulation's computational speed by approximately 21 %.

The similarity of the phase transition to the crystallization process predicted by CNT prompts the question of how well the intermediate crystalline states generated by the biased simulation correspond to physically sound transition states. To evaluate this question, the thermal stability of the obtained intermediate and final structures of rutile was tested. To this end, 16 atomic structures were extracted from the simulated trajectories at times ranging from 1.3 ns to 1.6 ns, with a temporal distance of 0.02 ns. These structures served as the starting point for simulating the TiO_2 system as an NpT ensemble at 2500 K and 1 atm without the application of any bias. Because no bias was active during the simulations, the

crystallization process completed only if the nucleation seed exceeded the critical nucleus size. Otherwise, the nucleus melted and the system returned to the liquid phase. The results of the equilibrium simulations demonstrated a strong correlation between the initial nucleus size and the successful crystallization. Fig. 6.10 shows the evolution of MAE in the equilibrium simulations for atomic configurations acquired at different simulation times from the biased simulations. For all initial structures extracted from the biased simulation before the 1.42 ns threshold, the crystallization seed underwent a phase transition to the liquid state and the system reverted to liquid TiO_2 . Conversely, every initial structure extracted from the biased simulation at or after 1.42 ns transformed completely into the stable crystalline rutile phase, indicating that these structures had overcome the free energy barrier. Consequently, at approximately 1.42 ns, the crystallization nucleus reached the size of a critical nucleus. These results demonstrate that the final crystalline phase is thermodynamically stable and that the identified transition states could provide valuable insights into liquid-to-solid phase transitions, e.g., through the determination of the committer probabilities of transition structures.

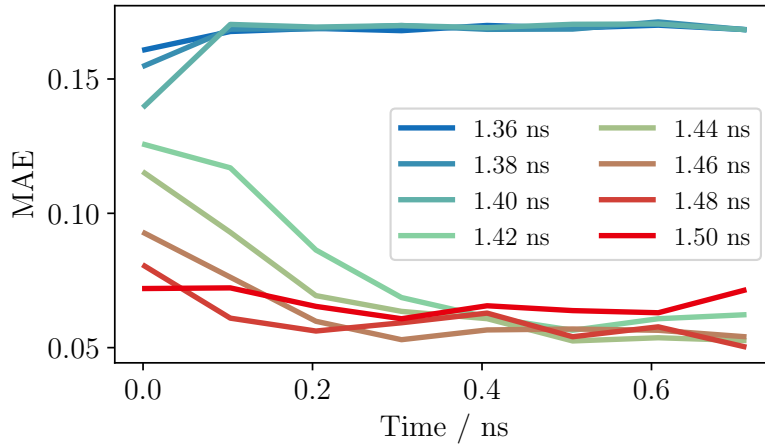


Figure 6.10: Evolution of the MAE of rutile nuclei in equilibrium simulations. The colors indicate the extraction time from the biased simulation, with blue colors indicating earlier and red colors later simulation times. For structures extracted before 1.42 ns, the MAE converges to the value characteristic of the liquid phase. At later times, crystallization completes and the MAE reaches a minimum.

■ 6.3.2.4 Crystallization of water

This section evaluates the algorithm's efficacy in enabling homogeneous crystallization of water in MD simulations. Inducing homogeneous crystallization in MD simulations serves as a prerequisite for investigating crystallization in mesoporous confinement. In contrast to

the simulated atomic TiO_2 systems, water is organized in molecules. Therefore, in addition to the position of the molecules, molecular orientation is essential during crystallization. Depending on temperature and pressure, water ice crystallizes in several polymorphs. In this study, the objective is to induce the formation of hexagonal ice I_h , which is the most stable form of ice at ambient pressures and temperatures.

To generate a target RDF of hexagonal ice, a NpT ensemble of hexagonal ice was simulated at a temperature of 10 K and 1 atm. The water molecule interaction was modeled with the TIP4P/ICE model.¹⁸⁸ The atomic form factor weighted target RDF was calculated over a radius ranging from 0 Å to 8.05 Å with a bin size of 0.07 Å. Subsequently, the target RDF served as input to the maximum relative entropy algorithm. The biased NpT system was set to a temperature of 360 K and 1 atm pressure. A temperature above the freezing point of water at 273 K was selected to enhance the mobility of water molecules, facilitating their reorganization into a crystalline structure. The liquid-to-solid phase transition occurred despite the elevated temperature because the induced bias lowered the free energy of the crystalline state, as discussed in Sec. 6.3.2.1. The Lagrange parameters were updated at 1000 time step intervals by averaging the instantaneous RDFs every 10 time steps. The time step size was 1 fs. The update parameter was set to $\xi = 5.0$ and no virial weighting was applied, i.e., $\kappa_b = 1.0$. In the initial simulation, the exponential scaling parameter was set to a value of $p = 1.0$.

The evolution of the MAE during the biased simulation is depicted in Fig. 6.11. The inset shows the target RDF (black) in comparison to the RDF at the start of the simulation at 0 ns (blue) and the RDF at the end of the simulation at 8 ns (red). The snapshots above the plot depict the position of the oxygen atoms bound in the water molecules. Similar to the preceding section, all oxygen atoms with average bond order parameter of $\bar{q}_6 \leq 0.07$ were classified into liquid atoms (blue). All oxygen atoms with $\bar{q}_6 > 0.07$ were classified as hexagonal ice atoms (red). The threshold of $\bar{q}_6 = 0.07$ for discriminating between liquid and crystalline atoms was determined from Fig. 6.12, which shows a histogram of bond order parameters for oxygen atoms in liquid water (blue) and the crystalline ice at the end of the biased simulation (purple). The threshold of $\bar{q}_6 = 0.07$ is indicated by the black line. Two issues emerge concerning the mediation of water crystallization with the maximum relative entropy algorithm. First, the system transitioned slowly, as indicated by the slow decrease in MAE. Second, many small crystallites formed instead of a single large crystal.

