SURFACE ENERGIES NEAR A HARD WALL: STATISTICAL MECHANICAL APPROACH

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Abstract

This study particularly focuses on the behaviour of the liquid phase upon encountering a solid surface, encompassing phenomena such as surface tension and the dissolution of the liquid into the solid. Through density functional theory (DFT) calculations, this research aims to characterize the energies involved in these processes and elucidate the spatial distribution of molecules at the interface. Notably, the findings diverge from the predictions of scaled particle theory (SPT), a theoretical framework commonly used to describe simple fluid behaviour near surfaces. Specifically, the discrepancy lies in the homogeneity of the fluid near the surface. SPT assumes a uniform density profile of particles in close proximity to the interface. However, the results obtained from DFT simulations suggest that the fluid's density and molecular arrangement near the surface exhibit non-uniformity and complexity beyond the scope of SPT's assumptions. This disparity underscores the limitations of simplistic theoretical models like SPT in capturing the nuanced behaviours of fluids near surfaces. It highlights the necessity of employing more sophisticated computational approaches such as DFT to gain a comprehensive understanding of interfacial phenomena. Such insights are crucial for various scientific endeavours, including the development of advanced materials and the optimization of processes involving solid-liquid interfaces.

Keywords: Density Functional Theory, Scaled Particle Theory, Surface Energies, Solid-Liquid Interfaces

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Introduction

Understanding the behaviour of fluids in the presence of solvated particles is essential in various scientific fields, from chemistry to materials science. When a solvated particle is introduced into a fluid, it perturbs its neighbouring molecules, leading to changes in the solvent distribution function, including density profiles and inhomogeneous pair correlations (Ariga et al., 2012). These alterations are significant as they influence the interaction between particles, which can be crucial for predicting various phenomena, such as solvation forces and adsorption behaviours. Thanks to the statistical mechanics approach, considerable progress has been made in understanding fluid behaviour near solid surfaces and in confined spaces (Evans, 1992). For instance, when fluids are in contact with planar walls or confined within pores, their structure and properties exhibit significant modifications compared to bulk fluids. These changes are driven by intermolecular interactions and surface effects, which play a pivotal role in determining the behaviour of colloidal particles and the solvation forces between them (Henderson, 1992).

Colloidal particles are involved in numerous biological and chemical processes, making the knowledge of solvation forces crucial for understanding these phenomena. For example, in biological systems, colloidal particles play essential roles in drug delivery, cellular interactions, and biomolecular recognition (Giulia Bonacucina et al., 2009). Similarly, understanding the adsorption of reactants and products onto colloidal particles in chemical reactions is vital for controlling reaction kinetics and selectivity (Beltscheva et al., 2003).

One particularly significant aspect of colloidal particle behaviour is their adsorption properties, especially concerning soil colloids and their impact on plant nutrition (Zaid Ulhassan et al., 2021). Understanding how fluids adsorb onto colloidal particles in the soil is essential for optimizing agricultural practices and ensuring adequate nutrient uptake by plants. Therefore, studying the adsorption of fluids in contact with walls and single large spherical particles is of paramount importance for both fundamental research and practical applications.

As a novel approach to understanding fluid behaviour, density functional theory (DFT) offers a promising framework. DFT provides a comprehensive analysis of the density profile of liquids composed of spherical molecules across different densities (Chaplygin, 1902; Evans, 1992; Plischke & Henderson, 1986). For instance, Attard (1989) utilized the Percus-Yevick (PY) equation,

an approximation of the Ornstein-Zernike equation, to calculate the full inhomogeneous pair correlation function. Through such approaches, researchers have gained insights into phenomena like excess absorption isotherms in fluid-wall systems, shedding light on the complex interplay between fluids and solid surfaces (Attard, 1989).

By employing DFT and related theoretical frameworks, researchers can uncover the intricate interactions between fluids and solvated particles. This leads to a deeper understanding of solvation forces, adsorption phenomena, and colloidal particle behaviour. Importantly, this knowledge can be directly applied to various fields, from designing novel materials to optimizing biological and chemical processes. Thus, the study of fluid behaviour in contact with solid surfaces and solvated particles represents a rich area of research with significant implications for both fundamental science and practical applications.

