

UNIVERSITÉ D'ORLÉANS
ÉCOLE DOCTORALEÉnergie, Matériaux, Sciences de la Terre et de l'Univers
Institut des Sciences de la Terre d'Orléans (ISTO)

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soutenue le : 21 mars 2024

pour obtenir le grade de : Docteur de l'Université d'Orléans

Discipline/ Spécialité : SCIENCES DE L'UNIVERS

Modelling contact line dynamics in multiphase porous media

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Acknowledgement

I am deeply grateful for the invaluable guidance and support provided by my supervisors throughout this thesis. Prof. Mohamed Azaroul's counsel on the scientific method was instrumental in shaping my research. Dr. Philippe Leroy, with his meticulous comments and expertise in the subject of the electric double layer. Last but certainly not least, Dr. Cyprien Soulaïne, whose emphasis on organization and structure has been pivotal in shaping the coherence of this report. This thesis would not have been possible without their exceptional mentorship and encouragement.

During this PhD, I have been fortunate to have the acquaintance of my colleagues and friends here at ISTO. Whether engaging in technical discussions or offering friendly support, their presence has been invaluable. I would like to extend special thanks to Saideep, Laurez, Kristijan, Armin, and Amirhossein for their support and friendship.

I owe a debt of gratitude to my father; I started this PhD with his blessing, and his spirit continued to help me to keep on. I am sincerely thankful to my mother, who traveled distance, visited, and stayed with me for weeks. My heartfelt appreciation goes to my family, including my sister and brothers, for their constant encouragement and support.

Résumé

La mouillabilité caractérise la capacité d'un liquide à s'étaler sur une surface solide ou à maintenir sa forme. Elle résulte de l'interaction des forces de surface de la phase de dispersion (phase mouillante) contre la phase non-mouillante sur le substrat solide. La mouillabilité apparaît dans les écoulements multiphasiques pour décrire l'interaction entre les phases fluides (huile/eau, eau/CO₂, ...) et le substrat rocheux. Le rôle de la mouillabilité dans cette thèse se concentre principalement sur la piégeage des fluides dans le réservoir souterrain, par exemple, le piégeage du CO₂ dans les aquifères, ainsi que l'amélioration de la récupération des fluides dans les réservoirs géologiques tels que le gaz de houille ("coal bed methane", CBM) et les réservoirs pétroliers, et enfin la modélisation générale de l'écoulement biphasique, où le problème de singularité des contraintes se situe au contact de l'interface de deux phases fluides avec le solide, appelé la ligne de contact triphasique.

La séquestration du CO₂ dans les aquifères souterrains ou les réservoirs pétroliers épuisés a attiré l'attention comme une solution plausible pour lutter contre le réchauffement climatique en atténuant le surplus de dioxyde de carbone dans l'atmosphère. Il est impératif de comprendre le mécanisme impliqué et d'être capable d'estimer la capacité à long terme d'une formation géologique pour la séquestration du CO₂. De plus, une analyse de la capacité de stockage permettra de comparer différentes solutions en termes de préférence économique et de faisabilité de l'opération. La capacité effective d'un réservoir géologique à stocker le CO₂, que ce soit sous forme libre ou dissous dans la saumure, diffère de la capacité théorique à mesure que les mécanismes de piégeage évoluent avec le temps. Différents mécanismes interviennent après l'injection de CO₂ dans un réservoir, tels que le piégeage structural et stratigraphique, le piégeage résiduel du CO₂, le piégeage par solubilité, le piégeage minéral et le piégeage hydrodynamique. Ces mécanismes de piégeage sont significativement influencés par la mouillabilité du système. La mouillabilité dans de tels cas peut changer par rapport à l'état initial en raison de l'interaction du CO₂ avec la saumure du réservoir et avec le solide, ce qui en fait un effet secondaire difficile à gérer pour la séquestration du CO₂ dans les aquifères salins.

Dans les réservoirs pétroliers, l'injection d'eau à faible salinité ou l'injection de CO₂ est considérée parmi les opérations de Récupération Assistée par Injection ("enhanced oil recovery", EOR) en modifiant la mouillabilité pour libérer la phase piégée. Il y a déjà eu plusieurs essais pilotes d'injection d'eau à faible salinité sur le terrain. Certains d'entre eux ont rapporté des résultats prometteurs en termes d'augmentation de la récupération de pétrole. Cependant, tous les cas sur le terrain n'ont pas observé d'amélioration significative. Cela indique que le succès de l'injection d'eau à faible salinité dépend du cas spécifique. Plusieurs facteurs mentionnés dans la littérature contrôlent l'altération de la mouillabilité et le succès global de l'opération, notamment le rôle des minéraux de la roche, la pression, la température, et les paramètres salins tels que la salinité et le pH de l'eau porale.

L'analyse de la mouillabilité dans les processus souterrains peut être réalisée à différentes échelles. La mouillabilité est essentiellement un phénomène de surface. Pendant ce temps, l'écoulement multiphasique dans les aquifères ou les réservoirs est modélisé dans de gros blocs de roches. Par conséquent, l'effet de la mouillabilité n'est pas directement visible à plus grande échelle. En revanche, à une échelle plus petite, les détails concernant les surfaces des phases sont résolus, ce qui permet d'inclure directement la mouillabilité dans l'analyse. Enfin, une altération de la mouillabilité indique une altération des forces de surface à l'échelle moléculaire.

Cette recherche vise à développer un simulateur à l'échelle des pores efficace pour l'écoulement biphasique qui tient compte de l'altération de la mouillabilité lorsque les propriétés du système changent (salinité, pH, rugosité de surface). Le cadre de modélisation tiendra compte des interactions intermoléculaires.

laire dans l'analyse à l'échelle des pores. Ce lien entre la région intermoléculaire et les microcanaux dans les milieux poreux est obtenu via l'approximation de lubrification combinée à la pression de disjonction.

De plus, dans la littérature, la plupart des analyses de la mouillabilité basées sur les interactions intermoléculaires et la pression de disjonction négligent la véritable géométrie de la phase mouillante près du point de contact. L'expression quantifiant l'interaction intermoléculaire dans une telle analyse suppose un film mince parallèle pour la région proche du contact. Cette région, cependant, est plus fidèlement représentée par un coin. Cette recherche vise à étudier les interactions intermoléculaires pour la géométrie en forme de coin près du contact.

Nous sommes confrontés à un problème qui concerne différentes échelles d'analyse. Par conséquent, nous avons l'intention de nous concentrer sur l'échelle sous-microscopique pour étudier le rôle des forces intermoléculaires dans la région de la ligne de contact triphasique. Cela nous permet de traiter l'ambiguïté causée par différents comportements de l'angle de contact lorsque le fluide rencontre différentes salinités et pH, ainsi que l'effet de la vitesse de la ligne de contact sur l'angle de contact. Un film mince de différentes épaisseurs peut approximer la région proche du contact.

Les questions scientifiques que nous essayons d'aborder dans cette thèse sont les suivantes :

- Quelles sont les principales interactions intermoléculaires qui sont importantes pour déterminer l'altération de la mouillabilité due aux changements dans les propriétés chimiques et thermodynamiques du système ?
- Quels sont les paramètres clés dans la construction d'un modèle de mouillabilité robuste capable de relier l'échelle moléculaire à l'échelle des pores ?
- Comment l'intégration de l'échelle moléculaire dans la modélisation de la mouillabilité améliore-t-elle la compréhension des écoulements multiphasiques dans les milieux poreux ?

Dans cette thèse, nous utilisons la théorie de la lubrification pour incorporer l'effet de l'interaction intermoléculaire et étudier la dynamique du film près du contact. L'interaction intermoléculaire que nous utilisons reflète la géométrie en forme de coin de la région près du contact.

Lorsqu'un liquide se propage sur une surface sèche ou en contact avec la vapeur du liquide, la différence d'énergie de la surface solide correspond au travail d'adhésion. Cette énergie provient de l'interaction par paire des constituants de différentes phases. La nature de cette interaction est électromagnétique et peut se produire entre deux charges, dipôles ou dipôles induits. Les forces dipôle-dipôle, dipôle-dipôle induit et dipôle instantané sont appelées forces de Van der Waals (VDW) et sont généralement considérées comme attractives. L'énergie adhésive pour un fluide non polaire peut être estimée avec l'attraction VDW.

L'énergie due à l'interaction VDW (W_{VDW}) pour un film plat d'épaisseur h est l'intégration de deux potentiels de corps en paire de tous les éléments dans deux plaques, ce qui donne

$$W_{VDW} = -\frac{A_{123}}{12\pi h^2},$$

où A_{123} , appelée la constante de Hamaker, décrit la polarisabilité des phases. L'équation est applicable lorsque la condition d'additivité est vérifiée. Cela signifie que la contribution de chaque paire d'atomes peut être intégrée et chaque paire n'affecte pas l'autre paire. Cela peut être vrai pour le cas des gaz raréfiés; cependant, pour les liquides, la constante de Hamaker doit être calculée selon la théorie de Lifshitz.

Cependant, pour des films non uniformes avec des surfaces arbitraires, le potentiel VDW, en plus de l'épaisseur du film, dépend de dérivées supérieures de l'épaisseur du film, y compris la pente et la

courbure de l'interface. Par exemple, le film non uniforme est essentiel lors de l'étude de l'interaction VDW à proximité du point de contact pour la propagation d'une gouttelette. Plusieurs études dans la littérature tentent d'obtenir l'expression appropriée de VDW pour la géométrie en coin à proximité du contact. Ces équations peuvent être formulées sous une forme générale :

$$W_{VDW}(h, h_x) = -A_{123} \left(\frac{1}{12\pi h^2} + \frac{g(\theta)}{12\pi h^2} \right),$$

Le potentiel VDW pour la géométrie en coin devrait converger vers l'expression du film plat lorsque l'angle de contact tend vers zéro. De plus, lorsque l'angle de coin atteint $\pi/2$, la géométrie ressemble à nouveau à un film plat; par conséquent, l'expression du film plat devrait être obtenue à nouveau. Cependant, les équations dans la littérature manquent de ce comportement caractéristique.

Pour comparer l'exactitude des expressions pour VDW dans la littérature, nous avons comparé l'angle de contact obtenu par ces équations via le travail d'adhésion et l'équation de Young-Dupré

$$\cos(\theta) = -\frac{W_{svl}}{\sigma_{lv}} - 1.$$

avec l'angle de contact mesuré expérimentalement. Ici, nous nous sommes concentrés sur la propagation d'alcane non polaire sur des polymères pour ne considérer que l'énergie VDW. La comparaison montre un écart significatif entre la valeur expérimentale de l'angle de contact et celles mesurées via l'interaction VDW. De plus, cet écart montre une tendance avec l'angle de contact lui-même, pointant vers la dépendance du potentiel VDW à l'angle de contact, comme suggéré par différentes études citées dans ce chapitre.

En ce qui concerne la mesure expérimentale, il est crucial de réaliser différents ensembles d'expériences systématiques avec un éventail plus large de fluides, similaires aux alcanes n-sur des substrats polymères, pour éviter la contribution d'autres forces intermoléculaires et, en même temps, obtenir une gamme de mesures d'angle de contact jusqu'à 90 degrés. Cette expérience peut nous aider à discerner avec précision la dépendance du potentiel VDW à l'angle de contact. Effectuer des mesures pour obtenir les propriétés du fluide et du substrat, c'est-à-dire l'énergie de tension superficielle et la constante de Hamaker, utilisées dans l'expérience est également vital, car il existe une gamme de valeurs différentes rapportées dans la littérature pour un système en raison de différentes conditions, de la pureté et de l'exactitude de l'expérience.

Traditionnellement, la pression de disjonction est exprimée comme une fonction de l'épaisseur de la phase de mouillage seule. Ce faisant, l'effet du profil réel de la phase de mouillage est négligé, c'est-à-dire sa pente et sa courbure. Certains efforts ont été déployés pour obtenir une expression analytique pour la composante de dispersion de la pression de disjonction qui tient compte de la pente et de la courbure. Cependant, l'expression analytique pour la composante électrostatique, appelée composante de la double couche électrique (EDL), est assez complexe et utilise de nombreuses simplifications, telles qu'une charge ou un potentiel constant sur la surface. Pour surmonter cela, nous avons résolu numériquement l'équation de Poisson-Boltzmann (P-B) pour obtenir un résultat plus précis pour la force électrostatique.

Nous avons discrétisé et résolu numériquement l'équation P-B en utilisant la méthode des éléments finis. L'élément est une ligne et un triangle pour les cas unidimensionnels et bidimensionnels, respectivement. En MEF, l'équation P-B est multipliée par une fonction de pondération et intégrée sur le domaine. La fonction de pondération est également une fonction d'interpolation pour la valeur inconnue sur l'élément.

La résolution de l'équation P-B nécessite des conditions aux limites, généralement un potentiel con-

stant ou une charge constante. Ces hypothèses sont acceptables pour des films suffisamment épais pour que les deux EDL aux limites du film n'interagissent pas entre elles. Cependant, dès que le film devient mince et que deux interactions EDL deviennent perceptibles, l'hypothèse de charge constante ou de potentiel constant n'est plus valide. Par conséquent, la condition aux limites doit être modifiée. Cette procédure est connue sous le nom de régulation de charge. Nous avons mis en œuvre un modèle de complexation de surface (SCM) pour tenir compte de la régulation de charge à la surface. La charge à la surface entre deux phases est liée au potentiel électrostatique à cet emplacement via l'équilibre d'action de masse.

La solution P-B est couplée au SCM. Le SCM corrige la condition aux limites utilisée sur le solveur P-B, et le solveur P-B donne la valeur de densité de charge sur la couche diffuse utilisée dans le SCM. Il s'agit d'une procédure itérative, et elle se poursuit jusqu'à la convergence.

Nous validons la mise en œuvre du couplage entre le solveur EDL et le modèle de complexation de surface à triple couche-TLM pour le film unidimensionnel. Nous avons validé le couplage pour l'interface quartz/eau avec une étude comparative de la littérature. En revanche, l'interface air/eau est validée en comparant les résultats avec le potentiel zêta mesuré lors de l'expérience. Après la validation de tous les composants du modèle, nous avons étudié le système quartz/eau/air dans un cas unidimensionnel correspondant à une géométrie de film et des cas bidimensionnels correspondant à la zone proche du contact.

Nous avons observé que la contrainte normale due à l'interaction électrostatique dépend de l'angle du coin ainsi que de l'épaisseur de la phase de mouillage (ou de la distance au point de contact). Nous avons également observé et calculé la composante tangentielle de la pression électrostatique, dont la valeur dépend également de l'angle du coin. Cela montre que l'interaction électrostatique à proximité du point de contact dépend de l'angle de contact et de la distance au point de contact. De plus, la composante tangentielle provoque un changement de tension superficielle à proximité du point de contact, ce qui entraîne un glissement local.

Pour les travaux futurs, l'interaction électrostatique obtenue ici peut être combinée avec un modèle de lubrification utilisant une interaction intermoléculaire dépendant de la pente pour étudier la dynamique de la région de contact. La composante tangentielle provoquera un effet Marangoni à proximité du contact, évalué par un glissement local sur la frontière.

Les forces intermoléculaires sont exprimées par la pression de disjonction, qui comprend les forces de van der Waals (VDW), de double couche électrique (EDL) et structurelles (str).

$$\Pi = \Pi_{VDW} + \Pi_{EDL} + \Pi_{str}.$$

Nous avons développé un modèle de lubrification physiquement ancré pour obtenir la propagation des films minces près du TPCP. Nous utilisons cette propagation pour modéliser l'altération de la mouillabilité et remplacer le concept d'angle de contact. Ce modèle nous fournit l'équation d'évolution de l'épaisseur du film :

$$\frac{\partial h}{\partial t} = \frac{\partial}{\partial x} \left(M(h) \frac{\partial}{\partial x} \left(-\sigma \frac{\partial^2 h}{\partial x^2} + \rho g h - \Pi(h, h_x) \right) - \mathbb{T}(h) \right).$$

où $M(h)$ est la mobilité du fluide et $\mathbb{T}(h)$ tient compte de la contrainte de cisaillement mutuel à l'interface fluide-fluide. Le terme de mobilité, M , dépend des limites fluide-solide.

Nous résolvons numériquement cette équation, et les étapes sont expliquées dans ce chapitre (voir Section 5.3). L'équation de lubrification pour les films minces est résolue sur une surface solide horizontale unidimensionnelle pour étudier la propagation d'une gouttelette et l'impact des conditions de

mouillabilité. Cela est réalisé en discrétisant une équation de lubrification adimensionnelle avec la méthode des différences finies et en la résolvant avec un programme MATLAB interne. Nous avons utilisé un maillage non uniforme, grossier dans la plupart des parties du domaine et de plus en plus fin près du TPCP. Comme l’emplacement du TPCP change avec la propagation du film, nous avons mis en place un schéma de raffinement de maillage adaptatif (AMR) pour suivre le mouvement du TPCP et raffiner dynamiquement le maillage près du point de contact.