During the evolution of the MAE no abrupt phase transition occurred, as had been observed for TiO_2 . A slight acceleration in the decrease of MAE occurred at simulation times of approximately 3.5 ns. The slow crystallization process halted before full crystallization occurred. The stalling of the crystallization process is indicative of diminished molecular

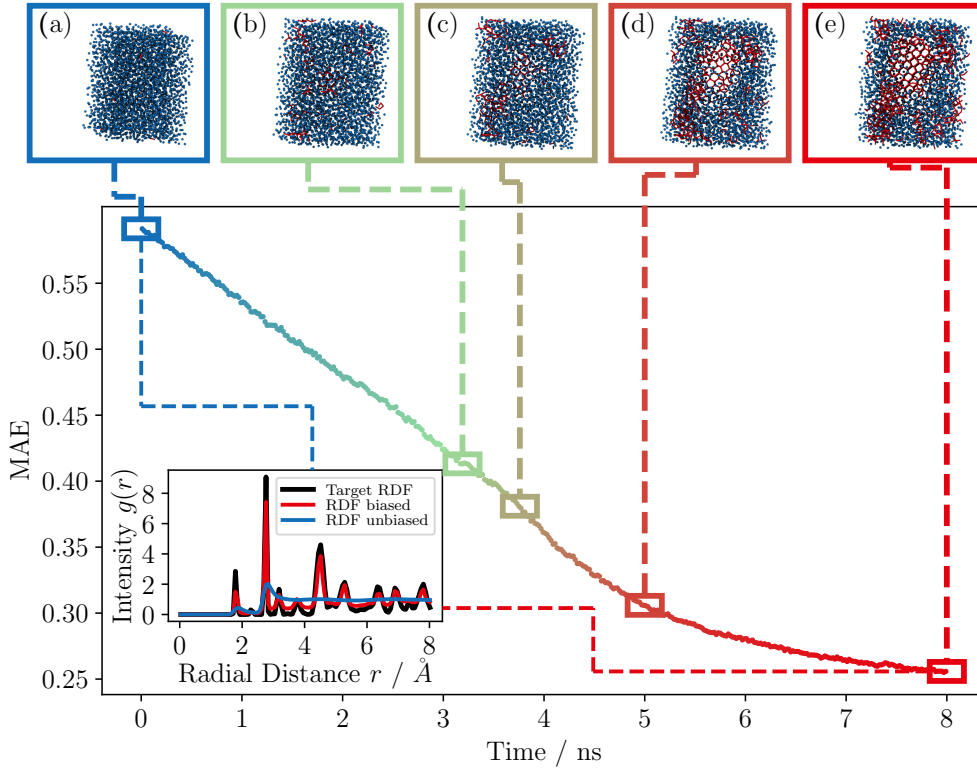


Figure 6.11: Crystallization of liquid water to hexagonal ice with exponential scaling of $p = 1$. The mean absolute error (MAE) between the RDF of the biased water system and the target RDF is shown in blue for higher values and red for lower values. The positions of the oxygen atoms are depicted in the above snapshots, from left to right at 0 ns, 3.19 ns, 3.76 ns, 5 ns, 8 ns. The atoms in the liquid and ice phase are colored blue and red, respectively. The inset shows the RDF of the unbiased liquid simulation (blue) and the final state of the system (red) against the target RDF (black).

dynamics under the larger applied bias. Fig. 6.13 displays the mean squared displacement of oxygen atoms bound in water molecules during the simulation. As shown in the figure, the change in mean squared displacement decreased as the simulation time increased and the biasing became stronger. After 3 ns, only little dynamics were observed in the system. As discussed in Sec. 6.3.1, the decrease in dynamics originated from the applied constraints, which drive the system toward reproducing the target RDF. Consequently, to achieve full crystallization, a very small update parameter has to be used to conserve the remaining dynamics. However, this approach would result in extended simulation times to obtain a fully crystallized system. During the simulation, the Lagrange parameters λ_b are optimized independently. Due to the exponential scaling parameter $p = 1$, the increase in bias per update is directly proportional to the difference between the target RDF $\tilde{g}_b^{\text{target}}$ and the average instantaneous RDF $\langle g_b \rangle$ for every bin b . Consequently, certain bin-specific Lagrange

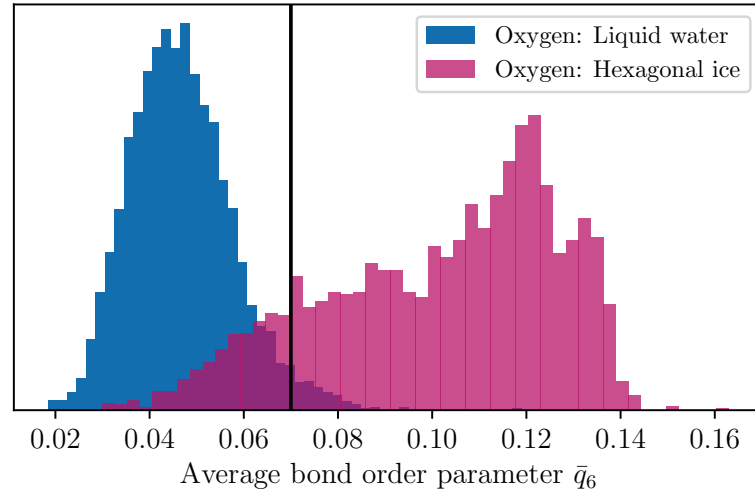


Figure 6.12: Histograms of the average local bond order parameters $\bar{q}_6$ for the water system. The histograms were calculated from the oxygen atoms of the unbiased liquid water system (blue) and the final biased water system (purple). The black line marks the threshold value $\bar{q}_6 = 0.07$.

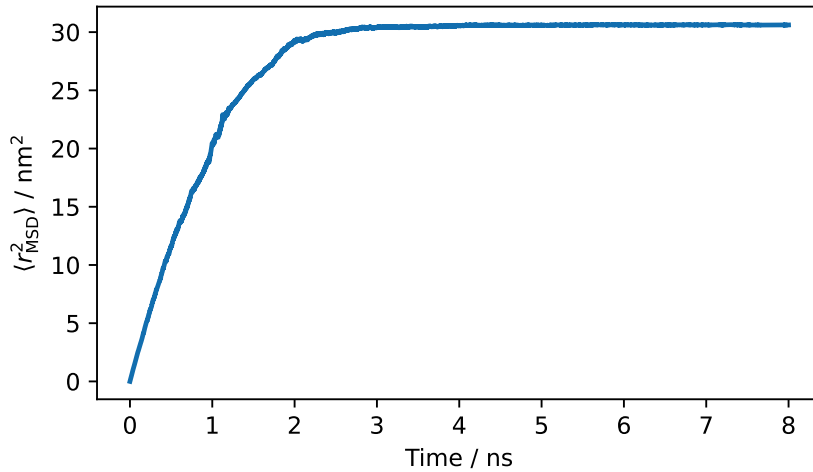


Figure 6.13: Evolution of the mean squared displacement of the oxygen atoms bound in the water molecules during the biased simulation.

parameters receive updates of larger magnitudes than others. Therefore, these bin-specific Lagrange parameters exert a stronger influence on the system dynamics. However, as discussed in Sec. 6.2.3, no theoretical justification exists for individual update speeds of the bin-specific biases. Therefore, the crystallization behavior of water could be enhanced by adjusting the exponential scaling parameter p to a value less than one. This adjustment has the potential to alleviate the significant constraints on the system's dynamics imposed

by Lagrange parameters associated to individual bins. Fig. 6.14 depicts the evolution of the MAE of systems with exponential scaling parameters of values $p < 1$. As evident from Fig. 6.14, the introduction of an exponential scaling parameter $p < 1$ produced phase transitions with more pronounced decreases in MAE during the transition. As such, the behavior was more analogous to the TiO_2 systems. Consequently, a decreased exponential scaling parameter can reduce the required simulation time to mediate a liquid-to-solid phase transition.