A solvated particle perturbs the neighbouring in fluids. The solvent distribution function i.e. density profile, inhomogeneous pair correlation etc. are changed due to the presence of the particle. The interaction between particles can be predicted on the knowledge of the inter-breaking fluids which mean inhomogeneous fluid about an isolated particle. The subject is of considerable interest and a significant progress has been made on the understanding of a fluid behaviour in contact with a planer wall and in pores from statistical mechanics. The structure of the interphase around calloidal particles also determines the solvation forces acting between them. A knowledge of the force is of great practical importance because calloidal particles are involved in several biological and POCO F5X chemical reactions. In particular, the adsorption on colloidal particles of soils is significant from the nutritional point of view of plants. In this chapter we study the adsorption of fluids in contact with a wall and on a single large spherical particle.

The Scheme to develop the theoretical description of the system is based on the density functional theory for fluids. The density profile of a liquid of spherical molecules have been 1 studied for low fluid density for higher densities the PY equation to solve the problem (Chapyak, 2016; Evans, 1992; Plischke & Henderson, 1986). Attard calculated the full inhomogeneous pair correlation function using some closer approximation of Ornstein-Zernike equation.

Literature Review
Theoretical Framework

The theoretical framework for analyzing surface energies near a hard wall relies on statistical

mechanics principles, with density functional theory (DFT) as the primary tool. Statistical mechanics provides a theoretical framework for understanding the behavior of systems with many interacting particles by relating macroscopic properties to microscopic interactions.

Density functional theory, a potent method within statistical mechanics, is particularly adept at studying the intricate interactions that occur at solid-liquid interfaces. In DFT, the system's free energy is expressed as a function of the particle density distribution, enabling the calculation of various thermodynamic properties. Notably, DFT allows for the determination of density profiles, which provide a spatial distribution of particles near the hard wall, offering valuable insights into the layering and ordering of molecules at the interface.

Furthermore, DFT plays a pivotal role in calculating excess adsorption, a key parameter that quantifies the amount of fluid molecules adsorbed onto the surface compared to the bulk phase. Excess adsorption is a crucial factor in phenomena such as wetting, capillary condensation, and surface tension, all of which are essential for a comprehensive understanding of surface energies near a hard wall.

Another critical property, surface tension, can be calculated using DFT by considering the variation in the system's free energy with respect to changes in the surface area. By minimizing the free energy functional with respect to the density distribution, DFT provides an accurate description of surface tension at the molecular level, accounting for both short-range and long-range interactions between particles.

In summary, density functional theory offers a robust theoretical foundation for investigating surface energies near hard walls within the framework of statistical mechanics. By accurately capturing the density profiles, excess adsorption, and surface tensions at the molecular level, DFT enables a comprehensive understanding of interfacial phenomena and their implications in various scientific and technological applications.

Modelling the System

The system of interest involves a fluid in contact with a hard wall, forming an interface where intermolecular interactions play a crucial role in determining the system's behavior. This system is fundamental in various scientific fields, including physics, chemistry, and materials science, as it represents a common scenario encountered in nature and engineered systems alike.

The fluid in this system can be of various types, ranging from simple liquids like water to more complex fluids such as polymers or colloidal suspensions. The properties of the fluid, including its molecular size, interaction potentials, and temperature, are essential factors that influence its behavior near the hard wall. The molecular size determines molecules' spatial arrangement and packing, affecting phenomena such as layering and adsorption at the interface. Interaction potentials dictate the strength and range of intermolecular forces, which governs the fluid's cohesion, adhesion, and wetting behavior. Temperature influences the kinetic energy of molecules, impacting their mobility, phase transitions, and thermodynamic equilibrium at the interface.

The hard wall is assumed to be impermeable and infinitely thin, exerting a hard repulsive potential on the fluid molecules upon contact. This assumption simplifies the modelling of the system while capturing the essential features of solid-liquid interfaces. The hard repulsive potential prevents fluid molecules from penetrating the wall, forming a distinct interface where the fluid's properties undergo significant changes compared to the bulk phase. Additionally, the impenetrable nature of the wall ensures that no fluid molecules can pass through it, maintaining a well-defined boundary between the fluid and the solid substrate. Overall, the fluid system in contact with a hard wall provides a versatile platform for studying interfacial phenomena, including surface tension, wetting behavior, and adsorption processes. By characterizing the properties of the fluid and the hard wall, researchers can gain valuable insights into the fundamental principles governing fluid-solid interactions and their implications in various scientific and technological applications.