Pour valider le modèle et sa mise en œuvre, tout d’abord, nous avons considéré la propagation d’une goutte d’huile sous l’effet de la tension superficielle où nous avons accès à l’équation analytique (Sections 5.4.1). Les résultats sont en excellent accord avec la solution de référence, ce qui confirme la robustesse de la discrétisation bi-laplacienne avec AMR. Ensuite, nous avons poursuivi avec la propagation d’une gouttelette avec tension superficielle et gravité (Section 5.4.2). Ce cas vise à vérifier la mise en œuvre de la gravité et de la courbure dans le modèle de lubrification. Comme il n’y a pas de solution analytique pour un tel cas, la vérification est obtenue en comparant la propagation des gouttelettes obtenues avec le modèle de lubrification et une approche basée sur le Volume de Fluide. Cette dernière est une approche de capture d’interface basée sur les équations de Navier-Stokes utilisée comme solution de référence pour vérifier la pertinence du modèle de lubrification d’ordre réduit. En plus de valider les résultats, nous pouvons retrouver l’angle de contact au TPCP et obtenir le comportement de Tanner pour l’angle de contact apparent en raison du pliage visqueux hydrodynamique.

Enfin, nous avons étudié l’effet de l’altération de la mouillabilité sur la propagation d’un film avec différentes salinités et pH (Section 5.4.3), où nous avons étudié la propagation de l’eau sur une surface de carbonate en présence d’huile. Les différents comportements observés pour les trois eaux sont expliqués en utilisant la dérivée de la pression de disjonction : un film d’une épaisseur supérieure à environ ~ 10 nm est stable pour les cas de faible salinité, tandis que pour l’eau à haute salinité, des films plus épais que environ 1 nm sont instables et finiront par se rompre en introduisant une perturbation.

Les résultats pour différentes salinités et niveaux de pH de l’eau mettent en évidence les capacités de notre modèle de lubrification pour les films minces à simuler l’altération de la mouillabilité due à un changement des propriétés du fluide. En effet, le changement de pH et de salinité modifie la double couche électrique (EDL) et, dans une certaine mesure, la force d’hydratation, ce qui influence la stabilité du film précurseur et conduit finalement à trois comportements de propagation : propagation avec mouillage complet, immobilisation de la goutte par rupture du film et immobilisation sans rupture par équilibre des forces. Nous avons également montré que l’épaisseur initiale du film précurseur impacte fortement la propagation d’une goutte.

Le modèle peut être modifié pour aborder la propagation sur une surface avec rugosité et étudier le système chimique hors équilibre où la salinité/le pH de la phase de mouillage change pendant la propagation du film. La dynamique du fluide non mouillant doit être abordée dans ce travail. Les futures lignes de recherche concernent le couplage de notre modèle de lubrification avec un solveur basé sur les équations de Navier-Stokes pour prendre en compte l’hydrodynamique à plus grande échelle et la contrainte de cisaillement mutuel à l’interface fluide-fluide.

Les travaux futurs de cette thèse peuvent être catégorisés en deux branches. La première se concentre sur l’inclusion d’autres composants dans le modèle de complexation en surface, tandis que la deuxième voie consiste à coupler le modèle de lubrification avec d’autres outils de modélisation à plus grande échelle.

- La solution du CO_2 dans l’eau et son effet sur la force intermoléculaire peuvent être étudiés facilement en ajoutant la spéciation de surface appropriée dans notre solveur couplé PB-SCM. Il est également possible de considérer d’autres paires de fluides en prenant en compte la spéciation de

surface correspondante dans le modèle SCM, par exemple, le système huile/saumure/carbonate. De plus, grâce au modèle de lubrification, l'effet dynamique sur la mouillabilité peut également être observé pour de tels systèmes.

- Les résultats de l'expansion du film obtenus à partir du modèle de lubrification peuvent être comparés aux données expérimentales obtenues par microscopie électronique. La microscopie électronique est capable de fournir des mesures *in situ* à l'échelle moléculaire. Ces mesures peuvent être utilisées pour valider le modèle et calibrer l'interaction intermoléculaire.
- Le couplage du modèle de lubrification avec un simulateur d'écoulement biphasique est essentiel car nous pouvons étudier d'autres effets, tels que la contrainte de cisaillement due à la phase non mouillante. De plus, l'effet de la pression de disjonction peut être observé à plus grande échelle, comme un réseau de pores et d'étranglements interconnectés.

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Chapter 1

Introduction

1.1 Importance of Wettability in Subsurface Processes

Wettability characterizes the ability of a liquid to spread across a solid surface or maintain its shape. It is the result of the interaction of surface forces of the spreading phase (wetting phase) against the non-wetting phase on the solid substrate. Fig. 1.1 shows three different behaviors for liquid droplets spreading against air on Berea sandstone. On the left, the liquid droplet spreads and even gets imbibed into the rock sample as soon as it is placed there, representing a complete wetting case. In the middle, the liquid droplet from an angle of 60° with the rock surface, which describes a partially wetting case. On the right, the liquid droplet maintains its shape while forming an angle of 125° with the rock surface, which is the non-wetting case.

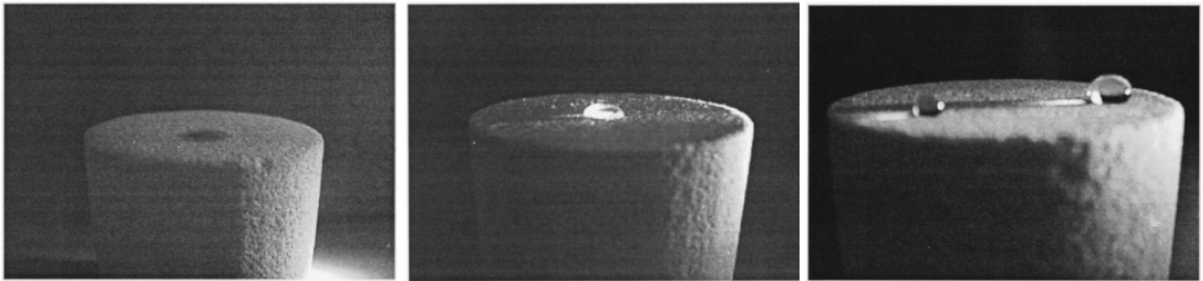


Figure 1.1: Spreading of a liquid droplet on the rock (sandstone) in complete-wetting, partial-wetting, non-wetting. The change in wettability is achieved by treating the sample. Reproduced with permission from reference [Li and Firoozabadi, 2000]. Copyright, 2000, SPE.

Wettability appears in multi-phase flow to describe the interplay between the fluid phases (oil/water, water/ CO_2 , ...) and the rock substrate. The role of wettability in this thesis is focused mainly on:

- the fluid trapping in the subsurface reservoir, for example, CO_2 trapping in aquifers,
- the improvement of the recovery of the fluid in geological reservoirs such as Coal bed methane (CBM) and petroleum reservoirs,
- the general modeling of two-phase flow where the problem of stress singularity lies at the contact of the interface of two fluid phases with the solid, called the three-phase contact line.

First, we further explain wettability's role in the sub-surface processes, including Carbon Capture and Storage (CCS), Enhanced Oil Recovery (EOR), and CBM. Then, we investigate different scales to

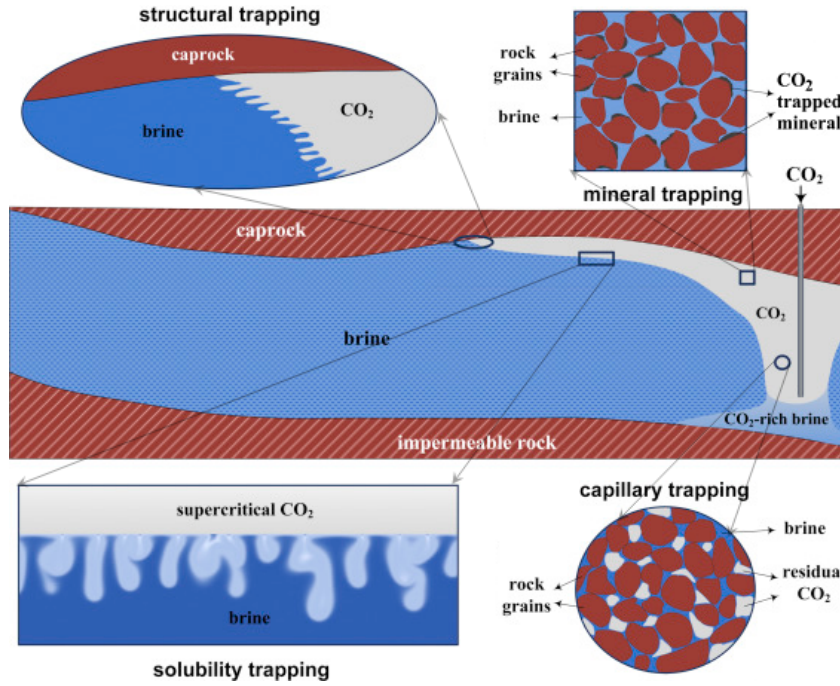


Figure 1.2: The different trapping mechanisms for CCS. Reproduced with permission from reference [Emami-Meybodi et al., 2015]. Copyright, 2015, Elsevier Science. Structural trapping of CO_2 under the caprock. The solubility trapping occurs all along the interface. The residual (capillary) trapping happens where the flow of CO_2 occurs.

determine which level of analysis is more suitable to model and explain wettability and its alteration. In particular, the pore and molecular scales are mentioned to describe the wettability and alteration. As measured and studied, the wettability lies somewhere between pore-scale and molecular scale. It encapsulates the inter-molecular interactions between the two fluid phases (*e.g.* liquid and gas) with the solid wall. At the pore scale, it reappears as a necessary condition for describing multi-phase flow.

1.1.1 Carbon capture and storage

CCS in underground aquifers or depleted petroleum reservoirs attracted attention as a plausible solution for global warming by mitigating the excess carbon dioxide in the atmosphere. It is imperative to understand the mechanism involved and be able to estimate the long-term capacity of a geological prospect for CCS. Furthermore, an analysis of storage capacity will enable the comparison of different solutions in terms of economic preference and feasibility of the operation.

The effective capacity of a geological reservoir to store CO_2 either as a free phase or as dissolved into the brine differs from the theoretical capacity as the trapping mechanisms change across time (Fig. 1.3). Different mechanisms take place after the injection of CO_2 into a reservoir, *e.g.* structural and stratigraphic trapping, residual CO_2 trapping, solubility trapping, mineral trapping, and hydrodynamic (Fig. 1.2) [Bradshaw et al., 2007].

After the injection into the aquifer, the plume of CO_2 rises due to the density difference and buoyancy force until it reaches an impermeable layer known as caprock. This is called structural trapping. Structural trapping is the dominant mechanism regarding storage capacity in the first decades after injection. This trapping mechanism is similar to how the hydrocarbon fluid is initially stored in a typical oil/gas reservoir. However, at larger time scales (10 to 1000 years), it becomes less relevant and will

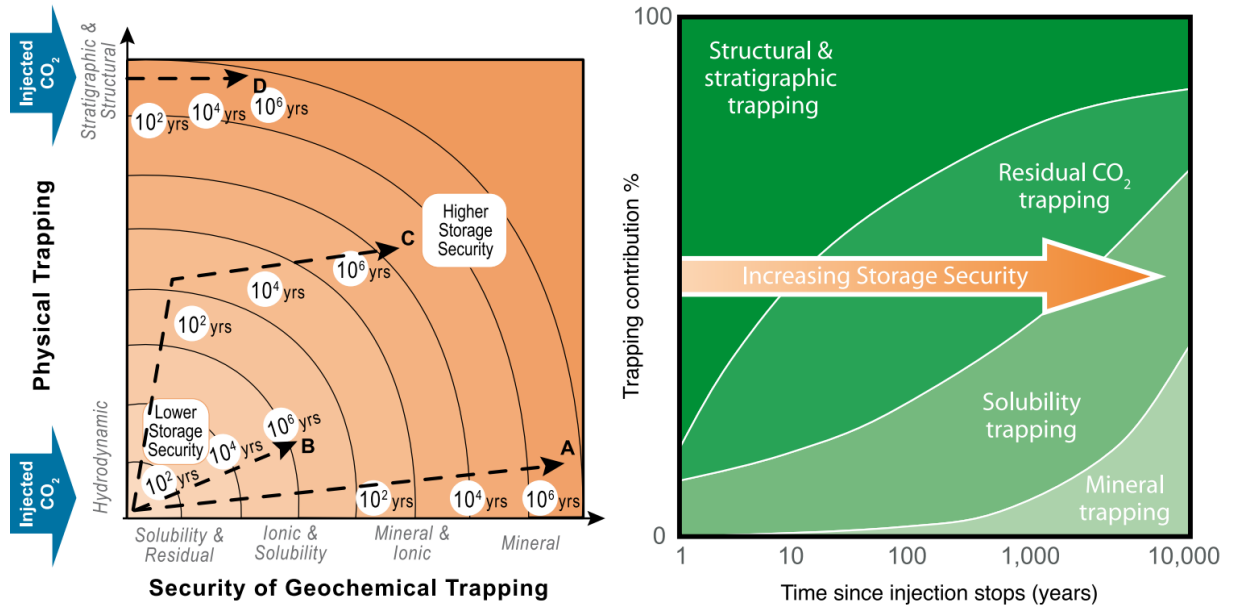


Figure 1.3: Contribution of different trapping mechanisms and their security versus time since injection in CCS. Structural trapping is the main mechanism at the start of injection; as time passes, the contribution of other mechanisms becomes significant also [Benson, 2005].

be overcome by the other competing mechanisms. When CO_2 moves through the aquifer, it can get trapped due to capillary force (for example, due to a snap-off in the constriction of a throat by the brine), called residual trapping. Solubility trapping occurs when CO_2 dissolves into the brine. Both residual and solubility trapping become the dominant mechanism after the first decades. Dissolving CO_2 into brine can encourage mineralization due to changes in water pH and causing the CO_2 to get trapped in the mineral form, which is the mineral trapping. Mineral trapping becomes noticeable after many centuries [Bradshaw et al., 2007]. Mineral trapping in sedimentary rocks is a slow process. However, reports of fast mineralization occur less than two years after CO_2 injection in basaltic rock in Iceland [Snæbjörnsdóttir et al., 2017, Matter et al., 2016]. In summary, in the short term (less than a decade), structural trapping is the main contributor to CO_2 sequestration in sedimentary rock. As time passes (10 to 1000s years), solubility and residual trapping also become important.

These trapping mechanisms, especially in the case of residual trapping and structural trapping, are influenced significantly by the wettability of the system. The wettability in such cases can change from the initial condition due to the interaction of CO_2 with the reservoir brine and with the solid, making it a challenging side effect for CCS in saline aquifers [Song and Zhang, 2013, Yang et al., 2005a, Chiquet et al., 2007]. An alteration in wettability could lead to a change in the predicted storage capacity of a geological structure by changing the capillary threshold pressure of the caprock. A modeling study conducted by Kassa et al. [2022] showed the role of wettability alteration in long-term exposure to CO_2 in CCS. They assumed a generic alteration of the wettability condition from strongly water-wet to intermediate-water-wet based on the exposure time to the CO_2 . Despite a simplified field-scale simulation, they obtained a map of different wettability across the reservoir. They also observed a backflow of CO_2 towards the injection site due to the wettability alteration. In this particular simulation, the effect of wettability alteration on the caprock is minimal, yet the loss of containment is still observable. As the CO_2 moves slowly through the very dense caprock, it changes the wettability of the caprock. Changing the wettability to a more CO_2 wet can decrease the sealing capability of the caprock.

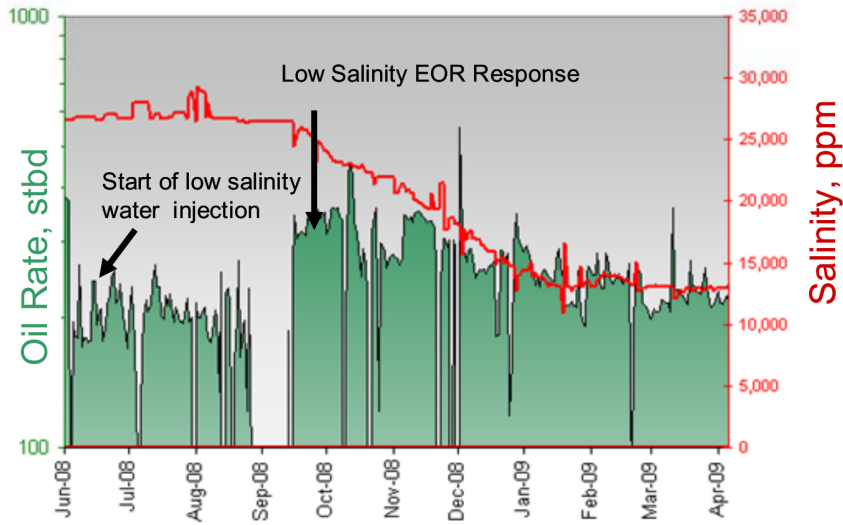


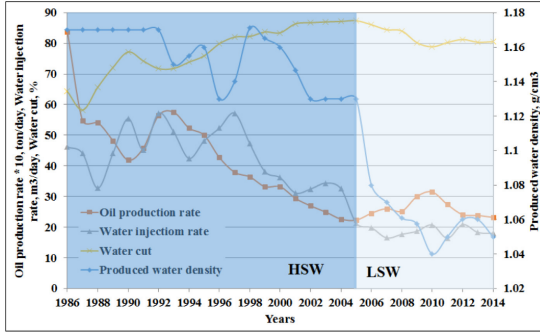
Figure 1.4: Increase of oil rate production after low salinity water injection in a field in Alaska and an increase of 13 % in oil recovery factor. The time the switch in injecting fluid occurred is shown in the figure, and the response of the new injecting fluid is detected through the reduction in salinity of produced water [Seccombe et al. [2010]].