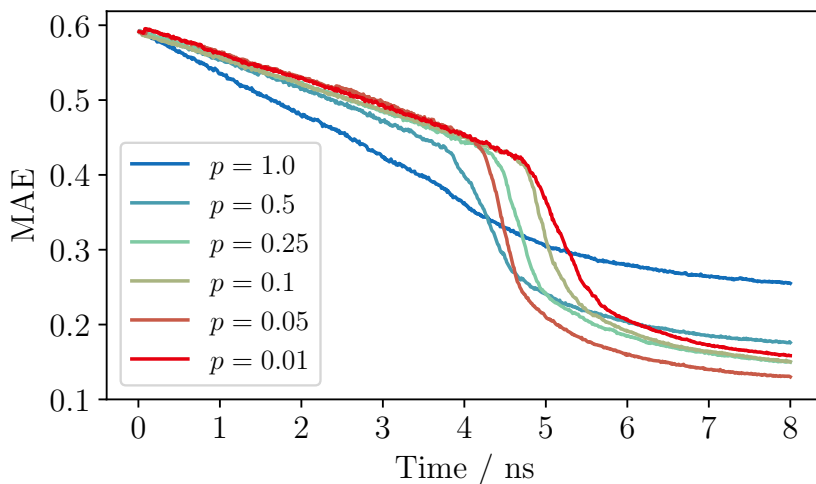


Figure 6.14: Evolution of the MAE of water during the biased simulations. The colors indicate different values of the exponential scaling parameter p , with blue colors indicating higher and red colors indicating lower values, respectively.

The second issue, which involves the formation of numerous crystallites rather than a large single crystal, is more challenging to resolve. The introduction of the exponential scaling parameter improved the crystallization dynamics of the system. However, the crystallized system still comprises numerous crystallites with varying orientations. Fig. 6.15 depicts the final configuration of oxygen bound in water after 8 ns biased simulation with $p = 0.01$. The formation of crystallites is hypothesized to result from the absence of orientation-related information in the RDFs, which only provide data on the atom positions. To overcome the free-energy barrier, the system requires a relatively strong bias which exceeds the original water interactions. This bias stabilizes crystallite formation, regardless of molecular orientation. Once formed, the water molecules remain fixed in the crystallites and cannot rearrange their positions to eliminate grain boundaries during the phase transition.

One strategy to mitigate this effect is to reduce the bias once the first crystalline structure was formed. To this end, an atomic configuration was extracted at 4.7 ns from a former

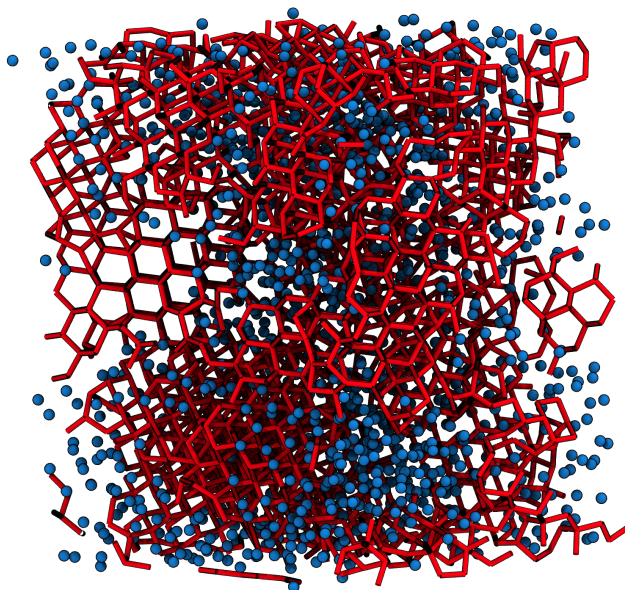


Figure 6.15: Final configuration of oxygen bound in water after 8 ns of biased simulation with exponential scaling parameter of $p = 0.01$.

simulation trajectory employing an exponential scaling parameter of $p = 0.01$. At the point of extraction, the atomic configuration exhibited an initial hexagonal ice structure. This atomic configuration served as the initial condition for a subsequent simulation. However, in this simulation, a constant bias was applied. The constant bias was extracted from the same simulation the initial structure was extracted from, but at an earlier time of 3.4 ns. The constant bias is not strong enough to spontaneously crystallize liquid water with high probability. However, the bias was sufficient to stabilize the existing small crystalline structure and enabled further crystallization. Fig. 6.16 shows the evolution of the MAE from this constant bias simulation. As demonstrated by the evolving MAE, a phase transition occurs even under the weaker applied bias. Although the simulation did not form a single defect free crystal, the resulting ice exhibited a significantly improved crystal structure, as evident from the snapshots in Fig. 6.16. The remaining defects are attributed to a combination of a residual bias that still limits the rearrangement of water molecules and finite-size effects of the simulated system.

The thermodynamic stability of the ice structure resulting from the constant bias was tested in an unbiased equilibrium simulation. Fig. 6.17 depicts the evolution of the MAE of the final ice structure, extracted after 5.5 ns, in equilibrium simulations with temperatures of 240 K, 250 K, and 260 K, respectively. To obtain the MAE the structure was compared to a perfect