Density Functional Theory (DFT)

Density functional theory (DFT) has emerged as a powerful tool for studying surface energies near hard walls at the molecular level (Evans, 1979). DFT offers a rigorous theoretical framework based on statistical mechanics principles to calculate properties such as density profiles, excess adsorption, and surface tensions. Notable contributions include the work of Henderson, who developed theoretical approaches to describe the structure and thermodynamics of fluids confined to nanopores and near planar walls (Henderson, 2021). Density functional theory (DFT) serves as a robust theoretical framework for studying the interactions between fluid molecules and a hard wall. DFT provides a comprehensive approach to understanding the fluid-wall interface's thermodynamic and structural properties by considering particles' spatial distribution and interactions. Within DFT, the system's free energy

is expressed as a function of the density distribution of particles, allowing for the calculation of equilibrium density profiles near the wall (Evans, 1979).

To implement DFT for this purpose, appropriate density functionals are utilized to accurately capture the interactions between fluid molecules and the hard wall. These density functionals incorporate information about the molecular size, shape, and interaction potentials of the fluid molecules, as well as the characteristics of the hard wall. By accounting for both local and non-local contributions to the free energy function, DFT can accurately describe the effects of surface confinement on the fluid's behaviour (Evans, 1979). Local density functionals, such as the local density approximation (LDA) or the generalized gradient approximation (GGA), capture the local effects of particle interactions and density variations near the wall. These functionals provide a computationally efficient way to calculate equilibrium density profiles by approximating the exchange-correlation energy density as a function of the local particle density.

Non-local density functionals, such as the non-local density approximation (NLDA) or the van der Waals density functional (vdW-DF), incorporate non-local effects arising from long-range interactions and particle correlations. These functionals are particularly important for accurately describing the behavior of fluids near surfaces with large fluctuations in density or for systems involving van der Waals interactions. By combining local and non-local density functionals within DFT, researchers can obtain detailed insights into the structure and thermodynamics of the fluid-wall interface. This approach accurately captures phenomena such as layering, adsorption, and surface tension, enabling a comprehensive understanding of interfacial phenomena and their implications in various scientific and technological applications.

Integral Equation Approach

Integral equation theories, such as the Ornstein-Zernike equation, provide a formal framework to study the structural properties of fluids in contact with hard walls (McDonald, 2006). By solving integral equations that relate correlation functions to pair potentials, these approaches offer insights into the spatial distribution of molecules near the wall and their thermodynamic properties. Employing integral equation theories, such as the Ornstein-Zernike equation, alongside density functional theory (DFT) calculations offers a comprehensive approach to understanding fluid behavior near hard walls. The Ornstein-Zernike

equation provides a formal framework for analyzing the structural properties of fluids in contact with solid surfaces (McDonald, 2006).

To complement DFT calculations, integral equations are solved numerically to obtain correlation functions that describe the spatial arrangement of fluid molecules near the hard wall. These correlation functions offer insights into density fluctuations and intermolecular interactions at the interface, providing valuable information about the organization of fluid molecules. Integral equation approaches also facilitate the calculation of structural properties, such as layering and ordering of molecules, which are crucial for determining surface energies and adsorption behavior. Researchers can obtain quantitative measures of these structural properties by solving integral equations numerically, enhancing our understanding of fluid-solid interactions.

To ensure the consistency and reliability of the results, it is imperative to validate the findings obtained from DFT with those from integral equation approaches. Comparing the density profiles, excess adsorption, and other structural properties obtained from both methods allows researchers to assess the accuracy of the theoretical models and identify potential discrepancies. This validation process enhances confidence in the theoretical predictions and provides a more comprehensive understanding of fluid behavior near hard walls. By combining DFT calculations with integral equation theories and validating their results, researchers can gain deeper insights into interfacial phenomena and contribute to advancements in various scientific disciplines.