1.1.2 Enhanced oil recovery

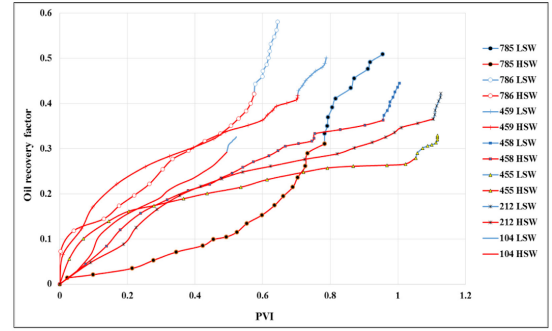
A petroleum reservoir's life cycle comprises different periods. The first period is the natural depletion in which the reservoir pressure is high enough to produce the hydrocarbon. After a while, with the production of hydrocarbon with natural drive, the reservoir pressure depletes, especially for a reservoir without an aquifer or a gas cap. In order to maintain production at this stage, different operations are performed, categorized as "improved oil recovery" (IOR) techniques. They include installing lifting pumps in the well to produce the hydrocarbon with a lower well pressure and maintaining the reservoir pressure by water injection, hence producing more hydrocarbon from the reservoir and increasing the recovery of the reservoir. The third period comes when IOR operations are not up to par. There is still a significant quantity of oil left in the reservoir. Enhanced oil recovery (EOR) operations alter fluid and rock interactions to release the trapped oil and increase the oil recovery.

Low-salinity water injection [Sheng, 2014] or CO_2 injection [Yang et al., 2005b] are considered among EOR operations by changing the wettability in a way that the trapped phase can be freed. There have already been several field-scale low-salinity water injection pilots. Some of them report promising results in terms of an increase in oil recovery. For example, an increase of 13% in oil recovery has been reported after low-salinity injection in a field in Alaska (Fig. 1.4). Abdi et al. [2022] summarised 13 field-scale studies of low salinity water injection EOR, dating from 2004 to 2018, out of which 9 cases showed incremental improvement in oil recovery by 5-50 %. Another example is a field test in Russia; along with the increase in oil production rate by 50 %, a decrease of water injection rate to half is also observed, which is due to the lower injectivity of low salinity water (Fig. 1.5a). However, lower injectivity does not lead to a lower production rate for both oil and water [Akhmetgareev and Khisamov, 2015]. In this long-term study, most wells show incremental improvement after switching to low-salinity water injection by 5-15 % (Fig. 1.5b).

However, not all field cases observed a significant improvement. This indicates that the success of the low-salinity water injection is case-dependent. Several factors mentioned in the literature control



(a) Increase in oil production rate for low salinity water injection following a long period of high salinity injection in a field in Russia [Akhmetgareev and Khisamov [2015]]



(b) The change in trend of oil recovery factor for different wells after switching to low salinity water injection in a field in Russia [Akhmetgareev and Khisamov [2015]]

Figure 1.5: Effect of low salinity water injection on the well recovery, oil and water production, and water injection rate

wettability alteration and the operation's overall success, including the role of rock minerals, pressure, temperature, and saline parameters, such as salinity and pH. Their effect is discussed more in section 2.3.

1.1.3 Coal bed methane

Coal bed methane (CBM) reservoirs are unminable coal seams that contain methane as an adsorbed phase. The coal seams are sometimes saturated with water. In order to produce methane, the water should be produced beforehand. The adsorbed methane in the coal bed can freely move after desaturating the coal from water. Injection of another gas into the seams to replace the adsorbed methane results in enhanced production of methane *i.e.* enhanced-CBM. CO₂ has been suggested as a candidate for injection since it is adsorbed more favorably by the seams compared to methane, and also, it is of interest from the standpoint of CCS [White et al., 2005]. Although wettability alteration has also been observed for the interaction between CO₂ and a wet coal sample with respect to the pressure [Siemons et al., 2006], its explanation is ongoing research. In this case, one possible explanation for wettability alteration is the decrease in water film stability with increasing pressure [Siemons et al., 2006]. However, the increase in adsorption of CO₂ on the surface as the pressure increases could also play a part in changing the wettability.

1.1.4 Ground-water remediation

The leakage and spillage of industrial waste or petroleum fluid on the ground surface can penetrate the vadose zone, pollute the groundwater aquifers, and pose significant health and environmental risks. These liquids are often non-aqueous; therefore, they are called non-aqueous phase liquids (NAPL) or dense NAPL. They can alter the initial wettability of the aquifers and remain trapped by means of capillary forces; therefore, flushing them out by pumping water and treatment will leave the NAPL phase trapped in the aquifer. Using surfactant, Javanbakht and Goual [2016] were able to release this trapped phase on the now weakly water-wet solid due to the wettability alteration of NAPL. Molnar et al. [2011] studied the role of wettability alteration due to NAPL in more detail; they found out different surfaces have different behavior. For example, in the case of the iron oxide surface, wettability remains strongly water-wet in contrast to the quartz surface, where it becomes wetter to NAPL.

1.1.5 Injectivity

Both CO₂ injection for the CCS and low-salinity water injection in EOR require injection wells to be drilled. Injection well performance, or injectivity, is obtained from well testing. During drilling, the leak-off test gives the fracture pressure of the formation, whereas, after drilling, the fall-off test is used to obtain fracture pressure and the properties of the induced fracture. The performance of the well is the ratio between the well-flowing rate and the pressure gradient between the well and reservoir, whereas, for an injection well, it is called injectivity. Injectivity is the flow rate at a well that can operate without inducing fracture. The performance of the injection wells depends on the interaction of rock and fluids. Since their interaction changes the porous media around the injection site, it will change the reservoir's life span, especially for injecting CO₂ into the aquifer. The influence of wettability and other physicochemical properties on the injectivity is discussed in a literature review focused on CCS by Hajiabadi et al. [2021]. They pointed out that wettability controls the salt precipitation due to CO₂ injection, which will reduce the well's permeability and injectivity and cause capillary backflow to the well. As mentioned earlier, this backflow is also observed in the simulation of Kassa et al. [2022]. Wettability alteration due to CO₂ is among the leading causes for fine migration, which eventually can cause blockage of channels and reduction in injectivity.

1.2 Scales of Analysis and Wettability

The analysis of wettability in subsurface processes can be done on different scales. The wettability is essentially a surface phenomenon. Meanwhile, the multi-phase flow in aquifers or reservoirs is modeled in large blocks of rocks. Therefore, the effect of wettability is not seen directly on larger scales. Whereas on the smaller scale, the details regarding the surfaces of the phases are resolved, which provides the means to include the wettability in the analysis directly. Finally, an alteration in wettability indicates an alteration in the surface forces in the molecular scale realm.

1.2.1 Field-scale

Reservoir models are the tools typically used to assess the recovery of a petroleum reservoir or storage capacity of CCS in the aquifer. Reservoir modeling often deals with length scales of tens of kilometers and time scales of several years. Therefore, the input parameters for these models describe the fluid and rock properties and interactions in an averaged manner using effective concepts such as relative permeability and capillary pressure. These parameters are measured in the lab for core samples that were taken from exploration wells. Then, these data are propagated throughout the reservoir using statistical analysis.

The flow in the reservoir is studied with the use of Darcy's law, which relates the velocity of the fluid, $\mathbf{u}$, to the pressure gradient, ∇P :

$$\mathbf{u} = -\frac{K}{\mu} \nabla P, \quad (1.1)$$

where μ is the fluid viscosity. The medium made of a network of pores and channels is seen as a continuous medium modeled using a permeability tensor (K) to describe the transmissibility as an average of the tortuosity of channels. This equation was derived when only one phase is present in the porous medium [Darcy, 1856]. If the porous medium contains more than one fluid, each phase is assumed to move through separate and distinct pathways [Ahmed et al., 2018]. The permeability of each phase is reduced compared to fully saturated media. The ratio of the new permeability to the saturated permeability is

called relative permeability. The ratio of the volume of one phase to total free volume (saturation, S_i) is used to calculate its relative permeability in the presence of other fluids.

Since the channels in the rock are less than ~ 1 mm, they can be considered as capillary tubes [Ahmed et al., 2018], and the capillary pressure is used to relate the pressure of the two phases to each other. Capillary pressure, like the relative permeability, is also a function of saturation [Leverett, 1941]. It reads,

$$P_c(S_w) = P_{nw} - P_w, \quad (1.2)$$

here, " w " and " nw " refer to the wetting and non-wetting phases, respectively. The wetting fluid spreads on the solid surface instead of the non-wetting fluid and occupies the smaller channels. The wettability is indirectly represented by capillary pressure and relative permeability as a function of wetting phase saturation.

Here, the capillary force can help us understand the residual trapping mechanism in CCS. It is worth mentioning that typically CO_2 is the non-wetting phase, and the brine is the wetting phase. Due to the capillary force, a residual saturation of CO_2 , $(1 - S_w)$, remains in the pore after its displacement. This saturation can determine the storage capacity of the residual trapping. However, due to the long-term interaction of the solid surface with the aquifer, which has become more acidic as a result of the dissolution of CO_2 , the residual saturation and capillary pressure curves for reservoir rock and caprock are most likely susceptible to change, and consequently, the relative permeability too. In Fig. 1.6, a case of change in the relative permeability of Berea sandstone due to alteration in wettability is shown. After the treatment, the sample wettability changed to a more gas-wet (intermediary wet to gas), causing the relative permeability of water to increase; meanwhile, the gas's relative permeability decreased. In a separate imbibition experiment, the alteration in wettability is shown to decrease the capillary pressure. The origin of wettability alteration may be of a different nature. A change in the roughness of the rock surface as a result of dissolution or a change in the electrostatic potential of the surface, which affects the surface forces, can explain the alteration of wettability. All these alteration mechanisms should be considered in field-scale simulations to predict a more realistic reservoir assessment.

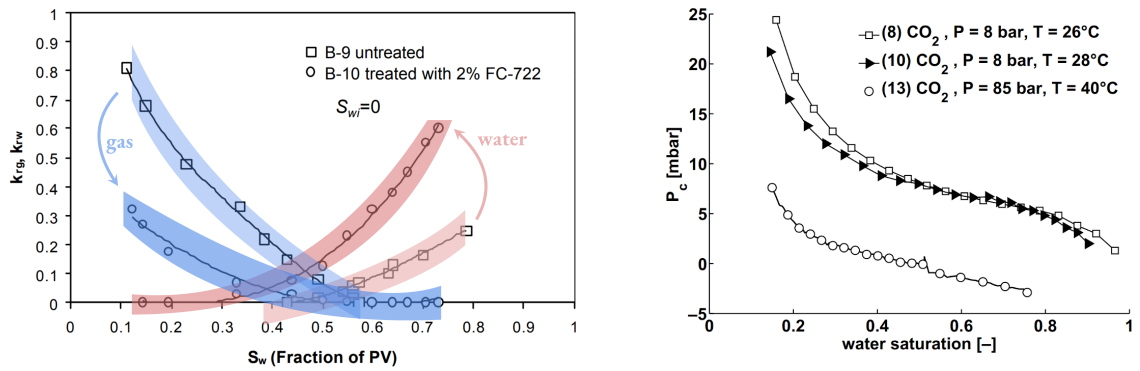


Figure 1.6: (a) Change in relative permeability of gas and water after alteration to gas-wet [Tang and Firoozabadi, 2002]. (b) Imbibition capillary pressure curve for CO_2 and water for unconsolidated quartz sand at different pressure and temperature conditions. The curve difference is explained by wettability alteration [Plug and Bruining, 2007]. Notice the change in endpoints for relative permeability, which indicates the residual saturation.

Since wettability is not directly linked in the field-scale approach, the effect of alteration in wettability can not be truly investigated with this approach. It is possible to try to model the permeability [Kassa

et al., 2021] and capillary pressure curves [Kassa et al., 2020] alteration as a result of wettability alteration, with the use of Lucas-Washburn equation for the flow in capillary tubes and include directly the wettability into the model as it is done in Kassa et al. [2022]. However, such approaches impose a big simplification for the complex network of pores in a porous medium.

1.2.2 Pore-scale

In order to fully address the effect of wettability on the fluid flow and phase trapping, it is essential to study the impact of wettability at the pore scale, where its effect is explicitly included in the model. In pore-scale analysis, the details of the interfaces between fluids in the porous media are preserved (Fig. 1.7). The Navier-Stokes equations govern the motion of the fluid through the porous medium, and wettability is included by imposing the surface forces on the interfaces as boundary conditions [Soulaire et al., 2021b]. Therefore, the interfaces between fluids and the solid substrate also change by changing the wettability. The wetting fluid tends to spread more on the solid surface and occupy the smaller pores and throats since the surface forces are more dominant there. The non-wetting phase tends to occupy the bigger pores. Hence, the phase connectivity and distribution (including trapping) are influenced directly by the wettability at the pore scale.

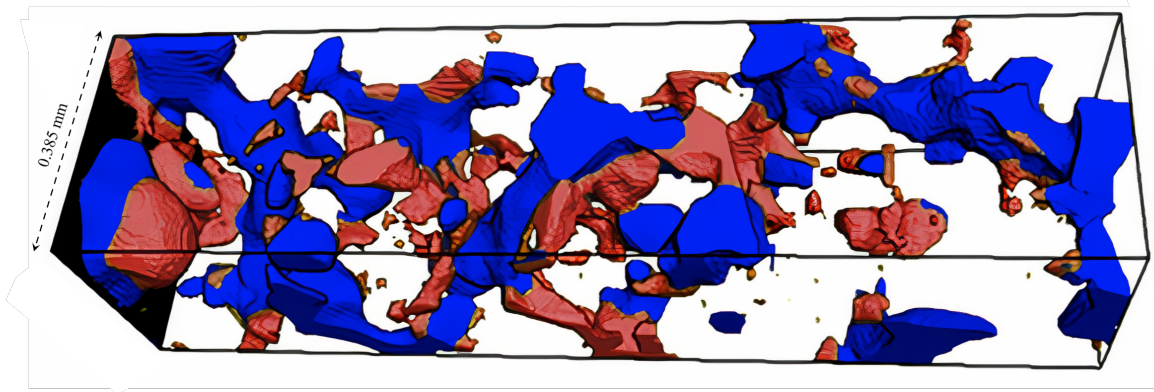


Figure 1.7: 3D X-ray image of two-phase flow of water (blue) and oil (red) in sandstone (white)[Zhang et al., 2022a].

The interface between two fluids (*e.g.* water and air) in a capillary tube or on a flat surface when it coincides with the solid surface forms an angle of θ with regard to the tangential line at the surface (see Fig. 1.8). The relationship between the surface forces is expressed by Young's equation,

$$\sigma_{lv} \cos(\theta) = \sigma_{sv} - \sigma_{sl}, \quad (1.3)$$

here l , v , and s are short for liquid vapor and solid, and θ is the angle between the tangent line on the solid and interface through the denser liquid (Fig. 1.8). This is the fundamental equation used for including wettability and surface forces as boundary conditions in pore-scale analysis. We will talk in more detail about the governing equations and the boundary conditions in section. 2.1. The acquisition method of wettability is discussed in section. 2.2.

We mentioned that wettability describes the surface forces near the point where fluids and solids meet. Therefore, analyzing the surface forces present at the molecular scale will allow us to improve our description of wettability at the pore scale.

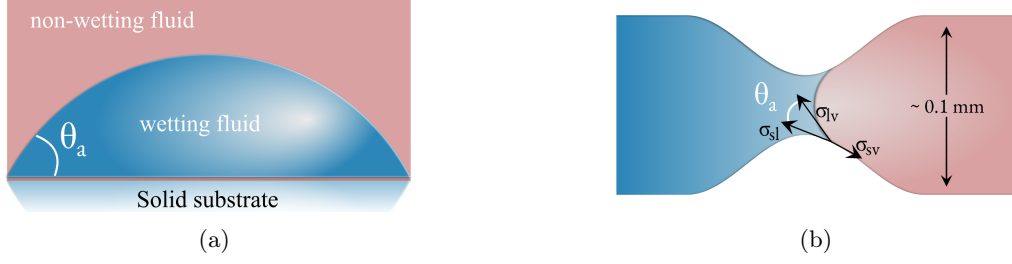


Figure 1.8: Pore-scale representation of wettability for (a) a flat surface and in (b) capillary tube (color blue and red represent wetting and non-wetting fluid respectively).