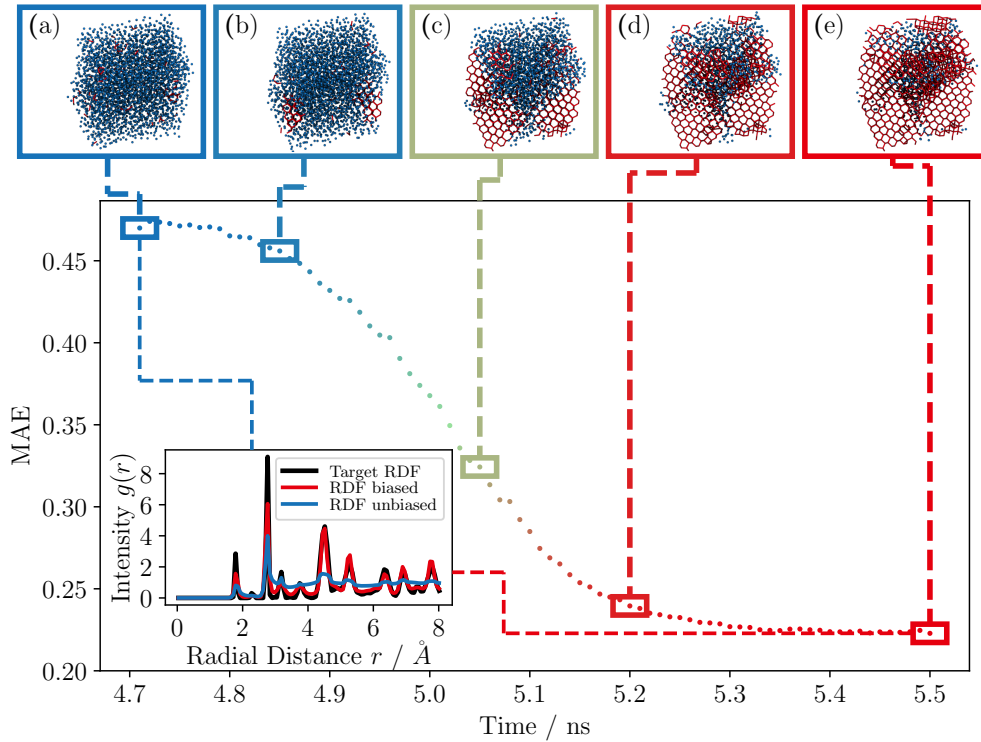


Figure 6.16: Crystallization of liquid water to hexagonal ice with an extracted initial atomic configuration and constant bias strength from a prior simulation. The mean absolute error (MAE) between the RDF of the biased water system and the target RDF is shown in blue for higher values and red for lower values. The positions of the oxygen atoms are depicted in the above snapshots, from left to right at 4.7 ns, 4.85 ns, 5.05 ns, 5.2 ns, 5.5 ns. The atoms in the liquid and ice phase are colored blue and red, respectively. The inset shows the RDF of the unbiased liquid simulation (blue) and the final state of the system (red) against the target RDF (black).

hexagonal ice crystal of equal temperature. Evidently, the final crystal structure melted at a temperature of 260 K, increasing the MAE. However, the crystal structure demonstrated stability at the remaining two tested temperatures, 240 K and 250 K, as indicated by the absence of an increase in the MAE. Conversely, the MAE decreased slightly, indicating that some of the crystal defects were corrected during the unbiased equilibrium simulations. The absence of significant molecular rearrangement at lower temperatures indicates that the crystal nucleus was too small to be stable at 260 K or above, but otherwise physically sound. Therefore, according to CNT, at 260 K, the surface energy contribution exceeded the volume energy contribution to the Gibbs free energy and the system did not overcome the free energy barrier. Consequently, the crystal structure is expected to maintain stability at elevated temperatures when the volume of the defect-free nucleus is increased. To obtain a larger nucleus size, the overall system size must be increased to minimize finite-size effects.

Furthermore, an additional reduction of the bias strength should result in an even lower density of grain boundary defects.

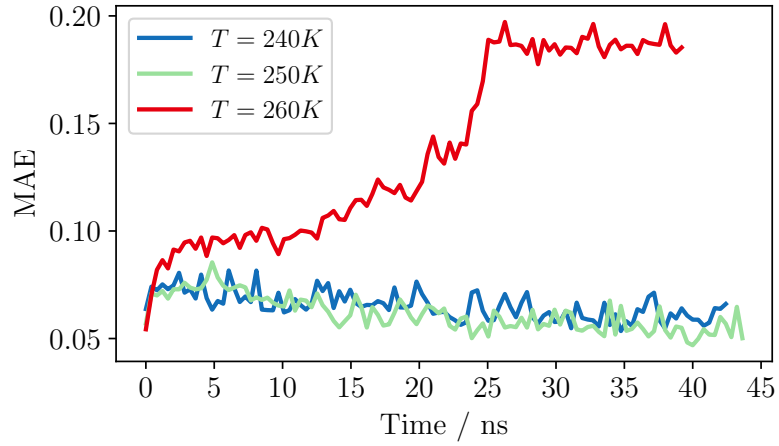


Figure 6.17: Evolution of the MAE of the extracted ice configuration in equilibrium simulations at temperatures of 240 K (blue), 250 K (green), and 260 K (red).

WATER IN MESOPOROUS MATERIALS: CONCLUSION AND FUTURE POSSIBILITIES

This thesis examined the capillary flow dynamics of water in ordered, cylindrical mesopores and the resulting imbibition-induced elastocapillarity with MD simulations. Furthermore, an algorithm was developed to address the challenges associated with simulating liquid-to-solid phase transitions. This chapter presents conclusions drawn from the findings and discusses implications for future research and applications, for the investigated effects and the algorithm, as well as for water in mesoporous materials in general.

7.1 Strategies for the analytical modeling of capillary flow dynamics of water in cylindrical mesopores on nanosecond time scales

To investigate imbibition dynamics of water imbibing into a pore matrix of ordered, cylindrical pores non-equilibrium MD simulations have been conducted. Specifically, 20 independent MD simulations of water imbibing into MCM-41 with pores of around 3 nm diameter were conducted. The individual simulation runs exhibited a low variance in the averaged capillary flow dynamics. During the analysis of the capillary flow dynamics two distinct imbibition regimes were identified, that require interpretation: a linear regime and a viscosity-dominated regime. The linear imbibition dynamics were observed during the initial 3.3 ps of the imbibition process. Two possibilities for the origin of the observed linear imbibition dynamics exist. The origin of the linear imbibition dynamics could stem from a systematic error arising from the initial atomic configuration at the start of the simulations or from an inertia-dominated liquid flow. Since the inertia-dominated liquid flow is predicted by the pressure balance determining capillary flow and the temporal extent of the linear imbibition dynamics falls within the predicted inertia-to-viscosity transition range of 0.08 ps to 7 ps, it is likely that the linear imbibition dynamics arise from an initial inertia-dominated liquid

flow. Therefore, this interpretation of the linear regime is adopted.

Comparison of observed capillary flow dynamics with several capillary flow models, namely, the original Lucas-Washburn model, the Bosanquet model, and the modified Lucas-Washburn model, provided valuable insights into modeling capillary flow processes on the nanosecond scale in mesoporous matrices of ordered, cylindrical nanopores. The analysis demonstrated that none of the models accurately describe the sub-nanosecond imbibition process, which involves flow regimes dominated by inertia and viscosity. This outcome aligns with the design of the original Lucas-Washburn model, which intentionally disregards the inertia-dominated flow contribution. However, the Bosanquet model is purposely designed to model the inertia and viscosity-dominated regime. In this case, the inaccurate replication of the capillary flow process appears to stem from the assumption of a static contact angle. The modified Lucas-Washburn model, on the other hand, explicitly incorporates a dynamic contact angle, yet it remains inadequate for simulating the full imbibition process, that includes the inertia-dominated regime. This conclusion may seem counterintuitive as in contrast to the original Lucas-Washburn model, the modified Lucas-Washburn model is derived by explicitly including the inertia of the liquid. However, a linear approximation of the capillary flow dynamics is employed to make the modified Lucas-Washburn model analytically describable. After this approximation, the modified Lucas-Washburn model exhibits the same fit capacity as the original Lucas-Washburn model, augmented by an initial time offset t_0 . Because the original Lucas-Washburn model neglects inertia in capillary flow, the modified version also fails to describe inertia-dominated capillary flow. Therefore, the most effective strategy to analytically model capillary flow with a dynamic contact angle is likely to treat the inertia-dominated and viscosity-dominated regimes separately.