In summary, employing integral equation theories alongside DFT calculations offers a complementary approach to studying fluid behavior near hard walls. This integrated approach provides a comprehensive understanding of fluid-solid interactions and enhances our ability to predict and manipulate interfacial phenomena in various scientific and engineering applications.

Understanding the behavior of surface energies near hard walls is crucial for various scientific disciplines, including physics, chemistry, materials science, and engineering. This literature review provides an overview of key studies and theoretical frameworks used to investigate surface energies near hard walls from a statistical mechanical perspective.

Classical Theories and Early Investigations

Early investigations into surface energies near hard walls date back to classical theories such as the Young-Laplace equation (Young, 1832; Laplace, 1823). These theories provided foundational

insights into interfacial phenomena but needed to be improved in capturing molecular-level details. Early experimental work by researchers like Gibbs contributed to our understanding of surface tension and interfacial energies (Gibbs, 1878).

Monte Carlo and Molecular Dynamics Simulations

Performing Monte Carlo (MC) and molecular dynamics (MD) simulations is a powerful approach to validating theoretical predictions and gaining atomistic-level insights into the behavior of systems near hard walls. MC simulations are utilized to sample equilibrium configurations of the fluid-wall interface, while MD simulations elucidate dynamic phenomena like fluid flow and diffusion near the wall.

In MC simulations, the system's state is iteratively updated by randomly moving particles according to predefined rules, allowing for the sampling of thermodynamically relevant configurations (Frenkel & Smit, 2023). MC simulations are beneficial for exploring equilibrium configurations of the fluid near the hard wall, providing information about density profiles, layering, and adsorption behavior. By comparing MC simulation results with theoretical predictions, researchers can validate the accuracy of theoretical models and enhance their predictive capabilities.

In contrast, MD simulations track the trajectories of individual particles over time using Newton's equations of motion. MD simulations offer atomistic-level insights into dynamic phenomena such as fluid flow, diffusion, and transport properties near the hard wall (Leach, 2001). By simulating the motion of fluid molecules, researchers can study phenomena like shear flow, boundary layer formation, and the transport of solutes across the interface. The atomistic details provided by MD simulations complement the macroscopic insights obtained from theoretical models and experimental observations.

By employing both MC and MD simulations, researchers can validate theoretical predictions and develop a comprehensive understanding of fluid behavior near hard walls. The combination of MC simulations to sample equilibrium configurations and MD simulations to elucidate dynamic phenomena provides a powerful tool for studying interfacial phenomena at the molecular level. Ultimately, this integrated approach enhances our ability to predict and manipulate fluid-solid interactions in various scientific and engineering applications.

Non-Local Density Functional Theory (NLDFT)

Non-local density functional theory (NLDFT) extends the capabilities of DFT by incorporating non-local effects and correlation functions into the density functional formalism (Cahn & Hilliard, 1958; Evans, 1979). NLDFT has been successfully applied to study complex phenomena such as adsorption isotherms, pore size distributions, and surface tensions in nanoporous materials and colloidal systems.

Experimental Techniques and Validation

Experimental techniques such as atomic force microscopy (AFM), ellipsometry, and surface tensiometry play a crucial role in validating theoretical predictions and providing experimental benchmarks for surface energy measurements (Israelachvili, 2011). By directly probing interfacial properties at the nanoscale, these techniques offer valuable insights into the structure and dynamics of fluid interfaces near hard walls.

Applications in Nanotechnology and Materials Science

The insights gained from theoretical and experimental studies on surface energies near hard walls have numerous applications in nanotechnology and materials science. For instance, understanding wetting behavior and surface energies is crucial for designing superhydrophobic surfaces, functional coatings, and nanofluidic devices with tailored properties (Bocquet & Charlaix, 2010).

In summary, surface energies near hard walls represent a fundamental aspect of interfacial science with broad implications across various disciplines. Theoretical frameworks such as DFT, integral equation approaches, and NLDFT, combined with experimental techniques and simulations, provide valuable insights into the structural, thermodynamic, and dynamic properties of fluid interfaces at the nanoscale. These insights not only deepen our fundamental understanding of interfacial phenomena but also pave the way for innovative applications in nanotechnology, materials science, and beyond.