1.2.3 Molecular-scale

The length and time scale at the molecular scale is in the range of $\sim 1 \text{ \AA} - 100 \text{ nm}$ and $10^{-15} - 10^{-12} \text{ s}$. The interaction between the fluid phases and the solid comes into play on the molecular scale through the surface forces. The surface forces are ultimately what determines the up-scaled properties such as surface tension. In the context of wettability, surface forces are dominant in the region close to the contact. Here, the surface forces on each interface interact—consequently, the up-scaled value of surface tension changes. The wettability is closely linked with the surface tension, which is described by the Young equation. Therefore, it is essential to take into account these forces in order to adequately describe the region close to the contact for the wettability determination. Furthermore, a change in wetting phase (water) properties, such as pH and salinity, affects the surface forces.

In order to capture wettability alteration, the surface forces at the molecular scale should be studied and up-scaled to the pore scale. Disjoining pressure is an interesting proxy for transferring molecular-scale information to pore-scale boundary conditions. Disjoining pressure refers to the inter-molecular interactions of the surfaces. These interactions cause an excess pressure at the three-phase contact region, where the surfaces are close to each other, compared to the bulk.

1.3 Objectives and Scope of the Thesis

Understanding multi-phase behavior in the capillary-dominated flow is crucial. Processes such as Carbon Capture and geological Storage, water resources remediation, and Enhanced Oil Recovery are among such cases. Realistic modeling of these cases requires an appropriate understanding of the physicochemical mechanisms influencing fluid displacements at the pore scale. We noticed some challenges in two-phase flow, mainly concerning the flow behavior of the interfaces and the solid, typically explained by wettability. The rock wettability can vary with a change in pore water composition (pH, salinity) and interfacial physicochemical properties through inter-molecular interactions.

This research aims to develop an efficient pore-scale simulator for two-phase flow that accounts for wettability alteration when there is a change in the system properties (pore water salinity, pH, surface roughness). The modeling framework will account for inter-molecular interactions in the pore-scale analysis. This link from the inter-molecular region to the microchannels in porous media is obtained via the lubrication approximation combined with disjoining pressure concept.

Moreover, in the literature, most wettability analyses based on inter-molecular interactions and disjoining pressure disregard the true geometry of the wetting phase close to the contact point. The expression used to quantify the inter-molecular interaction in such analysis assumes a thin parallel film for the region close to the contact [Burelbach et al., 1988, Oron et al., 1997, Yeh et al., 1999, Abu-Al-Saud et al.,

2020]. This region, however, is more closely represented by a wedge. This research aims to investigate the inter-molecular interactions for the wedge-shaped geometry close to the contact.

1.4 Scientific Questions

The questions that we are trying to address in the thesis are:

- What are the main inter-molecular interactions that are important in determining the wettability alteration due to changes in the chemical and thermodynamic properties of the system?
- What are the key parameters in constructing a robust wettability model that can link the molecular scale to the pore scale?
- How does integrating the molecular scale into wettability modeling improve the understanding of multi-phase flows in porous media?

1.5 Outline of Thesis

Chapter 2 starts by pinpointing the wettability in pore-scale modeling. Then, the wettability quantification through the contact angle concept is introduced. Some methods for measuring contact angle in the experimental setting are listed with their advantages. After, we show some evidence of controversial contact angle measurements in different settings such as pH, salinity, and pressure. Finally, we introduce molecular-scale analysis through the concept of disjoining pressure and its different components. We conclude this chapter with the methodology that we plan to account for wettability modeling and its alteration in the pore-scale model.

Chapter 3 focuses on the dispersion component of the disjoining pressure known as Van der Waals potential. We introduce different expressions for the dispersion component for near-contact line regions, including models from the literature and a new potential for wedge-shaped structures. The models and their contact angle predictions are compared with experimental measurements from the literature.

Chapter 4 focuses on the electrostatic component of disjoining pressure. We introduce the electric double layer's underlying mechanisms and briefly explain the surface complexation models. We couple these two models to evaluate the electrostatic component of disjoining pressure in a wedge-shaped structure using an in-house finite element code. The code is developed in MATLAB and validated using reference solutions. Then, we study the significance of the contact region concerning the excess pressure due to the electrostatic component of disjoining pressure for a water/gas/quartz system.

In Chapter 5, we use a lubrication model to study the dynamics close to the contact region by modeling the thin-film spreading. First, we explain the steps required to implement disjoining pressure into a lubrication model, resulting in a thin film evolution equation. Second, we describe the numerical scheme for solving the evolution equation and validate the model with the reference solutions. Then, we investigate the effect of pH and salinity on the spreading of a droplet.

Finally, in Chapter 6 we summarize the important findings of this work and the possible future work.

Chapter 2

Pore-scale modelling, contact angle, and molecular insights

At the pore scale, the flow is resolved in each pore and throat. Each phase obeys the conservation of mass and momentum (Navier-Stokes equations) along with appropriate boundary conditions at the fluid-fluid and fluid-solid interfaces. A standard approach to account for wettability at the fluid-solid boundary uses the concept of contact angle. In this chapter, we highlight that the contact angle measurements in the lab strongly depend on the experimental conditions such as fluid salinity and pH. Contact angle might not be the most effective way to describe wettability alteration. We point out that inter-molecular interaction is the key to accounting for changes in wettability due to changes in fluid and rock properties. We propose a methodology to include the molecular interactions in pore-scale models.

2.1 Modeling at the pore-scale

In this section, we introduce the governing equation for the flow at the pore scale, followed by the proper boundary conditions that describe the fluid/fluid and fluid/solid interface. For the flow in porous media (Fig. 2.1), each phase is described by the Navier-Stokes equations. Meanwhile, the continuity of stress is applied to the interface between two fluids, and wettability influences the fluid/solid/fluid.

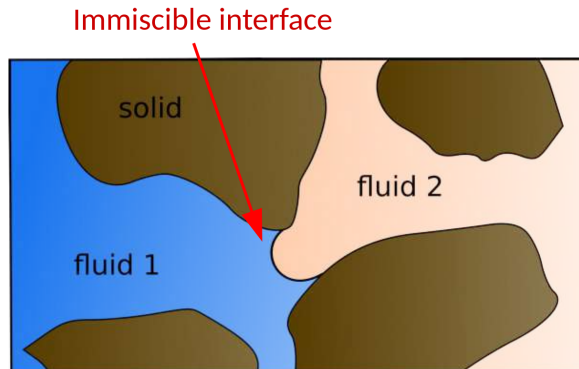


Figure 2.1: Illustration of two-phase flow in the porous media [Soulaine et al., 2018]

2.1.1 Introduction to Navier-Stokes equations

The governing equation describing the two-phase flow in pore-scale consists of the differential equation for the bulk of each phase

We can write the equation of continuity for the two phases (a, b) as:

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{u}_i) = 0, \quad i = a, b. \quad (2.1)$$

In the case of incompressible fluid, it becomes:

$$\nabla \cdot (\mathbf{u}_i) = 0, \quad i = a, b. \quad (2.2)$$

Here, ρ_i is the density of the phase i , and $\mathbf{u}_i = (u, v, w)$ is the velocity vector of phase i .

The conservation of momentum for the incompressible Newtonian flow is (Newton's 2nd law) applied to a fluid:

$$\rho_i \left(\frac{\partial \mathbf{u}_i}{\partial t} + \mathbf{u}_i \cdot \nabla (\mathbf{u}_i) \right) = -\nabla p_i + \nabla \cdot [\mu_i (\nabla \mathbf{u}_i + (\nabla \mathbf{u}_i)^T)] + \rho_i \mathbf{g}, \quad i = a, b. \quad (2.3)$$

where μ_i is the fluid viscosity, p_i is the pressure and $\mathbf{g}$ is the gravity. This equation is called Navier-Stokes.

2.1.2 Fluid-fluid interfacial condition

On the interface of the two fluids, there is a jump in stress due to the surface tension, which is explained by the momentum balance on the interface and the continuity of the stress :

$$(\mathbf{T}^{(2)} - \mathbf{T}^{(1)}) \cdot \mathbf{n} = -\kappa \sigma \mathbf{n} + (\mathbf{I} - \mathbf{n} \mathbf{n}) \cdot \nabla \sigma, \quad (2.4)$$

where $\mathbf{n}$ is the normal vector, $\mathbf{T}^{(1)}$ and $\mathbf{T}^{(2)}$ are the stress tensor in the fluid 1, 2, $\kappa = \nabla \cdot \mathbf{n}$ is the interface curvature, σ is the surface tension and $\mathbf{I} - \mathbf{n} \mathbf{n}$ is the projector on the plane tangent on the interface. In the right-hand side of Eq. 2.4, the first term is the surface tension force, $\mathbf{F}_C$, due to the curvature of the interface, and the second term is attributed to the change in interfacial tension across the interface.

2.1.3 Fluid-solid boundary conditions

Because the fluid cannot penetrate into the solid surface, the normal component of the fluid velocity is always,

$$\mathbf{u} \cdot \mathbf{n}|_{wall} = 0. \quad (2.5)$$

Far from the triple line, the condition at the fluid-solid interface can be a no-slip condition, i.e., the normal and tangential components of the velocity are zero on the solid wall [Stokes, 1846, Stokes et al., 1851],

$$\mathbf{u} \cdot \mathbf{t}|_{wall} = 0, \quad (2.6)$$

or a partial slip (also called Navier slip), i.e., the tangential component of the fluid velocity on the wall is proportional to the shear rate [Navier, 1823]:

$$\mathbf{u} \cdot \mathbf{t}|_{wall} = \lambda \left. \frac{\partial u}{\partial y} \right|_{y=0}. \quad (2.7)$$

where λ is the slip length, note that the partial slip condition encompasses the no-slip condition if $\lambda = 0$. On the point where the interface and the solid coincide, the normal of the interface with respect to the wall tangent forms an angle θ , which is the contact angle. Here, the effect of wettability and contact angle is directly linked to the model that describes the flow.

Problem of moving contact line

For the case of one-phase flow, the normal and tangential velocity component on the solid surface is assumed to be zero (no-slip). However, for the case of two-phase flow, the three-phase contact line boundary condition, which utilizes the contact angle, gives rise to the moving contact line problem. The moving contact line problem in two-phase flow modeling is twofold.

The *first* point is related to the no-slip boundary condition that is assumed on the solid surface. It means that the contact of the two fluids and the solid, known as the three-phase contact line, has a zero slip velocity. This is paradoxical because the fluid phases are moving [Huh and Scriven, 1971]. The no-slip condition will become unrealistic in the vicinity of the contact line because the three-phase contact line is moving while it is on the solid [Neto et al., 2005]. Therefore, it was suggested that near the contact line, a slip is allowed to relax stress and velocity. Another proposed method to deal with this problem is to assume a precursor film on the solid, giving rise to the "apparent contact line." However, for the physical situations where the system is partially wetting, the precursor film does not exist.

The *second* problem is known as the "dynamic contact angle." The dynamic contact angle indicates that the contact angle measured during the movement differs from the static contact angle. Some attempts were made to correlate the dynamic contact angle with respect to the flow velocity.

Static vs dynamic contact angles

The dynamic contact angle measured in the experiments differs from this static contact angle. The difference between static and dynamic measurements can be explained by a scaling issue: the static contact angle provides a measurement of the triple-line at the nano-scale, while dynamic measurement gives an apparent value valid at the resolution of the measurement, which is often micro-scale. Between the nano and micro-scale, hydrodynamic forces deform the fluid-fluid interface – a phenomenon known as viscous bending – which results in an apparent contact angle that is different from the static measurements and varies with the contact line velocity (see Fig 2.2).

Slip models assume that the change in the contact angle is due to the contact line velocity, U , and some characteristics of the media, k_1, k_2 [Hoffman, 1975, Dussan, 1979]:

$$\theta_d = f(\theta_s, U, k_1, k_2, \dots), \quad (2.8)$$

Moreover, for the f to have an inverse function:

$$U = F(\theta_d, \theta_s, k_1, k_2, \dots). \quad (2.9)$$

different forms for this function have been proposed and summarised in table 2.1.

Tanner [1979] studied the spreading of the silicone oil drop on a surface with precursor film. The slope of the tangent line that passes through the inflation point of film thickness is considered as θ_d . They further obtained the following equation for the dependency of the apparent contact angle on the velocity

$$U = k_1 \theta_d^3, \quad (2.10)$$

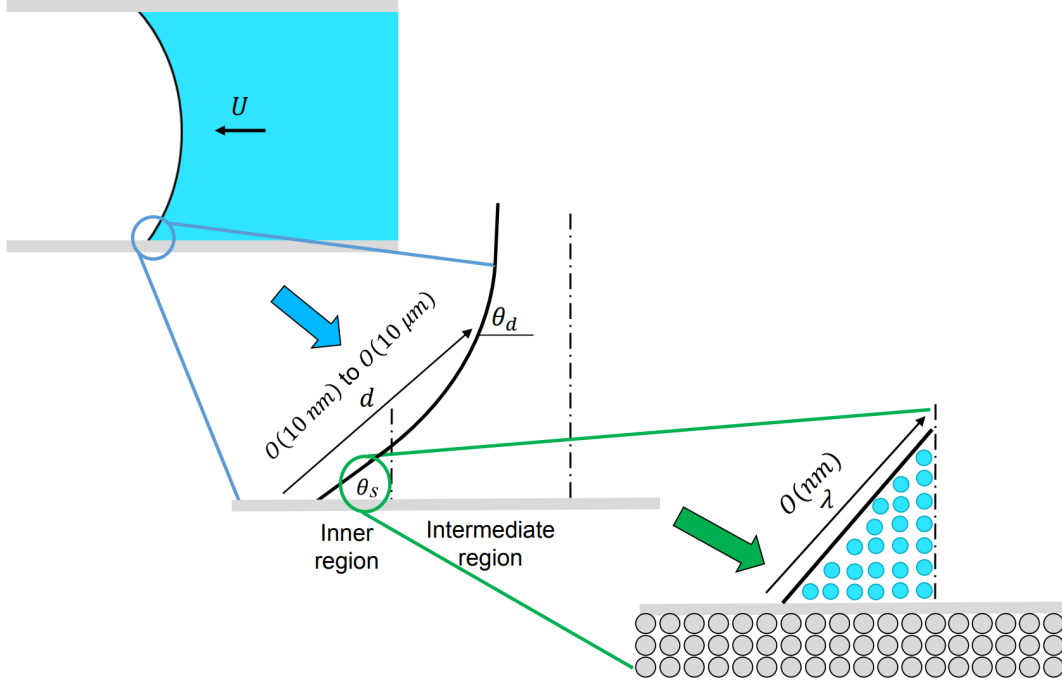


Figure 2.2: Depiction of apparent and measured contact angle [Abu-Al-Saud et al., 2017]

Table 2.1: Slip Models for the three-phase contact line boundary condition

Model	Equation	Example
Power law	$U = k_1(\theta_d - \theta_s)^{k_2}$	Ehrhard and Davis [1991]
Molecular-kinetic theory	$U = 2K\lambda \sinh\left(\frac{\lambda^2 \sigma_{1,eq}(\cos\theta_s - \cos\theta_d)}{2kT}\right)$	Blake and Haynes [1969]
Friction force	$U = \frac{\sigma_{1,eq}}{\mu_{cl}}(\cos\theta_s - \cos\theta_d)$	Ren et al. [2010]

where k_1 is a constant to be determined from the interaction of phases and solid.

How to model the contact line dynamics?

The models that have been proposed to deal with these two problems in the literature can be summarized as the following:

- Slip models: (Not to be confused with the slip velocity) Here, the boundary condition for the velocity of the contact line is linked to the static and dynamic contact angle with the form of $U = a(\theta_d - \theta_s)^b$. Also, a slip condition is assumed on the surface of the solid.
- Precursor film: In the case of the complete surface wetting, at low contact line speed, a very thin film is observed experimentally, which prewets the surface. The thickness of this film is in the range of 50 to 300 nm.
- Hybrid models: This combines a model for the vicinity of the contact line and a continuum approach for the bulk phase. For example, the molecular dynamic simulation provided the continuum model with the local slip parameters and dynamic contact angle [Zhang et al., 2017].
- Diffuse interface: The interface between the fluids is considered as a layer of infinite thickness as opposed to a sharp interface. This will allow for a variation of density in the diffuse layer and can alleviate the moving contact problem. [Bonn et al., 2009]
- Interface formation: Here, the dynamics of formation or disappearance of the interface is modeled by accounting for the flux of liquid to the interface or away from it obtained from the Navier-Stokes equations. [Shikhmurzaev, 2007]

2.1.4 Numerical solution of two-phase Navier-Stokes equations

Solving the Navier-Stokes equations for arbitrary geometry and multi-phases is achieved numerically. Volume of Fluid is widely used in computation fluid dynamics to simulate two-phase flow. In the Volume of Fluid (VOF) method, the two fluids are substituted with a phase indicator function. The phase indicator function is used to reconstruct and capture the interface between fluids. The phase indicator has a value of one in one phase and zero in the other phase. The integration of the governing equation over a controlled volume will result in the inclusion of surface tension in the governing equation as a volume force. In addition, this method is conservative in mass since the governing equation is integrated over the control volume. The VOF method is explained in more detail in App. A.1 followed by some two-phase simulation where we studied the effect of wettability on the flow.