To model the inertia-dominated regime, the linear model of Qu  r  ⁶¹ was found suitable, although this model does not consider a dynamic contact angle. The rationale for ignoring the explicit modeling of a dynamic contact angle arises from the short temporal extent of the inertia-dominated regime. Consequently, the change in contact angle during the linear imbibition process is considerably less pronounced than during the longer viscosity-dominated imbibition process. Therefore, the deviation of the imbibition dynamics from the linear model is small.

All three models demonstrated reasonable success in modeling the viscosity-dominated regime. However, when compared to the simulation snapshots, the static contact angles determined from the original Lucas-Washburn and Bosanquet models appeared to be in disagreement with the simulations. This result indicates the necessity of explicitly modeling the dynamic contact angle to accurately describe capillary flow on nanosecond time scales. As was demonstrated, the mere modification of the original Lucas-Washburn model with

an initial time offset, t_0 , provides the model with the capacity to model the contact angle dynamics during the capillary flow process. This property probably explains the agreement of the original Lucas-Washburn model and the Bosanquet model with the observed imbibition dynamics, even though both models consider only static contact angles. However, when analyzing capillary flow models, the resulting imbibition parameters must be interpreted as originating from the modified Lucas-Washburn model to derive valid physical parameters of the system. In particular, the determination of a static contact angle for the original Lucas-Washburn model can not be considered reliable. Other MD simulations⁷⁵ and experimental studies⁷⁴ report the equilibrium contact angle of water on silica to be $\theta = 0^\circ$. Consequently, all contact angles derived from the fitted capillary flow dynamics models exceed this equilibrium contact angle. This discrepancy may arise because the imbibition times considered were too short for the dynamic contact angle to converge to the equilibrium contact angle. Thus, the equilibrium contact angle of $\theta_{(M)LW} = 51.96^\circ$ obtained from the Lucas-Washburn models should be treated with caution. Despite this, all imbibition models examined demonstrated a reasonable agreement with the observed imbibition dynamics. This agreement is notable because the assumption of a perfectly cylindrical pore is only approximately valid for the modeled pore matrix. Therefore, it can be concluded that capillary flow models that assume cylindrical geometry can reliably predict capillary flow dynamics, even when the underlying assumption of cylindrical geometry is not perfectly satisfied.

Altogether, non-equilibrium MD simulations of capillary flow proved effective for investigating fluid dynamics in mesoporous materials at the atomic scale, especially at nanosecond timescales. To better understand how the dynamic contact angle influences the imbibition dynamics of water in MCM-41 and other systems, future simulations should extend the simulated capillary flow to timescales longer than the sub-nanosecond range considered here. Given the effectiveness of MD simulations in studying capillary flow dynamics, MD simulations are also recommended for investigating other effects driven by capillary flow. For instance, future studies could examine matter transport in capillary flows. Specifically, the simulation could be expanded to study chemical separation by introducing substances to the initial water reservoir. Alternatively, adding ions to the initial water reservoirs would enable the investigation of electrolyte transport in capillary flows. The ion transport mechanism could be of particular interest for harvesting electrical energy from wetting-drying cycles in mesoporous materials. Consequently, future non-equilibrium MD simulations of capillary flow could constitute a powerful tool for fundamental research on nanofluidics and for applications of matter transport.

7.2 Towards the understanding of imbibition-induced elastocapillarity

7.2.1 The elastic deformation model

As demonstrated, capillary flow of water in ordered, cylindrical mesopores causes imbibition-induced elastocapillarity in the pore matrix. The analytical model presented in this thesis attributes the resulting elastic deformation of the pore matrix to the Laplace pressure and the Bangham effect and predicts both the magnitude and the dynamics of the deformations. To the best of the author's knowledge, this model is the first to predict imbibition-induced elastocapillarity in ordered, cylindrical mesopores. The model was designed to describe the macroscopic deformation dynamics in two imbibition scenarios. First, a freely deformable pore matrix with liquid imbibing from one side was considered. This scenario is analogous to an imbibition experiment conducted on a monolithic pore matrix with a dilatometer. Second, a pore matrix was considered that was constrained in its lateral deformations, such that no shear deformations were possible and the lateral strain remained constant along the entire axial length of the pore matrix. In this scenario, the liquid imbibes from both sides of the pore matrix simultaneously. This imbibition scenario is analogous to the imbibition geometry of the conducted MD simulations. For both scenarios, the model considers the lateral and axial imbibition-induced macroscopic deformation dynamics. The developed model allows for multiple conclusions regarding the expected elastic deformations of pore matrices consisting of ordered, cylindrical pores during the imbibition of a liquid.

One central conclusion from the elastic model is that all deformation dynamics are expected to be proportional to the imbibition length of the liquid columns into the pore matrix during the active imbibition process. The axially induced macroscopic strain is expected to be monotonically expansive during the active imbibition process for both considered imbibition geometries, i.e. the freely deformable and constrained pore matrix. A contraction of small magnitude upon complete pore filling is predicted, originating from the Poisson effect of the disappearance of the Laplace pressure. For the freely deformable pore matrix, the lateral macroscopic strain depends on the axial distance from the liquid–vapor interface of the imbibing liquid column. Depending on the relative strength of the Bangham effect compared to the Laplace pressure effect, the laterally induced strain is either expansive over the entire axial pore length or exhibits an axial point of inversion where contractile strain turns into expansive strain as the distance from the liquid–vapor interface increases. A theoretical lower bound for the axial position of the point of inversion is determined by the model. For the constrained pore matrix, macroscopic contractile deformations in the lateral direction are predicted to be theoretically possible. However, the maximum attainable contraction

remains modest, even under conditions that are highly favorable for contractile behavior of the pore matrix. Consequently, the observed lateral deformations are likely to be primarily expansive in most systems during active imbibition. For unconstrained and constrained pore deformations, a substantial lateral expansion of the pore matrix is predicted once the Laplace pressure vanishes after the complete filling of the pore voids. This expansive effect is referred to as *Laplace jump*.