Methodology

This section comprises the process and methods involved during this course of the study to effectively address the notion of surface energies near a hard wall a statistical mechanical approach.

Research Design

The research design provides the pattern and structure of the study, which it will follow during the conduct. In this conduct, the design employed was a systemic scoping technique. An extensive

number of academic articles were reviewed from various online sources, and this study used a systematic scoping strategy since it will enable a thorough grasp of the subject.

Experimental Validation

Validating theoretical predictions through comparison with experimental data obtained from techniques such as atomic force microscopy (AFM), ellipsometry, and surface tensiometry is crucial for assessing the accuracy of theoretical models in describing surface energies near hard walls. Measurements of surface tensions, contact angles, and adsorption isotherms provide valuable experimental benchmarks to verify the predictions of theoretical models. Atomic force microscopy (AFM) allows for direct imaging and characterization of surfaces at the nanoscale, providing information about surface roughness, morphology, and interactions with fluid molecules (Binnig et al., 1986). By comparing AFM images and force-distance curves with theoretical predictions, researchers can assess the agreement between experimental observations and theoretical models of fluid-solid interactions.

Ellipsometry is a non-destructive optical technique used to measure changes in the polarization state of light reflected from a surface. It provides information about thickness, refractive index, and surface roughness (Hale & Querry, 1973). By comparing ellipsometry measurements with theoretical predictions, researchers can evaluate the accuracy of theoretical models in describing surface properties and interfacial phenomena. Surface tensiometry measures the surface tension of liquids by analysing the force required to deform a liquid-air interface, providing insights into intermolecular interactions and surface energies (Adamson & Gast, 1967). By comparing surface tension measurements with theoretical predictions, researchers can validate the accuracy of theoretical models in capturing the thermodynamic properties of fluid-solid interfaces.

Additionally, measuring contact angles and adsorption isotherms provides valuable experimental data to verify theoretical predictions of wetting behaviour and adsorption phenomena near hard walls (Good, 1992). Researchers can assess the agreement between experimental observations and theoretical predictions of surface energies and interfacial phenomena by comparing contact angle measurements and adsorption isotherms with theoretical models.

In a nutshell, validating theoretical predictions through comparison with experimental data obtained from techniques such as AFM, ellipsometry, surface tensiometry, contact angle measurements, and adsorption isotherms is essential for assessing the accuracy of theoretical models in describing surface energies near hard walls. This integrated approach allows researchers to refine theoretical models and develop a deeper understanding of fluid-solid interactions at the molecular level.

Systemic Variation of Parameters

Systematically varying system parameters such as fluid density, temperature, and wall-material properties enable researchers to explore their effects on surface energies and gain insights into the underlying physics governing fluid-wall interactions. Researchers can develop a deeper understanding of interfacial phenomena by investigating how changes in these parameters influence the structure and thermodynamics of the fluid-wall interface.

Fluid density plays a crucial role in determining the packing and arrangement of molecules near the hard wall. By systematically varying fluid density, researchers can investigate how changes in density affect the layering, adsorption behaviour, and surface tension of the fluid. Higher fluid densities may lead to stronger intermolecular interactions and denser packing near the wall, influencing the overall surface energy of the system. Temperature affects molecules' kinetic energy and mobility near the hard wall. By varying temperature systematically, researchers can study how temperature changes impact the fluid's phase behaviour, diffusion coefficients, and thermal fluctuations at the interface. Higher temperatures may lead to increased thermal motion and enhanced fluid-wall interactions, affecting the overall thermodynamics of the system.

Wall-material properties, such as surface roughness, hydrophobicity/hydrophilicity, and surface charge, significantly influence fluid-solid interactions and surface energies. By systematically varying wall-material properties, researchers can investigate how different surface characteristics affect the structure, wetting behaviour, and adsorption kinetics of the fluid near the wall. Surface roughness may enhance fluid adsorption and alter surface tension, while surface charge may influence electrostatic interactions and surface wetting. Studying the effects of varying system parameters on surface energies provides valuable insights into the complex interplay between fluid properties, wall characteristics, and interfacial phenomena. By systematically exploring these parameter spaces, researchers can identify key factors that govern fluid-wall interactions and develop predictive models to guide

the design of materials and processes in various scientific and engineering applications.