The level-set method developed by Osher and Sethian [1988] is another numerical tool for two-phase flow modeling. This method uses the advection of a level-set function. The level set function is a signed-distance function whose value is zero at the interface, negative in one phase, and positive in the other phase. This method provides a more accurate description of the interface (the normal and curvature property) compared to the VOF method [Mirjalili et al., 2017].

2.2 Contact Angle Measurement

The wettability of a system is directly measured by the contact angle, which relates the forces on the three-phase contact line with the visual angle formed by the interfaces. The visual measurement can be done by

taking images with a camera or other techniques that visually represent the interface. In this section, the common methods used to measure contact angle are summarized. We discussed some measurements in the literature for CO₂/brine/rock and oil/brine/rock, and we highlight that these measurements indicate the contact angle's dependency on the experiment's thermodynamic conditions.

2.2.1 Image

The two common and popular methods that are mainly used for contact angle measurements with imaging are the static/dynamic sessile drop method and the (tilted) pendant drop method (Fig. 2.3) [Huh and Reed, 1983]. In the first method, the images of the drop captured by the camera could be used directly to obtain the profile of the droplet and, consequently, the tangent line, which is then used to calculate the contact angle (goniometer contact angle measurement). The second method, known as axisymmetric drop shape analysis profile (ADSA), is indirect and utilizes the theoretical profile of the droplet and compares it with the experimental drop by changing the fitting parameters, *i.e.* surface tension, contact angle, droplet volume, surface area, and three-phase contact radius [Kwok and Neumann, 1999, Rotenberg et al., 1983]. Advancing and receding contact angle measurements are obtained by injection and withdrawal of fluid from the droplet or by a tilted setup.

These methods deal with macro-scale (millimeters and above). However, suppose we are to study the effect of surface geometry irregularities and impurities present even for a smooth surface such as mica. In that case, we need to have a higher resolution down to several nanometers since even though the roughness is in the order of nanometers, it can have significant implications on a larger scale, as seen in (d) in fig.2.3.

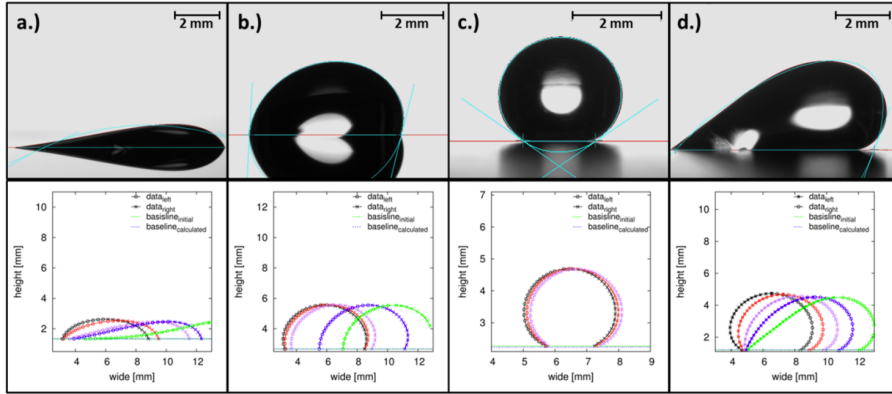


Figure 2.3: Contact angle measurement on a tilted plate fitting the image. The wetting condition changes to non-wetting from (a) to (c). Image in (d) represents a droplet on a non-wet surface with high hysteresis (rose-petal surface) [Heib and Schmitt, 2016]

2.2.2 X-ray

In this method, the interface between the fluids in the porous medium is captured through micro-CT imaging. One of this method's main advantages is performing *in situ* measurements. Andrew et al. [2014] used micro CT imaging to obtain a distribution of contact angle inside a rock sample initially saturated with brine during a supercritical CO₂ injection. The result obtained by this method points out a different observation than the other contact angle measurements, which predicted that supercritical CO₂-brine-carbonate systems are intermediate-wet (Fig. 2.4). Mascini et al. [2020] tried to measure the

contact angle with micro CT images at specific time events. They were able to narrow the distribution of measured CA. Zhang et al. [2022b] were able to show the wettability alteration during precipitation of asphaltene in the rock sample using micro CT imaging.

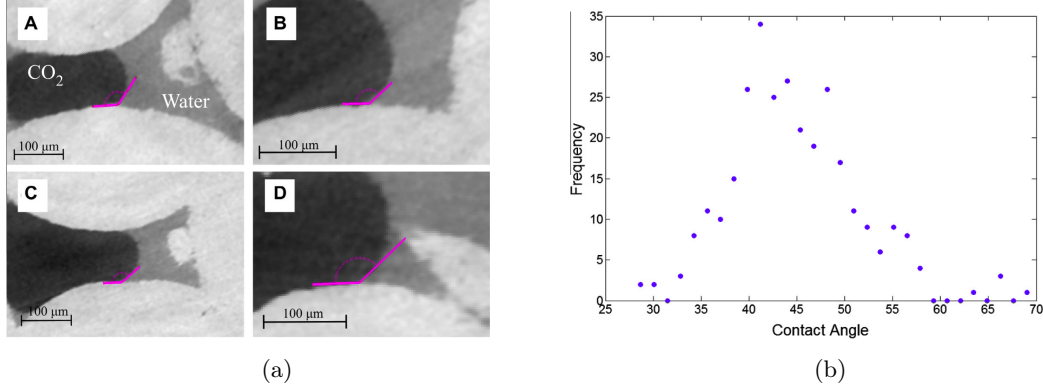


Figure 2.4: Contact angle measurement with X-ray micro-tomography for a system of supercritical CO_2 /brine/limestone, (a) the measured angle: A:53°, B:42°, C:39°, D:41°; (b) Distribution of measured contact angle [Andrew et al., 2014]

2.2.3 Atomic force microscopy

The previous methods rely heavily on the droplet's visual description, which limits how small the resolution can be. Atomic force microscopy (AFM) can go beyond the limits of the optical method. In other words, using AFM, one can access the scale where inter-molecular forces influence the contact line in the tapping mode of AFM, and an oscillating tip probes the droplet's surface. The attracting or repulsive force of the surface will change the amplitude of the oscillating tip, and the result could be converted into force. As the probe covers the droplet, the nano-scale profile of the region of interest is drawn and can be used to obtain the contact angle (Fig. 2.5) [Herminghaus et al., 2000]. AFM can also be used to obtain contact line tension [Pompe and Herminghaus, 2000] as well as the forces between particles and bubbles and to measure the contact angle for small particles [Preuss and Butt, 1999, Ecke et al., 1999].

Nguyen et al. [2003] pointed out that these measurements should be considered dynamic. The sharp, apparent three-phase contact line corresponds to a transitional region around the contact line as seen by AFM (see in Fig. 2.5a). In this region, the contact angle is changing. However, the contact angle measured by AFM further from this area offers the same value as the typical optical methods, with the caveat that AFM results in a much higher resolution and precision [Yu et al., 2013]. Advancing and receding contact angle has also been investigated by AFM [Chen et al., 2014]. Analyzing the contact angle on a rough surface of quartz mineral by AFM has resulted in varying magnitudes for even one droplet, which could be addressed by surface pre-treatment and droplet size [Deng et al., 2018].

2.2.4 Electron microscopy

Electron microscopy is another method that can indirectly obtain images at the nano-scale. In this method, a beam of electrons is emitted on the thin layer of the sample, and the response (reflected electron) is evaluated at the detector to produce an image of the sample [Qin et al., 2021]. The advantage of this method, compared with the AFM, is the ability to perform *in situ* measurements. Qin et al. [2021] performed such experiments to obtain contact angle at the nano-scale in spontaneous imbibition. They performed their measurements on a dolostone that was pre-saturated with oil so that the wettability of

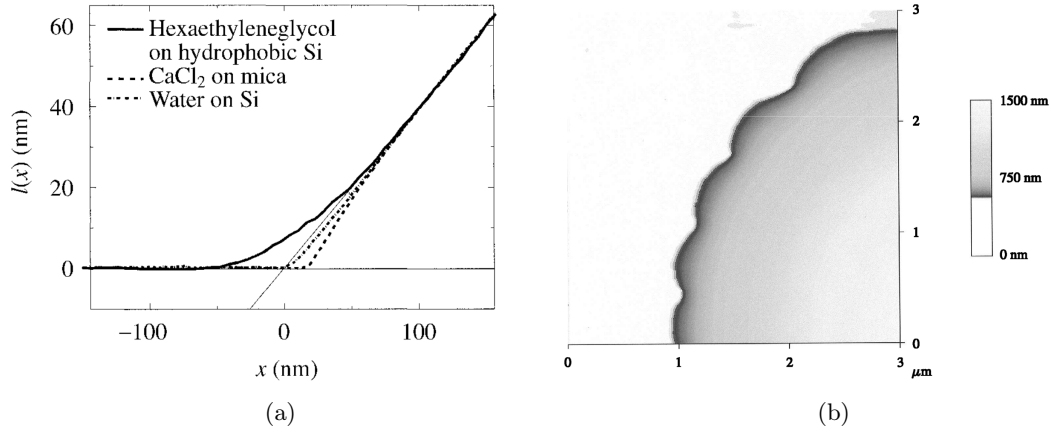


Figure 2.5: AFM topography image of hexaethylene glycol droplet, (a) profile of the droplet close to the contact line, showing deviation from the straight line in the transitional region. Notice the difference between the non-wet and wet curves; (b) 2d profile of the droplet, the corrugation of the contact line is due to the heterogeneity of the surface wettability [Herminghaus et al., 2000]

the rock changed in the oil-wet. Their measurements show a thin film that goes beyond the contact point (Fig. 2.6). This precursor film thickness is in the order of intermolecular forces.

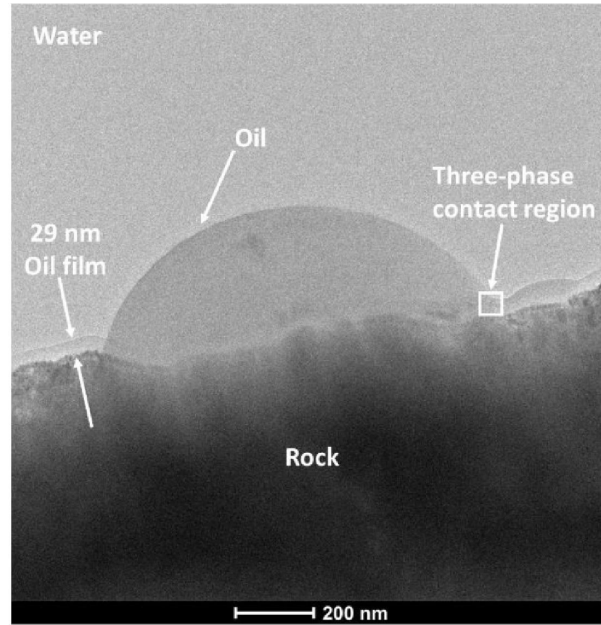


Figure 2.6: two-dimensional environmental transmission electron microscopy (ETEM) image of crude oil droplets produced by spontaneous imbibition of distilled water into a dolostone under equilibrium conditions. The rock sample was aged with oil to render it oil-wet. Reproduced with permission from reference [Qin et al., 2021]. Copyright 2021 Elsevier Science.

2.3 Observational controversies of contact angle

The value for the contact angle measured in the literature by methods described in section 2.2 differs from each other to a great extent, even for one type of solid and fluid. Here, we briefly explained the parameters and conditions that could affect the measurements.

2.3.1 Hysteresis and roughness

Some researchers have conducted experiments to understand how geometrical defects or impurities on the surface of the substrate change the spreading of the droplet (Fig. 2.7). Contact angle measurements on muscovite (representative of aluminosilicate mineral) for CO_2 and water are affected by the reaction of supercritical CO_2 with the surface and cause hysteresis [Wan et al., 2014]. The long-term interaction between all three phases could help to distinguish the contribution of the newly cut mineral surface to the hysteresis and mimic the realistic mineral surface [Wan et al., 2014]. A general increase of contact angle on the surface of mica was observed with regard to time in the literature [Jafari and Jung, 2018]. This change in contact angle has more to do with the initial heterogeneity on the surface *i.e.* the change is more pronounced in the case of mica surface compared to silica surface with a relatively homogeneous surface [Jafari and Jung, 2018, Chiquet et al., 2007].

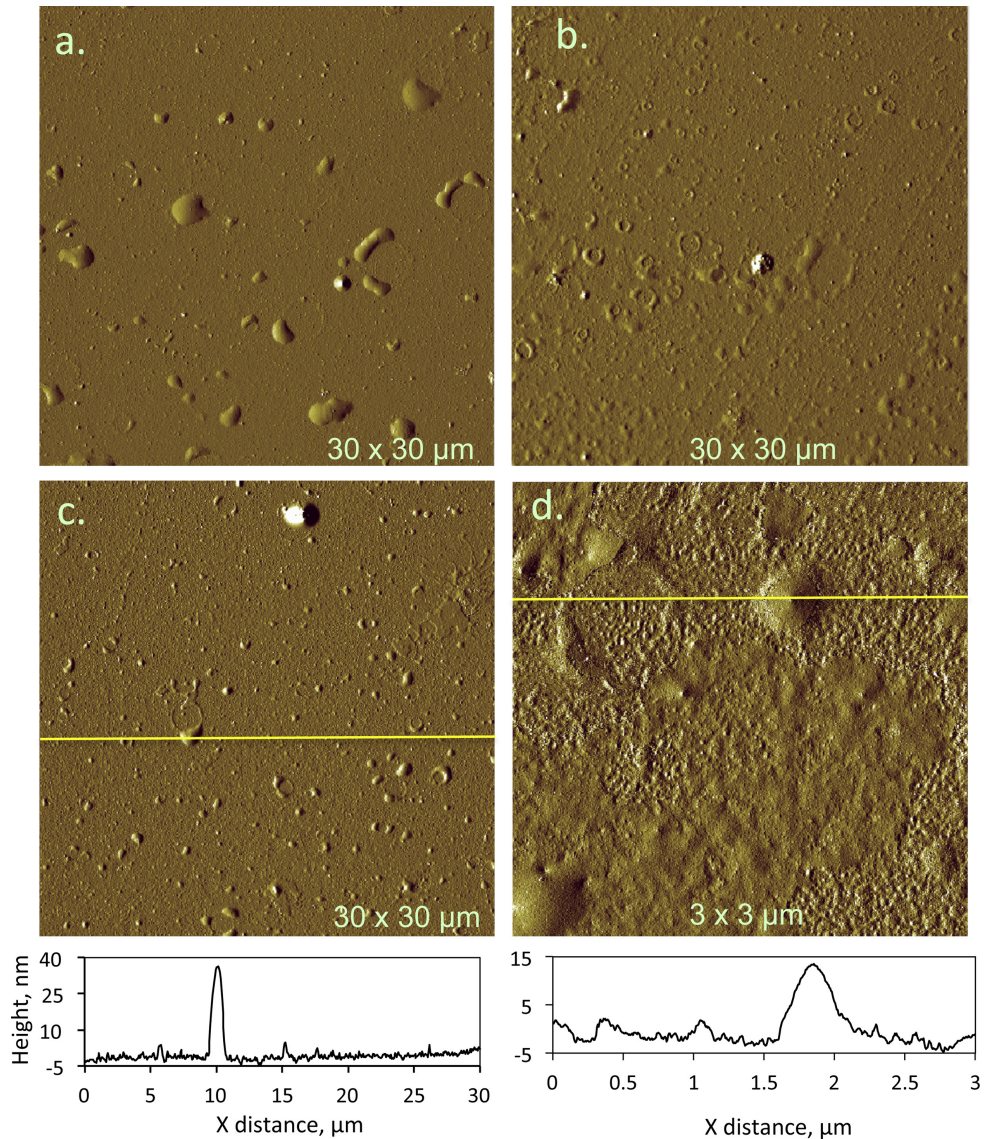


Figure 2.7: AFM images of mica surface reacted by supercritical CO_2 . (a) induced blisters. (b,c) the aftermath of the collapse of blisters and dissolution and precipitation features. (d) close up image of blisters. Reproduced with permission from reference [Wan et al., 2014]. Copyright 2014 Elsevier Science.

2.3.2 Salinity and pH

The role of salinity also varies with different surface (Fig. 2.8). The contact angle increases with salinity for silica surfaces [Jung and Wan, 2012], whereas in the case of mica surfaces, some reported an increase [Arif et al., 2016b,a] and some reported unclear behavior [Wan et al., 2014, Jafari and Jung, 2018].