In addition to predicting the deformation behavior in matrices of ordered, cylindrical mesopores, the elastic model offers new opportunities to extract properties related to imbibition-induced elastocapillarity from the observed deformations. For instance, the determination of both the acting Laplace pressure and the effective Bangham pressure is possible from the observed deformation dynamics in the ordered, cylindrical mesopores. Additionally, the surface stress release can be estimated when the pore radius is known. Notably, the Laplace pressure and the Bangham pressure can be determined independently through two different approaches. Both quantities can be determined from the deformation dynamics during active capillary flow. Furthermore, the Bangham pressure can be calculated from the final deformation upon complete filling, whereas the Laplace pressure can be determined from the observed Laplace jump. Other properties of the liquid or the pore matrix could also be determined from the deformation dynamics, such as the surface tension of the liquid, the contact angle, the pore radius, the porosity, Young's modulus, or the Poisson ratio.

7.2.2 Comparison of predicted and simulated imbibition-induced elastocapillarity

Quantification of the imbibition-induced strain in the pore matrix of the conducted MD simulations permitted a direct comparison between observed imbibition-induced deformation dynamics and theoretically predicted deformation dynamics. Analysis of the simulations demonstrated that the deformation dynamics of the lateral and axial pore matrix directions can be classified into three distinct deformation regimes. These regimes are designated as the active imbibition regime (I), the equilibration regime (II), and the final equilibrium regime (III). The analysis of each of these deformation regimes allows for insights about the nature of imbibition-induced elastocapillarity.

During the active imbibition regime (I), the simulations exhibited a time-dependent expansive strain in the lateral and axial directions. The observed strain followed the functional form of the modified Lucas-Washburn equation. These results confirm two central prediction of the elastic model. First, that the imbibition-induced deformations during the active imbibition process are predominantly expansive. Second, that the induced deformations are directly proportional to the imbibition length of the liquid column. The proportionality

of the deformation dynamics to the imbibition length merits further consideration. Because the elastic model describes deformation dynamics by assuming a constant Laplace pressure, the model assumes a static contact angle of the imbibing liquid column during the imbibition process. However, analysis of capillary flow dynamics provided strong evidence that the contact angle varied dynamically during imbibition. A dynamic contact angle causes the Laplace pressure to change dynamically which should result in deformation dynamics that are not proportional to the imbibition length of the liquid column. This contradicts the predictions of the model as well as the observations from the simulations. This apparent contradiction can be resolved by considering that the contact angle undergoes the most significant changes during the initial stages of imbibition. However, during that period, the wetted area of pore matrix surface is small, resulting in only a limited amount of deformation. During later times, the rate of change in contact angle decreases and the assumption of a constant Laplace pressure turns into a reasonable approximation. As a result, the dynamic evolution of the contact angle and, consequently, the evolution of the Laplace pressure during the capillary-flow process are expected to have a limited impact on the deformation dynamics of the pore matrix, explaining the simulated deformation dynamics correctly predicted by the elastic model.

To further verify the elastic model, the observed deformation dynamics during the active imbibition of water were used to calculate the Laplace pressure and the effective Bingham pressure. The magnitude of the attained Laplace pressure agreed with theoretical predictions from imbibition models, whereas the values calculated for the effective Bingham pressure and the surface stress release were significantly smaller than the values determined from the final equilibrium strains. These deviations indicate that the assumption of a continuous stress-strain equilibrium in the pore matrix during active imbibition may not be valid. Consequently, a delay in the observed strain relative to the induced stress could occur in the simulations. This delay between stress and strain should manifest as additional expansive strain during the equilibration regime of the pore matrix. Note that the delayed expansive strain is expected to occur in addition to the predicted expansive strain that arises from the Laplace jump.

During the equilibration regime (II), a substantial expansive strain, in agreement with the predicted Laplace jump, was observed in the lateral pore matrix direction. Consequently, another key prediction of the presented elastic model was confirmed. However, the magnitude of the Laplace jump exceeded the elastic model's predicted magnitude. A reduced contact angle caused by the collision of two menisci of opposite direction explains part of the excess deformation, yet additional mechanisms for expansive strain are needed to account for the full observed strain. Consequently, the excess strain indicates that the assumed continuous

stress-strain equilibrium was in fact violated during the simulations. This violation caused a delayed additional expansion of the pore matrix after the pore space was entirely filled by the liquid. Another discrepancy between the simulations and the model's predictions could also be explained by a delayed additional expansion in the axial direction. Specifically, the elastic model predicts a slight contraction in the axial direction during the equilibration of the pore matrix. Instead, a minor expansion was observed. Because the predicted contraction is small, a delayed axial expansion could exceed it and thus explain the discrepancy.

In the equilibrium regime (III), the pore matrix exhibited a constant final strain in every direction. The induced stresses that caused these deformations were determined to be of similar magnitudes in the lateral and axial pore matrix direction. Consequently, the simulation results align with the predictions of the elastic deformation model. The final observed strain values were used to derive the effective Bangham pressure and surface stress release. The calculated surface stress release exceeded the change in surface energy predicted by Young's relation. This result indicates that, during imbibition, the dynamic contact angle may not have converged to the equilibrium contact angle. This conclusion agrees with the analysis of capillary flow dynamics, which also indicated that the contact angle may not have reached the equilibrium contact angle during the active imbibition process. Additionally, the derived surface stress release values were compared with surface energies reported in the literature. The determined values for the surface stress release also exceed the literature values for surface energy release. However, in this case, the discrepancy was less pronounced than the discrepancy observed between the surface energies derived using Young's relation and may be attributed to inaccuracies in the literature values or deviations in the modeling of the system. Additionally, the tendency towards an increased surface stress release in the simulations could be an indication that the assumption of a perfectly smooth cylindrical pore geometry in the elastic model is too restrictive. In this case, the observed increase in surface stress release would arise from the amplification of the Bangham effect caused by an increased roughness of the pore surface.