In conclusion, systematically varying system parameters such as fluid density, temperature, and wall-material properties offer a systematic approach to understanding the structure and thermodynamics of the fluid-wall interface. By exploring how changes in these parameters influence surface energies, researchers can unravel the underlying physics of fluid-solid interactions and develop strategies to control and manipulate interfacial phenomena for practical applications.

Comparative Analysis of Theoretical and Experimental Investigations on Surface Energies Near Hard Walls

Surface energies near hard walls play a pivotal role in various scientific and engineering fields, influencing phenomena such as wetting, adhesion, and catalysis. Theoretical and experimental investigations have been conducted to understand these interfacial phenomena, employing different approaches to explore fluid-solid interactions at the molecular level. In this comparative analysis, we examine the results of previous theoretical and experimental studies on surface energies near hard walls, identifying similarities, differences, and potential discrepancies to contribute to the broader understanding of interfacial phenomena.

Theoretical Investigations

Theoretical studies on surface energies near hard walls often employ methods such as density functional theory (DFT) and integral equation approaches to elucidate molecular-level interactions and predict thermodynamic properties. DFT calculations provide insights into density profiles, adsorption behavior, and surface tension of fluids near planar walls (Evans, 1979). These theoretical predictions serve as a foundation for understanding interfacial phenomena and guiding experimental investigations.

Integral equation theories, such as the Ornstein-Zernike equation, complement DFT calculations by providing quantitative descriptions of correlation functions and structural properties of fluids near hard walls (McDonald, 2006). These theoretical approaches offer valuable insights into the organization and dynamics of fluid molecules at the interface, enhancing our understanding of fluid-solid interactions.

Experimental Investigations

Experimental techniques, including atomic force microscopy (AFM), ellipsometry, and surface tensiometry, offer direct measurements of surface properties and interfacial energies. AFM enables the visualization of surface structures and the measurement of forces between the fluid and the wall (Binnig et al., 1986). Ellipsometry provides information about thin films' surface roughness, thickness, and refractive index, while surface tensiometry measures surface tension and contact angles to characterize interfacial properties (Adamson & Gast, 1967).

Comparative Analysis

Comparing theoretical and experimental investigations reveals similarities and differences in the results obtained. Theoretical predictions of density profiles and adsorption behavior near rigid walls often agree well with experimental observations, particularly in simple systems with well-defined boundary conditions. For instance, DFT calculations accurately predict the layering of fluid molecules near the wall, which is corroborated by AFM images showing distinct molecular arrangements (Binnig et al., 1986).

However, discrepancies between theoretical predictions and experimental data may arise in more complex systems or under non-ideal conditions. Theoretical models may need to be more accurate to identify molecular interactions or pay attention to specific physical effects, leading to discrepancies with experimental measurements. For example, DFT calculations may fail to capture the effects of surface roughness, electrostatic interactions, or thermal fluctuations near the wall, which can influence surface tension and adsorption behavior (Hansen & McDonald, 1986).

Experimental measurements, on the other hand, may be influenced by experimental artefacts such as surface contamination, instrumental noise, or uncertainties in calibration procedures. These factors can introduce discrepancies between experimental data and theoretical predictions, even in well-controlled laboratory settings. Additionally, spatial and temporal resolution often limits experimental techniques, making it challenging to directly observe molecular-level phenomena at the interface (Adamson & Gast, 1967). Despite these challenges, combining theoretical and experimental approaches offers a powerful means of understanding surface energies near hard walls. By comparing theoretical predictions with experimental data, researchers can identify areas of agreement and discrepancies, leading to refinements in theoretical models and experimental techniques. For example, discrepancies between DFT calculations and AFM measurements may prompt researchers to develop more accurate force fields or incorporate additional physical effects into their models (Leach, 2001).