Standnes and Austad [2000] studied the wettability alteration of chalk substrate when there is a change in salinity or pH of the water. The contact angle on a calcite crystal as a representative mineral for chalk at two different temperatures was measured to investigate the effect of temperature. They observed a change from slightly water-wet (contact angle less than 90) to water-wet in samples previously saturated with oil. The change was more substantial in cationic surfactant than anionic surfactant (12-28 degrees to 39-63 degrees). They proposed two mechanisms for cationic and anionic surfactants. Cationic surfactants can stick to negatively charged organic material deposited on the surface, desorbed, and move into the oil phase. By doing so, they expose the surface to water ions and wet the surface. However, in the case of anionic surfactants, they cannot detach organic groups. Instead, they make an intermediary zone between the organic deposited and the oil phase, creating a weak capillary force that lowers CA. Both surfactants caused an increase in effect by increasing temperature. The same behavior is observed for the concentration. However, there is a critical concentration after which the effect is reversed, meaning the contact angle increases.

The surface of calcite is slightly negatively charged while in contact with water (calcite saturated solution, pH=8.3), although excess charges could be found at surface defects [Lee et al., 2016]. The surface charge can differ by having the calcite surface in contact with brine with a different concentration ratio of Ca^{2+} and SO_4^{2-} . Strand et al. [2006] proposed an explanation for the wettability alteration of carbonates in contact with brine with a higher sulfate concentration by competition of sulfate ion versus organic carboxylic group in adsorption onto the surface. By adsorbing sulfate ions on the surface, the surface is less positively charged and releases the adsorbed carboxylic group. Since there is a high concentration of Ca^{2+} , it would result in a reaction between the carboxylic group and Ca^{2+} . It is worth mentioning that the oil-water interface is negatively charged with the magnitude depending on the pH of water [Marinova et al., 1996].

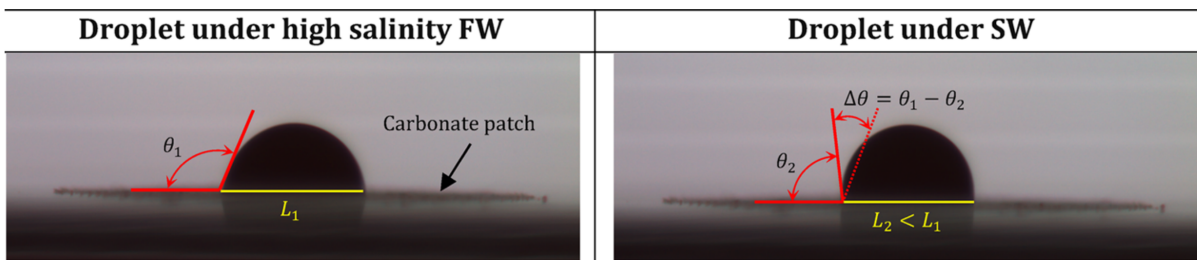


Figure 2.8: Oil droplet on limestone with different salinity of formation water. Reprinted with permission from [Mahani et al., 2015]. Copyright 2015 American Chemical Society.

In the case of wettability alteration in regard to CO_2 , the change in pH in water has been proposed as the mechanism [Chiquet et al., 2007]. As the pH decreases, the brine/ CO_2 interface (negative) charge goes to zero, and it vanishes for a pH lower than 3. Therefore, the repulsive electrostatic force between the water-solid interface and the water- CO_2 interface disappears and results in an increase in contact angle. This can be observed in the change of the CO_2 bubble shape in Fig. 2.9. Farokhpour et al. [2013] investigated the temporal effect on the CO_2 bubble profile as well as the contact angle for a mica-brine- CO_2 system, and observed an increase in contact angle after 41 days (Fig. 2.10).

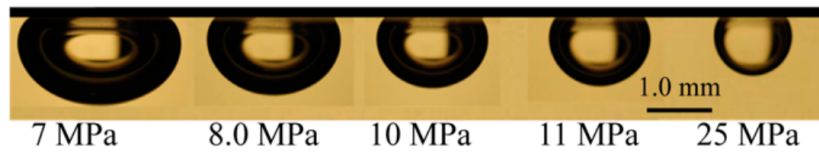


Figure 2.9: Change in CO_2 bubble shape and size with pressure for the system of silica-water- CO_2 . Reprinted with permission from [Jung and Wan, 2012]. Copyright 2012 American Chemical Society.

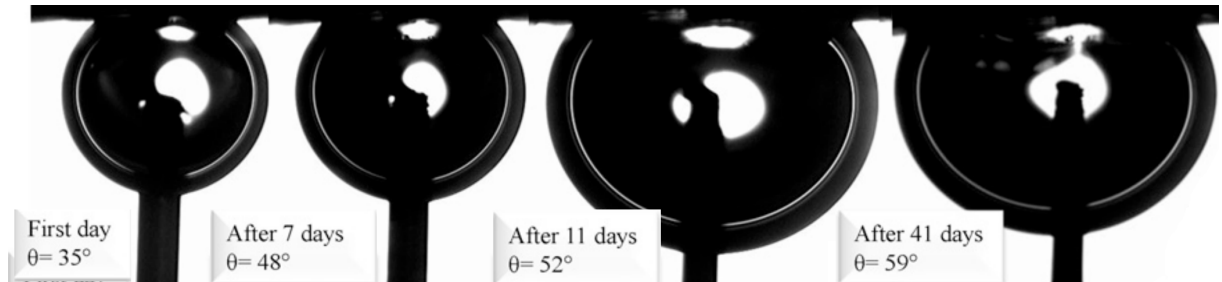


Figure 2.10: Droplet of gas in a system of mica-brine- CO_2 . Reproduced with permission from reference [Farokhpour et al., 2013]. Copyright 2014 Elsevier Science.

2.3.3 Pressure

The change in contact angle is observed while increasing CO_2 pressure for a coal sample (Fig. 2.11). The water- CO_2 -coal system also exhibits an alteration in contact angle with regard to the pressure; for the atmospheric pressure, the system is more water-wet, and by increasing the pressure, it changes to a higher contact angle [Siemons et al., 2006]. Siemons et al. [2006] suggested that the water film at the coal surface is less stable at higher pressures with a higher pressure of CO_2 . However, the increase in adsorption of CO_2 on the surface as the pressure increases could change the wettability. In addition, the dissolution of CO_2 and its compressibility could also play a role.

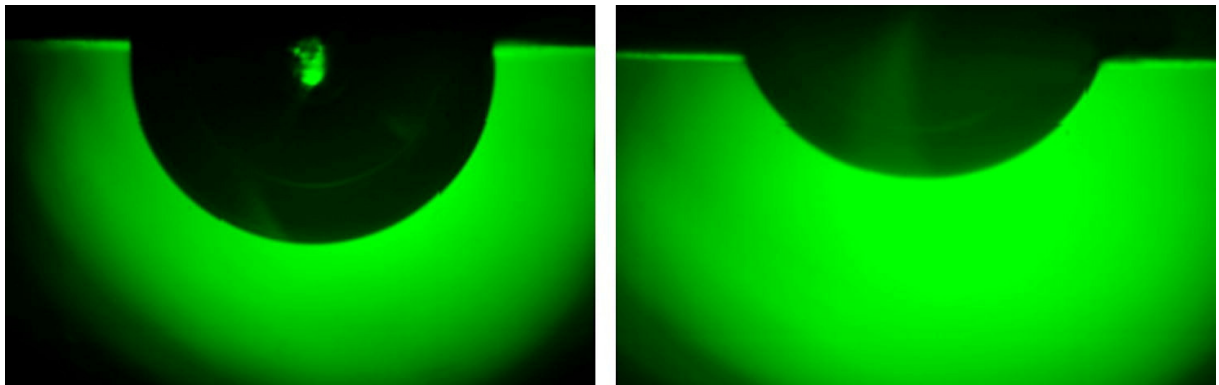


Figure 2.11: Change in shape in CO_2 bubble on coal surface in the presence of water as pressure increases from left to right. Reproduced with permission from reference [Kaveh et al., 2011]. Copyright 2014 Elsevier Science.

2.3.4 Droplet size

For small enough droplets, the contact angle measured even for the same surface and fluid depends on the droplet size [Méndez-Vilas et al., 2009]. For a single droplet, the contact angle measured at different

points of the contact circle is different [Deng et al., 2018].

Table 2.2: The contact angle reported in the literature for different thermodynamic conditions (in case of advancing and receding measurements, the average value is calculated)

phase 1	phase 2	solid	T (K)	P (MPa)	salinity	pH	contact angle	reference
s-cr CO ₂	brine	silica	318	7	0	-	35	Jung and Wan [2012]
					5 (M)		65	
				15	0		45	
					5 (M)		70	
CO ₂	brine	Mica (1)	343	15	0	-	~60	Arif et al. [2016b]
				15	20 % wt		~70	
				5	0		~20	
				308	0		~30	
		Mica (2)	343	15	0		~110	
				15	20 % wt		~110	
				5	0		~50	
				308	0		~70	
brine	oil	Limestone	298		3.66 (M)	6.9	~60	Mahani et al. [2015]
brine	oil				0.035 (M)	8.7	~40	
brine	oil	Dolomite			3.66 (M)	6.9	~130	
brine	oil				0.035 (M)	9.2	~130	

2.4 Molecular insights and wettability

Surface forces related to the interaction of molecules are considered short-range, meaning that on a larger scale, they decay to zero. However, their effects can be observed, for example, in surface tension or wettability. The overall interaction of all the molecules of different phases is already present in the surface tension force and Young’s equation (1.3) with two caveats. First, we can estimate upscaled surface tension and contact angle values, knowing the inter-molecular interaction. The second point is about the range of validity of the upscaled values. Surface tension is determined by the surface forces, which are short-range intermolecular forces. They can describe the averaged inter-molecular interaction of the interface provided the bulk of phases are large enough. However, suppose we are dealing with a very thin layer of liquid. In that case, the interfaces of the liquid are interacting with each other, and the surface tension of the liquid will deviate from the typical values. The same is true in the vicinity of the three-phase contact line, where different surfaces are now interacting. The range of validity of the Young’s equation (1.3) is outside of the short-range inter-molecular forces (≈ 100 nm) [de Gennes, 1985]. In order to explain these forces, we introduce cohesive and adhesive energy [Israelachvili, 2011].

2.4.1 Cohesive and adhesive energy

Cohesive energy, W_H , is the energy required to remove or introduce a mole of molecules to the bulk of the system. In a two-dimensional closed pack network structure of molecules in the bulk phase, each molecule has up to 6 neighbor molecules (Fig. 2.12). By introducing a new molecule in the already formed network, three former bonds need to break first, and then six bonds will form. Therefore, the net energy change is three times the pair-potential energy for each molecule (for a three-dimensional case, it will be six times the pair-potential energy). In other words, internal energy consists of the pair potential of the bonds in the system.

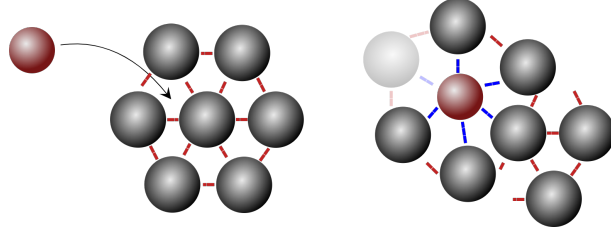


Figure 2.12: Molecular arrangement in a closed pack system. The center molecule has six bonds with the surrounding molecules. The red sphere is being introduced into the network. The new bonds are formed (shown in blue).

For the creation of a surface, the cohesive energy needs to be overcome, which will result in two surfaces. Therefore, the energy required to separate the bulk phase and create two surfaces in the process is half the cohesive energy:

$$\sigma_l = \frac{1}{2}W_{ll}. \quad (2.11)$$

σ_l is also called the surface energy and W_{ll} is the work of cohesion between phase l . Materials with high-energy bonds, such as metallic solids, have a high cohesive energy as opposed to molecular solids like hydrocarbons or ice/water. High-cohesive materials tend to have also high surface energy [de Gennes, 1985].

2.4.2 Work of adhesion

The work of adhesion is the energy required to create a surface between unlike molecules. Therefore, the work of adhesion of two phases l, v is:

$$W_{lv} = \sigma_l + \sigma_v - \sigma_{lv}. \quad (2.12)$$

In order for the two phases to adhere to each other, first, a surface is created in both of them. Then, the energy of the system is reduced by the interaction of the newly formed surface, quantified by surface tension σ_{lv} .

2.4.3 Work of spreading

We can similarly write the adhesion work of solid/liquid and solid/vapor. If a liquid spreads on the solid surface in the presence of vapor, it separates the solid from vapor and the liquid from itself and creates a surface with the solid and vapor. Therefore, the work of liquid spreading is [Israelachvili, 2011]:

$$W_{lsv} = W_{sv} + W_{ll} - W_{sl} - W_{lv} = -\sigma_{sv} + \sigma_{sl} + \sigma_{lv}. \quad (2.13)$$

The spreading coefficient is $-W_{lsv}$. Therefore:

$$S = \sigma_{sv} - \sigma_{sl} - \sigma_{lv}. \quad (2.14)$$

The derivation up to this point was made for the case of parallel layers of phases. It means that in the above equations, the surface area that is created between solid and liquid is equal to the surface area between liquid and vapor. However, for the cases mainly concerned with wettability, these two surfaces are not parallel, and the surface area is not equal. Therefore, in these cases, the work of spreading is

introduced as:

$$W_{tot} = \sigma_{lv}(A_c + A_f) - W_{lsv}A_f, \quad (2.15)$$

where A_f and A_c is the flat and curved area of the droplet (Fig. 2.13).

2.4.4 Young-Dupré equation

At the equilibrium, the change in the work is zero, and:

$$W_{lsv} = \sigma_{lv}(1 + \cos(\theta)), \quad (2.16)$$

which is also called Young-Dupré equation. If the liquid is spreading on the solid as opposed to the vapor,

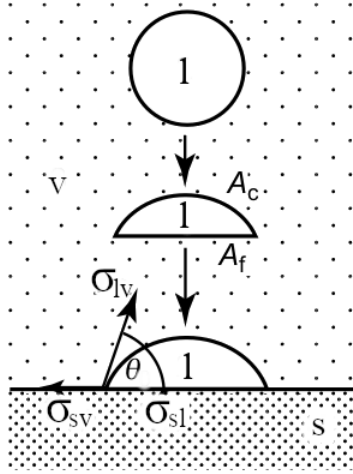


Figure 2.13: spreading when the fluid has a non-zero contact angle with the solid [Israelachvili, 2011]

then the above equation becomes:

$$W_{vsl} = \sigma_{lv}(1 - \cos(\theta)). \quad (2.17)$$

This equation relates the inter-molecular interaction with the wettability, which is represented by the contact angle.

2.4.5 Disjoining pressure and inter-molecular interactions

Alternately, it is convenient to define a "disjoining pressure," Π , as a gradient of the adhesion energy:

$$\Pi = -\frac{dW_{vsl}}{dh}, \quad (2.18)$$

where h is the distance to the interface, the etymology of the disjoining pressure refers to the excess pressure in the fluid close to the interface due to the inter-molecular interactions [Derjaguin, 1989]. The intermolecular interactions involved in thin films and colloidal suspensions are considered Van der Waals (VDW), electric double layer (EDL), and structural interactions.

Van der Waals This interaction is due to the attraction of polar or non-polar constituents of the different phases. The overall interaction of each pair of molecules leads to an expression of the surface force between fluid/fluid and solid/fluid interfaces.

Electric double layer This interaction is important when electrolytes are present in the fluid. The interaction of the electrolyte with the fluid/fluid and fluid/solid surface causes a redistribution of the ions different from the bulk. The new distribution exerts an excess pressure in the domain, which is the contribution of the electrostatic force in disjoining pressure.

Structural interactions This interaction is mainly concerned with the orientation and network of molecules very close to the interface. In the case of water, the hydration force is mainly considered.

The disjoining pressure is, therefore, the sum of these three contributions:

$$\Pi = \Pi_{VDW} + \Pi_{EDL} + \Pi_{str}. \quad (2.19)$$

The integration of disjoining pressure (Π) results in energy (W) associated with the inter-molecular interactions in the three-phase contact region. Combining the disjoining pressure with Eq. 2.17 can provide the contact angle. In Fig. 2.14, the disjoining pressure that corresponds to the different wettability conditions is shown. In this thesis, we intend to replace the concept of contact angle with disjoining pressure in a pore-scale model.