Altogether, substantial evidence was collected in favor of the presented model describing imbibition-induced elastocapillarity and many central predictions of the elastic model were confirmed. However, several limitations and open questions remain regarding the model and the conducted simulation study. A significant source of uncertainty in the comparison between model and simulation arises from the indication that the assumptions of elastic deformation theory are violated in the modeled MCM-41 structure. Specifically, the determination of the Young's moduli of the simulated porous structure revealed an apparent violation of elastic deformation theory. This effect probably arises from the x-y axis coupling introduced to stabilize the MCM-41 structure in the simulations. Despite this coupling, many qualitative

predictions of the elastic model regarding imbibition-induced deformation dynamics agree with observations from the imbibition simulation. This agreement supports the qualitative validity of the simulations. However, the impact of the deviation from elastic deformation theory on quantitative results, such as calculated values for the induced stresses, remains unclear. Therefore, the reported values should be interpreted with caution. Additional open questions arise from the discrepancy between dynamically and statically determined pressures and surface stress release, the observed expansion instead of contraction in the axial direction during equilibration, and the extensive magnitude of the Laplace jump. These effects were hypothesized to result from a delayed equilibration of the pore matrix to the surface stress release, but further investigations are necessary to substantiate this hypothesis. Another open question concerns the evolution of the dynamic contact angle during the simulated capillary flow. The analysis of the simulation study indicated that the contact angle did not converge to the equilibrium contact angle during the imbibition process, but the simulation analysis has not yet provided definitive proof of this hypothesis. Additionally, uncertainties about the deviations of the deformation dynamics from the model during the initial period of the imbibition process remain. Finally, two aspects of the model assumptions require further investigation. These aspects are the assumption of perfectly cylindrical pores and the possible effect of surface roughness on the magnitude of the deformations. These listed issues should be addressed in future studies to clarify the validity and limitations of the developed model of imbibition-induced elastocapillarity. These additional studies of imbibition-induced elastocapillarity could be based on simulations, in particular, on improved MD simulations, or experiments, such as dilatometry or X-ray scattering studies.

7.2.3 Future prospects of research and applications

The presented results encourage further investigation of imbibition-induced elastocapillarity and its potential applications.

Given the success in generating insights about imbibition-induced elastocapillarity, additional MD simulations of improved design would be worthwhile. Based on the analysis of the conducted imbibition simulations, these MD simulations should be improved in three key aspects relative to the simulation setup described in this thesis. First, it is essential that the investigated system satisfies the elastic deformation theory. In particular, the porous structure has to be sufficiently stable to eliminate the need for simulation box coupling and to ensure that elastic deformation theory remains valid. Second, the pore geometry should be simplified. In this context, examining pore structures of perfect cylindrical geometry would be worthwhile in order to further validate the presented elastocapillarity model. Subsequent

alterations of the pore surface or geometry could elucidate the impact of pore-wall roughness and pore geometry on the deformation dynamics and magnitudes. Finally, experiments with extended capillary flow times would likely provide valuable insights. As the imbibition velocity decreases continuously during viscosity-dominated capillary flow, the pore matrix deformations are expected to fully equilibrate to the imbibition-induced stresses at longer imbibition times. Consequently, for systems with significantly longer imbibition times, the assumption of stress-strain equilibrium constitutes a better approximation and should fit the developed deformation model more precisely. Additionally, longer imbibition times improve the agreement between the modeled and observed Laplace pressure effect because the dynamic contact angle approaches the equilibrium contact angle as the imbibition velocity decreases. In partial wetting conditions, the measurement of the converged equilibrium contact angle would enable the comparison of the surface stress release predicted by the elastic model with the surface energies derived from the Young relation.

In addition to the recommended supplementary MD simulations, exploration of other research avenues into imbibition-induced elastocapillarity could provide valuable insights. For instance, future studies should aim to obtain a more thorough understanding of imbibition-induced elastocapillarity in systems with distinct properties. The relatively stiff silica matrix limits elastocapillarity effects. Conversely, more flexible materials, such as polymers, are expected to exhibit more significant effects and therefore be more suitable for applications based on elastocapillarity.¹⁸⁹ Investigating imbibition-induced elastocapillarity in porous media with a larger variation of pore geometries represents another promising direction for future research. Ordered, cylindrical pores provide a simple geometry that suits initial studies of imbibition-induced elastocapillarity. However, a study of more complex geometries, including unordered porous media, could expand the range of future applications. Finally, several methods can regulate the intensity of interfacial effects. These methods include the use of distinct liquids or mixtures of liquids, functionalization of pore surfaces¹⁹⁰, and application of electrical potentials⁵⁶. Because elastocapillarity depends directly on the intensity of interfacial effects, these methods could control the deformation dynamics and magnitudes of porous materials during imbibition.

A comprehensive understanding of imbibition-induced elastocapillarity could serve as a foundational element for future applications. Two potential applications utilizing imbibition-induced elastocapillarity include sensory technology and actuation systems. For instance, measurements of the deformation of porous systems could be used to sense the filling fractions of porous systems. Conversely, the deformation of porous systems can be regulated by modifying the dynamics of the imbibition process. This capability could enable the porous materials to function as actuators. Ultimately, future measurements of imbibition-induced

elastocapillarity could streamline the characterization of liquids or porous systems.

7.3 Enabling liquid-to-solid phase transitions in MD simulations

The results presented thus far demonstrate the value of MD simulations as a tool for obtaining scientific insights into the capillary effects of water in porous materials. In light of these results, the final section of this thesis focuses on the development of a method for investigating liquid-to-solid phase transitions in mesoporous materials using MD simulations. To this end, an algorithm was developed that incorporates information from radial distribution functions into MD simulations via the principle of maximum relative entropy. The algorithm mediates crystallization by reproducing the RDF of the crystalline target in the simulated system. Consequently, the algorithm can mediate liquid-to-solid transitions and also manipulate the structure of liquids in simulations in general. To illustrate the practical benefits of the algorithm, two exemplary applications of the algorithm were presented.

In the first application, the algorithm was used to bias liquid water systems described by the TIP3P model to match the RDF of the TIP4P/2005 model. During this process, the agreement between the angular distribution function of the target liquid and the biased liquid also increased. Consequently, the algorithm may benefit applications that require structural alignment between two individual liquids. Concurrently, the application of the maximum relative entropy algorithm significantly impeded molecular dynamics through the restraining bias. Therefore, it is advisable to refrain from applying the algorithm when accurate reproduction of molecular dynamics is essential.

The second demonstrated application of the maximum relative entropy algorithm was the mediation of liquid-to-solid phase transitions of titanium dioxide and water systems in MD simulations. The results were particularly encouraging for the TiO_2 system, likely because the TiO_2 system is simulated by individual atoms. An outstanding issue concerns the strong required bias forces to induce crystallization, as these substantial forces cause a temperature increase within the simulated system. The temperature increase can be mitigated by reducing the length of the time steps or by increasing the damping parameters in the thermostat. However, future developments of the algorithm should prioritize the elimination of this simulation artifact. Nonetheless, the maximum relative entropy algorithm demonstrated the potential to direct the MD system to crystallize into the desired polymorphs with a low defect rate. Because the observed transition states are physically sound, the method may allow investigation of the committor probabilities of individual nucleation seeds. In summary, the results demonstrate that the presented maximum relative entropy algorithm can function as a powerful tool to extend MD simulations.