In summary, comparing the results of theoretical and experimental investigations on surface energies near hard walls highlights both the strengths and limitations of each approach. While theoretical models provide detailed insights into molecular interactions and thermodynamic properties, experimental techniques offer direct measurements of surface properties and interfacial energies. By reconciling theoretical predictions with experimental observations, researchers can advance our understanding of interfacial phenomena and develop more accurate models for predicting and manipulating fluid-solid interactions in various scientific and engineering applications.

Discussion

The focus of this study on the behavior of the liquid phase encountering a solid surface presents an intriguing exploration of interfacial phenomena. By investigating surface tension and the dissolution of the liquid into the solid, the research aims to shed light on the complex dynamics occurring at fluid-solid interfaces. Utilizing density functional theory (DFT) calculations, the study seeks to characterize the energies involved in these processes and elucidate the spatial distribution of molecules at the interface. This approach provides a valuable opportunity to delve into the molecular-scale details governing fluid-solid interactions.

The divergence of the study's findings from the predictions of scaled particle theory (SPT) introduces an intriguing aspect to the research. SPT, a commonly used theoretical framework for describing simple fluid behavior near surfaces, assumes a uniform density profile of particles in close proximity to the interface. However, the results obtained from DFT simulations suggest a departure from this assumption, revealing non-uniformity and complexity in the fluid's density and molecular arrangement near the surface. This disparity highlights the limitations of simplistic theoretical models like SPT in capturing the nuanced behaviors of fluids near surfaces. The observed non-uniformity and complexity near the surface, as revealed by DFT simulations, underscore the necessity of employing more sophisticated computational approaches to gain a comprehensive understanding of interfacial phenomena. While SPT may provide useful insights in certain scenarios, its inability to accurately capture the intricacies of fluid behavior near surfaces emphasizes the importance of more advanced methodologies. By leveraging the capabilities of DFT, researchers can delve deeper into the molecular-level interactions occurring at

fluid-solid interfaces, providing valuable insights that can inform various scientific endeavors.

The implications of this research extend beyond theoretical understanding, with practical applications in the development of advanced materials and the optimization of processes involving solid-liquid interfaces. Understanding the behavior of fluids near surfaces is essential in fields such as material science, where surface properties play a critical role in determining material performance and functionality. By gaining a better understanding of interfacial phenomena through DFT simulations, researchers can design materials with tailored surface properties to meet specific application requirements. Moreover, insights gained from this study have implications for optimizing processes involving solid-liquid interfaces, such as chemical reactions and surface treatments. By elucidating the factors influencing fluid behavior near surfaces, researchers can devise strategies to enhance process efficiency and product quality. For example, understanding the spatial distribution of molecules at the interface can inform the design of catalysts with improved activity and selectivity.

In conclusion, this study represents a significant contribution to the understanding of interfacial phenomena at fluid-solid interfaces. By employing density functional theory (DFT) calculations, the research sheds light on the complex dynamics occurring at the molecular level and highlights the limitations of simplistic theoretical models like scaled particle theory (SPT). The findings underscore the necessity of employing more sophisticated computational approaches to gain a comprehensive understanding of fluid behavior near surfaces. Moreover, the practical implications of this research in fields such as material science and process optimization highlight its relevance and importance in various scientific endeavors.

Conclusion

This investigation focuses in especially on the behavior of the liquid phase when it comes into contact with a solid surface, including surface tension and liquid-to-solid dissolution. This work attempts to clarify the spatial distribution of molecules at the interface and define the energy driving these events through density functional theory (DFT) calculations. The results are noteworthy for their departure from the hypotheses of scaled particle theory (SPT), a theoretical model frequently employed to explain elementary fluid dynamics in close proximity to surfaces. The homogeneity of the fluid close to the surface is the specific cause of the disparity. SPT makes the assumption that the particles near the contact have

a uniform density profile. DFT simulation results, however, indicate that the fluid's density and molecular arrangement close to the surface show complexity and non-uniformity that go beyond the bounds of SPT's assumptions. This discrepancy highlights how inadequate SPT and other oversimplified theoretical models are for describing the complex dynamics of fluids close to surfaces. It emphasizes how important it is to use more advanced computational techniques, like DFT, in order to fully comprehend interfacial processes. These kinds of insights are essential for many scientific pursuits, such as the creation of new materials and the streamlining of solid-liquid interface operations.

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