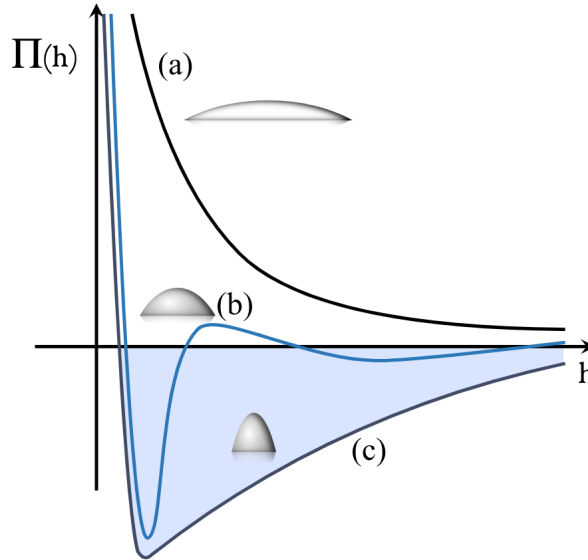


Figure 2.14: Disjoining pressure curves represent different wettability conditions. The area underneath curves determines the disjoining pressure integration and, eventually, the contact angle. (a) represent a complete wetting case, (b) corresponds to a partial wetting, and (c) belongs to a surface with higher contact angle.

2.5 Conclusions and methodology used in the thesis

2.5.1 Summary

- Wettability appears in the boundary condition at pore-scale modeling through the contact angle. The implementation of the contact angle in the pore-scale modeling will result in a moving boundary problem. In order to mitigate this problem, different models have been proposed, such as the slip model, flow on a precursor film, diffuse interface, and interface formation.

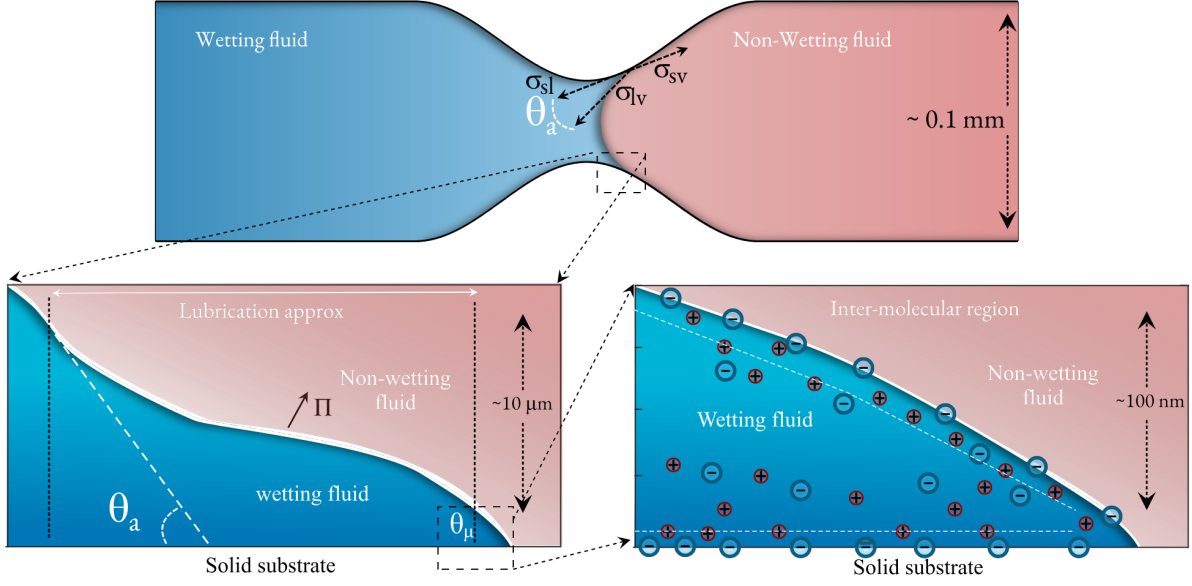


Figure 2.15: Illustration of interface for a micro and sub-micro scale

- Contact angle is influenced by different thermodynamic parameters (table.2.2) and down to the molecular level. Even so, the smoothest surface (such as mica), which has very small roughness affects contact angle measurements. It is also true if the surface contains some chemical impurity. The ions in the fluid in contact with the surface can alter the surface potential and, therefore, change the inter-molecular interaction between the fluid and the solid.
- Accounting for the inter-molecular interaction close to the contact region can alternatively be used to model the wettability behavior of the system. The inter-molecular interaction has been studied in colloids and thin films using the disjoining pressure concept. Furthermore, disjoining pressure can give insights into the alteration in wettability.

2.5.2 Methodology used in the thesis

We are dealing with a problem that concerns different scales of analysis. Therefore, we intend to focus on the sub-micro scale to investigate the role of inter-molecular forces in the region of the three-phase contact line (Fig. 2.15). This allows us to address the ambiguity caused by different behaviors of contact angle as the fluid encounters different salinity and pH and the effect of contact line velocity on contact angle. A thin film with varying thickness can approximate the region close to the contact.

In this thesis, we use the lubrication theory to incorporate the effect of inter-molecular interaction and study the dynamic of the film close to the contact. The inter-molecular interaction used reflects the wedge-shaped geometry of the region close to the contact.

Chapter 3

Van der Waals potential near the three-phase contact line

Abstract

The work of adhesion describes the energy of spreading of a liquid on either a dry surface or a surface in contact with the vapor of the liquid. This energy comes from the pair interaction of constituents of different phases. The nature of this interaction is electromagnetic and can be between two charges, dipoles or induced dipoles. The dipole-dipole, dipole-induced dipole, and instantaneous dipole interaction are called Van der Waals (VDW) forces, usually considered attractive. The adhesive energy for a non-polar fluid can be estimated with the VDW attraction. The work of adhesion is related to the wettability and contact angle through the Young-Dupré equation. In this chapter, we use different expressions of VDW potential and compare the results based on how accurately they predict the wettability measured in the experiment. A VDW potential derived with fidelity to the three-phase contact region predicts better results.

3.1 VDW energy of interaction between two species

VDW energy of interaction between two non-polar species can be approximated by their polarizability [de Gennes, 1985]:

$$P_E = \frac{C_{VDW}}{r^6}, \quad (3.1)$$

where r is the distance between two bodies and $C_{VDW} = -\frac{2}{3} \frac{\alpha_1 \alpha_2}{(4\pi\epsilon_0)^2} \frac{\hbar\nu_1\nu_2}{\nu_1+\nu_2}$. α_i is the polarizability of species i , $\hbar$ is the Planck constant and ν_i is the orbiting frequency of the electron of species i . Surfaces with high polarizability show more affinity for the liquid spreading, *i.e.* complete wetting. The same form of this equation can be used for the interaction of polar and dipole species with each other with different exponents for r .

3.2 VDW potential for two parallel surfaces

VDW potential for two parallel plates at a distance of h is the integration of two pair body potential of all the elements in two plates, assuming that the higher pair potential is negligible (assumption of

additivity). This assumption is fine when the two surfaces are interacting through the vacuum or rarefied gas.

3.2.1 Integration of the VDW energy between species

In order to obtain the interaction energy of two different surfaces, the pair-interaction of each constituent from the surfaces with each other is integrated:

$$W_{VDW} = \int \rho_{e2} \left(\int \rho_{e1} P_E dv \right) dz \quad (3.2)$$

where $\rho_{ei} = \frac{N_A}{Mw_i} \rho_i$ is the density of the particle in surface i . The inner integral results in the interaction of one particle from surface 2 with all the constituents of the surface 1. To obtain the inner integral, the

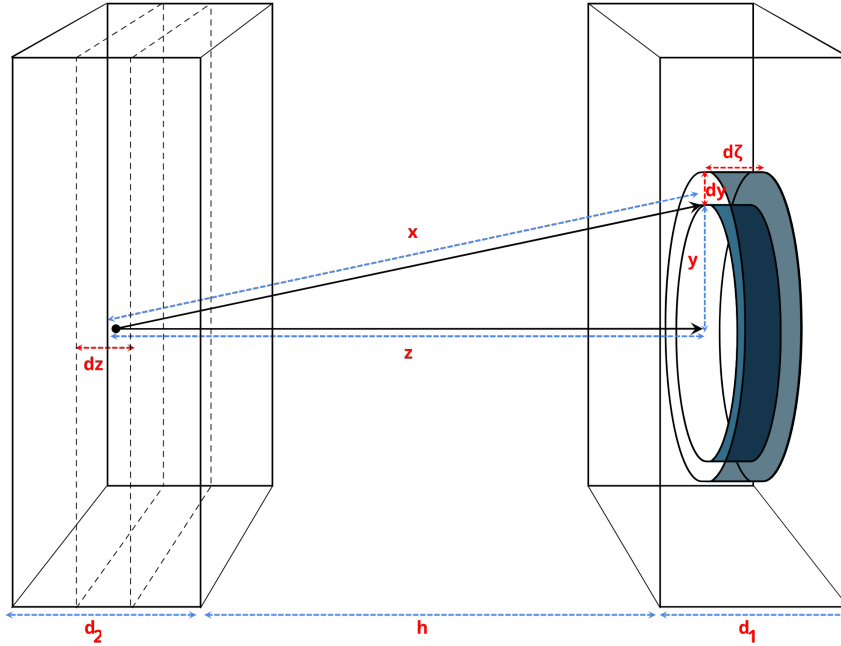


Figure 3.1: Integration of pair potential for two plates at a distance h

volume element is selected as a ring, $dv = 2\pi y dy d\zeta$ (fig.3.1), we have:

$$\int_{\zeta=0}^{\zeta=d_1} \int_{y=0}^{y=\infty} \frac{C_{VDW}}{x^6} \rho_{e1} dv, \quad (3.3)$$

Using the Pythagorean theorem, $x^2 = (z + \zeta)^2 + y^2$, and therefore:

$$\int_{\zeta=0}^{\zeta=d_1} \int_{y=0}^{y=\infty} 2\pi \rho_{e1} C_{VDW} \frac{y}{((z + \zeta)^2 + y^2)^3} dy d\zeta = \frac{\pi \rho_{e1} C_{VDW}}{6} \left(\frac{1}{z^3} - \frac{1}{(z + d_1)^3} \right). \quad (3.4)$$

Now, we can calculate the outer integral, which is the interaction of all of the particles from the first surface with the second surface:

$$W_{VDW} = \int_{z=h}^{z=h+d_2} \frac{\pi \rho_{e1} \rho_{e2} C_{VDW}}{6} \left(\frac{1}{z^3} - \frac{1}{(z + d_1)^3} \right) dz = -\frac{A_{12}}{12\pi} \left[\frac{1}{(h + d_1 + d_2)^2} + \frac{1}{h^2} - \frac{1}{(h + d_1)^2} - \frac{1}{(h + d_2)^2} \right], \quad (3.5)$$

and $A_{12} = \rho_{e1}\rho_{e2}C_{VDW}$ is called the Hamaker constant. If we assume the thickness of two planes is much larger compared to their distance, meaning $d_i \rightarrow \infty$, then the energy of interaction between two planes becomes:

$$W_{VDW} = -\frac{A_{12}}{12\pi h^2}, \quad (3.6)$$

Moreover, the VDW (dispersion) contribution of disjoining pressure for two plates is:

$$\Pi_{VDW} = -\frac{\partial W_{VDW}}{\partial h} = \frac{-A_{12}}{6\pi h^3}, \quad (3.7)$$

3.2.2 Lifshitz Theory of VDW

The equations for VDW potential derived so far are applicable when the condition of additivity holds. It means the contribution of each pair of atoms can be integrated, and each pair does not affect the other pair. This is for rarefied gases; however, for liquids, it does not hold [Israelachvili, 2011, Lifshitz and Hamermesh, 1992]. Instead of integrating the pair potential as it was explained before, Lifshitz and Hamermesh [1992] calculated the fluctuation in the electromagnetic field in the medium and used Maxwell stress tensor to arrive at a more general form for the inter-molecular interaction, which in the limit of rarefied gas and short distance is equal to VDW potential that was introduced before. According to this theory, for short distances, the inter-molecule interaction simplifies to [Lifshitz and Hamermesh, 1992, Derjaguin, 1989, Israelachvili, 2011]:

$$\Pi_{VDW} = -\frac{\hbar\bar{\omega}}{8\pi^2 h^3}, \quad (3.8)$$

where $\bar{\omega} = \int \frac{(\epsilon_1 - \epsilon_3)(\epsilon_2 - \epsilon_3)}{(\epsilon_1 + \epsilon_3)(\epsilon_2 + \epsilon_3)} d\zeta$ and ζ is the frequency. Therefore, the Hamaker constant can be rewritten as $A_{123} = \frac{3\hbar\bar{\omega}}{4\pi}$; we need to obtain the proper Hamaker constant. Hough and White [1980] calculated the Hamaker constant according to Lifshitz theory by using a refractive index for a variety of three-phase systems, such as water/hydrocarbons/quartz. For the case of spreading of thin film in contact with the vapor, we can write A_{svl} based on each pair interaction [Derjaguin, 1989, Israelachvili, 2011]:

$$A_{svl} \approx A_{vv} + A_{sl} - A_{sv} - A_{lv}, \quad (3.9)$$

where A_{ij} is the Hamaker constant between two phase i, j . However, it should be noted that in order to obtain the accurate result for the VDW interaction, the Hamaker constant should be calculated based on Lifshitz theory, the same as the work of Hough and White [1980] for the A_{svl} . Therefore, the dispersion component of disjoining pressure is:

$$\Pi_{VDW} = -\frac{A_{vv} + A_{sl} - A_{sv} - A_{lv}}{6\pi h^3}. \quad (3.10)$$

Another implication of Lifshitz's work is the change in the decay of VDW interaction for large distances, which is called retardation.

3.2.3 Retardive VDW

The dispersion potential is due to the polarization of the atoms. Suppose the separation of the two plates grows higher than the wavelength associated with the transition between the ground and excited states of the atom. In that case, the dispersion potential decreases more rapidly than $1/h^3$. The difference between retarded and non-retarded dispersion potential becomes noticeable for a distance higher than 2-3 nm.

According to Lifshitz's theory of VDW, for the limit of long distance, the interaction decays faster with respect to distance by $\frac{1}{h^3}$ instead of $\frac{1}{h^2}$. The approximation of the retardive and non-retardive VDW interaction that covers the limit of both short and long separation of two plates is given by Overbeek [1952, Chapter 6] and Gregory [1981]:

$$W_{VDW} = -\frac{A}{12\pi h^2} \left(\frac{1}{1 + bh/\lambda} \right), \quad (3.11)$$

where λ is the characteristic wavelength for retardation interaction, and the constant b is a fitting parameter. [Gregory, 1981] obtained $b = 5.32$ to have the best fit at the distance corresponding to $\frac{3\lambda}{2\pi}$.

3.3 VDW for non-uniform films

So far, we have discussed the potential of VDW for parallel interfaces. The equations written in the previous section are theoretically derived for two parallel plates. Alizadeh Pahlavan [2018], however, showed that in a partial wetting system where the contact angle is not zero, the inter-molecular potential should at least depend on the first order derivative *i.e.* slope of the film thickness. For non-uniform films with arbitrary surfaces, however, the VDW potential, in addition to the film thickness, depends on higher derivatives of the film thickness, including slope and interface curvature (Fig. 3.2). The region close to the contact is a special case for the non-uniform case; in the vicinity of the contact, the film resembles a wedge-shaped geometry (Fig. 3.3).