Regarding the mediation of liquid-to-solid transitions of water, the evaluation of the algorithm yielded mixed results. Compared with the TiO_2 system, producing defect-free crystals proved more challenging. During the crystallization process low crystallization dynamics were encountered, causing the phase transition to stagnate. The problem arose from overly restrictive restraints on the system, which were a result of individual bin-specific Lagrange parameters of significant magnitude. The issue was resolved by applying exponential scaling parameters with values less than one. With the reduced exponential scaling parameters updates to the Lagrange parameters become more uniform. This uniformity prevents excessive bin-specific Lagrange parameters, which cause low crystallization dynamics. A second issue concerned the formation of individual crystallites separated by grain boundaries. The crystallites likely formed because the RDF lacks crucial information about the orientation of the molecules in the ice crystals. As a consequence, the bias prevents the molecules from rearranging into defect free crystallites. It was demonstrated that applying a constant low bias potential to an atomic configuration that already exhibited initial crystalline structures lead to ice crystals with reduced defects. Therefore, to ensure the formation of well-formed ice crystals from a bias potential that does not include orientational information, it is essential to maintain the bias at a minimum level. Consequently, future algorithm enhancements should prioritize more advanced strategies to lower the influence of the bias potential during the process of phase transition. For instance, the applied bias could scale with the size of the crystallite in the system. In this scenario, the Lagrange parameters could be scaled as a function of the magnitude of the mean absolute error. As a result, crystal defects are minimized by decreasing the bias potential as the crystal forms. Therefore, establishing an effective functional relation between Lagrange parameters and MAE represents a promising avenue for further research, also with regard to the investigation of mediated phase transitions of water confined in porous media.

The maximum relative entropy algorithm has potential applications beyond reproducing RDFs in liquids and mediating liquid-to-solid phase transitions in MD simulations. One potential application is the training of machine learning interaction potentials (MLP). Training MLPs requires a versatile training data set encompassing a wide range of system configurations. As demonstrated, the maximum relative entropy method can bias MD systems to reproduce specific configurations or establish structural similarity. Consequently, the algorithm can generate high-value training data for the training of MLPs.

Additionally, as discussed the principle of maximum relative entropy can be applied to any observable derived from the ensemble average of a simulated thermodynamic system. Consequently, the approach is not limited in reproducing RDFs but can be used to reproduce many other observables in MD simulations. Two observables may prove to be of particular

interest in the future. These are the structure factor function $S(q)$ and the thermodynamic ensemble average of the average local bond order parameters.

Experimentally determined RDFs of atomic systems are derived from WAXS measurements by applying a Fourier transformation to the structure factor function. Artifacts from the Fourier transform are therefore typically introduced into the RDF. In contrast, the structure factor function is directly obtained in WAXS measurements. Eliminating the Fourier transformation by biasing the system to reproduce the structure factor function directly could facilitate the interpretation of WAXS data. In contrast to the commonly used RMC method for interpreting WAXS measurements, the obtained algorithm would not constrain the resulting system with a variance value that is not supported by experimental data. Additionally, the determined structure would benefit from the prior information contained in the original interaction potential of the system. Particularly, the combination of bias potential with machine learning algorithms trained to model diverse systems^{191,192} may yield accurate interpretations of WAXS measurements. Finally, the method of Lagrange parameters could be utilized to objectively determine the coupling parameter to balance the bias to the original potential energy of the system.

The maximum relative entropy approach could also be used to reproduce a thermodynamic ensemble average of the average local bond order parameters defined by Eq. (6.47). As demonstrated in this thesis, average local bond order parameters provide a robust method to classify the phase of individual atoms in simulated systems. Consequently, the system average of the average local bond order parameter serves as a powerful indicator of the phase composition in the system. One drawback of using the average local bond order parameters as target variable in the maximum relative entropy principle is that target values cannot be obtained from experiment. Therefore, this approach cannot combine experimental data with simulation results. However, the thermodynamic ensemble average of the average local bond order parameters can be employed to bias the thermodynamic system toward specific atomic configurations when these configurations are known. Consequently, this strategy should be well-suited for studies of phase transitions with known initial and final configurations. In such studies, average local bond order parameters are expected to offer advantages over RDFs because of two reasons. First, because spherical harmonics contribute to the calculation of the parameters, the parameters are sensitive to the orientation of molecules. Consequently, they are expected to demonstrate enhanced performance when applied to molecular crystals, such as water ice. Secondly, crystalline systems are well characterized by one or two individual bond order parameters. Therefore, only one or two Lagrange parameters need optimization, in contrast to the reproduction of all bins of the RDF. As a result, the relative weighting of the Lagrange parameters becomes less critical.

Crystallized water confined within MCM-41 pores of around 10 nm diameter is hypothesized to adopt a structure similar to cubic ice.^{109–112,193,194} Consequently, the application of a bias based on the ensemble average of average local bond order parameters, which discriminates cubic ice from confined liquid water offers a promising approach to simulate the freezing of water in porous confinement. As a result, applying biases based on average local bond order parameters could facilitate studies of the liquid-to-solid phase transition under strong confinement and the resulting elastocapillarity effects on the pore matrix. Therefore, future studies should focus on the application of the here-presented algorithm, or an updated form of it, e.g., with local bond order parameters as target variables, to investigate the proficiency of the algorithm to mediate liquid-to-solid phase transitions of water in confinement. After successful mediation of liquid-to-solid phase transitions of confined water, subsequent studies could examine the structure of confined ice and the elastocapillarity effects induced by phase transitions.

7.4 Shaping the future with water-driven materials

The findings of this thesis contribute to a more comprehensive understanding of capillary flow and the phenomenon of imbibition-induced elastocapillarity in water-driven mesoporous materials. The results indicate substantial potential for scientific progress and for the development of sustainable, scalable technologies through further investigation of water-driven mesoporous materials, especially in small-scale structures where interfacial effects are amplified. The resulting technologies could contribute to the realization of several United Nations Sustainable Development Goals. However, the minute structures of mesoporous materials and the confinement of water within the pore matrices limit the number of scientific methods that can contribute to a more profound understanding of capillary effects in mesoporous materials. As demonstrated in this thesis, MD simulations are particularly well suited to investigate capillary effects in mesoporous materials on small scales, because the simulations are comprised of individual atoms and their interactions. Consequently, capillary effects emerge naturally in these simulations, obviating the need for any a priori assumptions about the capillary effects. This feature renders MD simulations a powerful method for investigating previously unexplored capillary effects and their underlying mechanisms. However, it was shown that conventional MD simulations cannot model certain processes, such as liquid-to-solid phase transitions. One potential solution to this problem is to extend conventional MD simulation algorithms by integrating external, potentially experimentally derived information. As demonstrated, when integrating information, the principle of maximum relative entropy provides a suitable starting point for further extension of MD

simulations. Altogether, it is my hope that, the results and concepts presented in this thesis contribute to the development of sustainable, scalable water-driven mesoporous materials and thereby contribute to the global efforts toward peace and prosperity on a well-preserved planet.

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