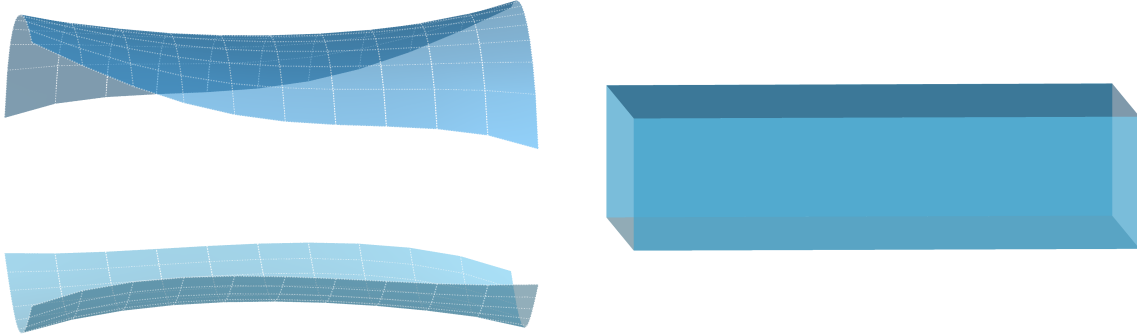


Figure 3.2: Illustration of non-uniform and uniform film

3.3.1 Two arbitrary curved surfaces

Wang et al. [2020] proposed the following equation for the VDW potential for two arbitrary curved surfaces, where one surface is infinite, and the other is the unit area:

$$W_{VDW} = \frac{A}{3} \frac{1}{sh^3}, \quad (3.12)$$

where the Hamaker constant here defined as $A = \pi^2 \rho_{s1} \rho_{s2} C$ and

$$s^2 = (c_1 + \tilde{c}_1 \cos^2(\theta) + \tilde{c}_2 \sin^2(\theta)) (c_2 + \tilde{c}_1 \sin^2(\theta) + \tilde{c}_2 \cos^2(\theta)) - (\tilde{c}_1 - \tilde{c}_2)^2 \sin^2(\theta) \cos^2(\theta)$$

and c_1, c_2 are two principal curvatures for the first surface and $\tilde{c}_1, \tilde{c}_2$ are the same for the second surface, and θ is the relative angle of the surfaces at the point of interest on both surfaces. The wetting film

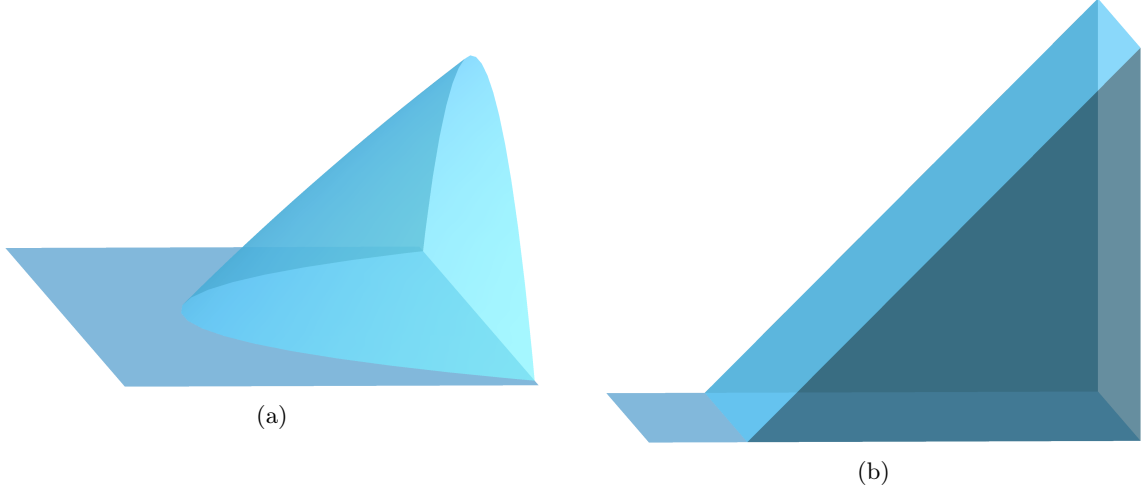


Figure 3.3: Illustration of the three-phase contact region (a) pore scale representation (b) molecular representation

in the vicinity of the three-phase contact resembles a wedge geometry with two semi-infinite surfaces. Therefore, this equation is not applicable to obtain the VDW interaction for the contact region. However, it can provide insight into the general form for VDW potential.

3.3.2 Two intersecting interfaces

For the particular domain of the three-phase contact region, Wu and Wong [2004] derived a VDW potential in the partial wetting film considering two intersecting interfaces. First, they obtained the VDW potential per volume for the molecules in the liquid (wetting phase). Second, they subtracted the total potential per volume at the region close to the wedge by the potential far from the substrate. Finally, by integrating this value from the solid surface up to the wetting surface, they obtained the excess energy:

$$W_{VDW} = \frac{A_{ff}}{4h^2} \left(\frac{(1 - \frac{A_{fs}}{A_{ff}})}{3} + \frac{(1 - \frac{A_{fg}}{A_{ff}})}{4} \left(1 - \frac{1}{\sqrt{1 + h_x^2}} \right) h_x \right), \quad (3.13)$$

where A_{ff} , A_{fg} , and A_{fs} are the Hamaker constant for fluid-fluid, fluid-gas, and fluid-solid and h_x is the slope of the intersecting surfaces.

Similarly and at the same time, Fuentes [2003] obtained an expression for VDW for a wedge geometry as well. They consider the non-wet phase as air. Therefore, they neglect the VDW due to air. Diaz et al. [2010] developed this expression to calculate the excess energy. They consider the same concept as the work of Wu and Wong [2004] but with a different method. There are two main differences in their method compared with the one used by Wu and Wong [2004]. The first is obtaining excess energy; they considered the wedge resting on an adsorbed film. The second difference is that they introduced a term dependent on the equilibrium contact angle. They reasoned that the slope-dependent term in VDW will result in a tangential force; therefore, as the wetting phase contact angle reaches its equilibrium value, the tangential force should reach zero. Finally, they obtained an equation for VDW potential to have the form:

$$W_{VDW} = -\frac{A_{fs} - A_{ff}}{12\pi(h+b)^2} + \frac{A_{ll}}{12\pi(h)^2} \left(-\frac{1}{2} + \frac{3}{4} \cos(\theta) - \frac{1}{4} \cos^3(\theta) \right), \quad (3.14)$$

where b is the thickness of the adsorbed film. Diaz et al. [2010] used this form of expression for a wedge

and pointed out that the cut-off distance for an advancing and receding moving contact line is different, which will result in a hysteresis. It is important to note that for the zero contact angle, the eq. 3.14 does not converge to the parallel plate expression.

3.3.3 Wedge with small slope

Dai et al. [2008] found out that the expression developed by Wu and Wong [2004] (eq. 3.13) in the limit of zero slope did not lead to VDW interaction for two parallel plates and derived a corrected expression with modifying the method. They derived the inter-molecular potential energy for two intersecting planes considering the slope of the interface by using the definition of interfacial energy. The idea is that the interfacial tension energy is the difference between the total pair potential between each particle in a domain when only one phase is present versus when both phases are present. They called the energy inside the film subtracted with interfacial energy, the excess energy per unit area. The expression that they derived is quite complex; however in the limit of small slope ($h_x \ll 1$), it simplifies to:

$$W_{VDW}(h, h_x) = -A_{123} \left(\frac{1}{12\pi h^2} + \frac{h_x^2}{16\pi h^2} \right), \quad (3.15)$$

and the disjoining pressure:

$$\Pi_{VDW} = -\frac{A_{123} (4 - 3h_x^2 + 3hh_{xx})}{24\pi h^3}, \quad (3.16)$$

where A_{svl} is the Hamaker constant for two phase (l, v refer to liquid and vapor) interacting with the third phase (s is solid) and $h_{xx} = \frac{\partial h_x}{\partial x}$. In the limit of zero slopes for the interface *i.e.* two parallel plates, the equation simplifies to eq.3.7.

However, two issues remain in the derivation. First, the VDW expression goes to infinity for the wedge angle approaching $\pi/2$. However, this does not seem plausible. Since we can imagine the wedge with the right angle as a film with a parallel plate, where the VDW potential no longer depends on the film's slope, the dependency on the slope should vanish as the angle reaches $\pi/2$. The second issue is related to their derivation. In order to obtain the excess energy due to the VDW interaction, they integrated the total energy for a molecule in the film subtracted with the interfacial energy. They replaced the distance of the molecules to the fluid-fluid interface with an equation based on the thickness of the film, " h ," at a location on the fluid-fluid interface. However, their choice of the location of " h " seems arbitrary since moving the " h " will change the integrated expression.

3.3.4 Generalization of VDW potential for a wedge structure

All the equations we mentioned so far do not adequately express the VDW interaction either close to zero contact angle or to $\pi/2$. However, these equations give insight into the dependency of the VDW potential on the film thickness and the contact angle. The VDW potential for the wedge geometry should converge to the expression for the parallel film when the contact angle goes to zero. Moreover, when the wedge angle reaches $\pi/2$, the geometry again resembles a flat film.

We propose, therefore, an expression based on a generic combination of the two mentioned approaches for the VDW potential to have a form:

$$W_{VDW}(h, h_x) = -A_{123} \left(\frac{1}{12\pi h^2} + g(\theta) \frac{h_x^2}{12\pi h^2} \right), \quad (3.17)$$

where

$$g(\theta) = \frac{1}{4}(1 + \cos(\theta)) \cos^5(\theta) \cos(2\theta). \quad (3.18)$$

This function simplifies to the eq. 3.15 for small angles, and it converges to VDW potential for the parallel plate for zero contact angle, and for the contact angle equal to $\pi/2$ also reduces to the parallel plates expression.

3.4 Comparison with experimental data

We proposed different equations for VDW interaction. Here, we compare these equations with a set of experimental data from the literature. First, we give a summary of the experimental setup. Then, we explain how the contact angle is computed using the VDW interactions. Finally, we compare and discuss the different CA predictions with the experimental dataset.

3.4.1 Experimental dataset

The contact angle measurement is carried out by [Zisman, 1964, Baier and Meyer, 1992]. Fox and Zisman [1950b] devised a methodological process to measure the contact angle, which includes the percolation of a non-polar liquid sample to remove the polar among other impurities, treating the surface of the polymer with high pressure, high temperature, and cleaning in acid solution with high temperature to remove surface irregularities and finally the careful placement of the liquid sample on the polymer surface. Their measurements ensured an advancing contact angle and a fast measurement for more volatile liquids (5 s). Baier and Meyer [1992] used the same procedure as the one that Zisman standardizes in the work of Shafrin and Zisman [1952], which is practically the same procedure as the one explained earlier, with one additional detail about the placement of a mono-layer of the liquid on the solid sample.

The properties of n-Alkanes used in the equations are listed in table 3.1.

Table 3.1: Properties of n-Alkanes [Hough and White, 1980, Drummond and Chan, 1997]

Alkane Number	Carbon	$A_{lvl} (\times 10^{-20} J)$	surface tension at 20 °	cut-off length $h_{c lvl}$ (nm)
5		3.74	16.01	0.176
6		4.06	18.20	0.172
7		4.31	20.01	0.169
8		4.49	21.61	0.166
9		4.66	22.98	0.164
10		4.81	23.72	0.164
11		4.87	24.61	0.162
12		5.03	25.42	0.162
13		5.04	26.44	0.159
14		5.09	26.70	0.159
15		5.15	27.02	0.159
16		5.22	27.39	0.159

The properties of the solid substrate are listed in table 3.2. The Hamaker constant for PTFE is 3.76×10^{-20} J, and the surface energy is 18.5 mN/m [Fox and Zisman, 1950a]. The Hamaker constant for FEP teflon is 3.57×10^{-20} J [Stark et al., 2015] and the surface energy is 18.8 mN/m [Wu, 2017]. Drummond and Chan [1997] reported the Hamaker constant for PDMS equal to 4.3×10^{-20} J. However, this is inaccurate since the equations predicted complete wetting for lighter n-alkanes. In the literature,

the measured Hamaker constant of mica and gold interacting across PDMS is 3.4×10^{-20} J [Rapp et al., 2015]. Using the Lifshitz theory, we can obtain the Hamaker constant for PDMS by using the Hamaker constant of mica-mica in vacuum (6.96×10^{-20} J) [Ackler et al., 1996] and gold-gold across vacuum (34.90×10^{-20} J) [Jiang and Pinchuk, 2016]. Based on this calculation, the Hamaker constant for PDMS is 3.27×10^{-20} J. The surface energy of PDMS is equal to 21.8 mN/m [Kuo, 1999, Drummond and Chan, 1997].

Table 3.2: Properties of substrate

Substrate	$A_{lv} (\times 10^{-20} J)$	surface tension at 20 °	cut-off length $h_{c lv}$ (nm)
PTFE	3.76	18.5	0.164
FEP	3.57	18.8	0.159
PDMS	3.27	21.8	0.141

3.4.2 Contact angle from VDW energy

The inter-molecular interaction is related to the microscopic contact angle with the eq.2.16 that was derived earlier in chapter 2.4,

$$\cos(\theta) = -\frac{W_{svl}}{\sigma_{lv}} - 1. \quad (3.19)$$

We can calculate the macro scale contact angle from this equation, provided that we know the inter-molecular interaction potential, W_{svl} . In this section, we mainly deal with non-polar liquid spreading on polymers. Since the interaction of n-alkanes with the polymer substrate only comprises the non-polar interaction, we can use the VDW potential as the inter-molecular interaction potential and neglect the other contributors such as electrostatic component.

The method of Hough and White Hough and White [1980] calculated the Hamaker constant based on Lifshitz theory and compared their result with the experiment of Fox and Zisman [1950a] for the spreading of alkanes on Polytetrafluoroethylene (PTFE). They further used the VDW potential for parallel plate for the interaction of solid, vapor and liquid, $W_{svl} = -\frac{A_{svl}}{12\pi h_c^2}$ and they used the same approximation to calculate the surface tension of the liquid as $\sigma_{lv} = -\frac{1}{2}W_{lv}$. They further assumed that the cut-off length h_c for the fluid-gas and fluid-solid interfaces is equal. Therefore, the equations are simplified into:

$$\cos(\theta) = \frac{2A_{svl}}{A_{lv}} - 1. \quad (3.20)$$

The method of Drummond and Chan In the derivation of Drummond and Chan [1997], different cut-off lengths are used for the interfaces. Therefore, the equation becomes:

$$\cos(\theta) = \frac{2A_{svl}}{A_{lv}} \left(\frac{h_{c|lv}}{h_{c|svl}} \right)^2 - 1, \quad (3.21)$$

where $h_{c|lv}$ and $h_{c|svl}$ are the cut-off length for fluid-vapor and fluid-solid-vapor VDW potential energy. They calculated the $h_{c|lv}$ using the surface tension energy of the fluid and using the VDW potential as:

$$h_{c|lv} = \sqrt{\frac{A_{lv}}{24\pi\sigma_{lv}}}. \quad (3.22)$$

They used the same equation to obtain the $h_{c|svs}$ by using the surface energy of the solid substrate. In order to obtain the cut-off length for fluid-solid-vapor, they used different geometric and arithmetic averages of $h_{c|lvl}$ and $h_{c|svs}$ and compared the calculated contact angle with several measurements in the literature. The geometric average matched the experiment best according to their comparison.

A new method using slope-dependent VDW Instead of using the VDW equation for parallel plates in eq. 3.19, we may use the eq. 3.15. It results in the following equation for the contact angle:

$$\cos(\theta) = 2 \frac{A_{svl}}{A_{lvl}} \left(1 + \frac{3}{4} \tan^2(\theta) \right) - 1. \quad (3.23)$$

Likewise, we obtain the following equation if we use the generalized VDW equation (eq. 3.17):

$$\cos(\theta) = 2 \frac{A_{svl}}{A_{lvl}} (1 + g(\theta) \tan^2(\theta)) - 1. \quad (3.24)$$

This equation is obtained by fitting the experimental data of the contact angle measurements for the spreading of n-alkanes on the PTFE surface.

3.4.3 Results

Now we compare the contact angles obtained by the mentioned equations with the experimental data for n-alkanes on the polytetrafluoroethylene (PTFE) surface [Fox and Zisman, 1950a] (table 3.3), on the FEP Teflon surface [Zisman, 1964] (table 3.4) and Polydimethylsiloxan (PDMS) surface [Baier and Meyer, 1992] (table 3.5).

The contact angle prediction for n-alkanes on the PTFE surface is shown in fig. 3.4 and table 3.3. It appears that considering the slope for VDW potential is important when the contact angle is small (smaller than 40). In fact, for the contact angle values less than ~ 40 , the usual VDW potential that

Table 3.3: Hamaker constant and measured contact angle for spreading of Alkanes on PTFE [Fox and Zisman, 1950a, Hough and White, 1980]

Alkane Carbon Number	A_{svl} ($\times 10^{-20} J$)	cut-off length $h_{c svl}$ nm	θ with eq.3.20	θ with eq.3.21	θ with eq.3.23	θ with eq.3.24	$\theta_{exp.}$
5	3.75	0.170	wetting	wetting	wetting	wetting	wetting
6	3.91	0.168	22.37	wetting	11.76	14.1	12
7	4.03	0.166	29.77	22.55	14.85	20.48	21
8	4.11	0.165	33.88	31.69	16.89	25.2	26
9	4.18	0.164	37.2	37.47	18.54	30.23	32
10	4.25	0.164	39.8	39.91	19.83	35.20	35
11	4.28	0.163	40.77	42.74	20.31	37.19	39
12	4.35	0.163	43.18	45.02	21.50	41.92	42
13	4.35	0.162	43.33	47.61	21.57	42.19	-
14	4.38	0.162	44.03	48.33	21.92	43.42	44
15	4.4	0.161	44.85	49.04	22.33	44.77	-
16	4.43	0.161	45.78	49.95	22.78	46.2	46

only relies on thickness shows a discrepancy with the experiment up to $\sim 80\%$. The highest difference corresponds to the n-hexane where the measurement is 12° while the parallel plates model shows a 22.37° . Furthermore, the predictions using the equation modified by Drummond and Chan [1997] suffer from the same discrepancy. This discrepancy can be explained as, for a small contact angle, the film

thickness variation just before the three-phase contact line takes a longer distance. Therefore, the slope of the film becomes important, whereas, for a higher contact angle, film thickness reaches the three-phase contact line more sharply. Using eq. 3.23, the calculated contact angle matches the two first points of the experimental data (contact angles less than 10). However, it deviates significantly from the experiments for higher n-alkanes (contact angles). Thus, one can conclude that for a small enough contact angle ($0 < \theta < 30$), eq. 3.15 describes VDW for the three-phase contact region in the film more accurately than eq.3.6. However, eq. 3.6 can be used for contact angles higher than ~ 40 . The slope-dependant term does not explain the VDW potential in the middle of this range. Therefore, we modified the slope-dependant term based on this experiment's measurements (eq. 3.17). Unlike other approaches, the contact angle based on this modification reproduces the whole range of the experiment without adding fitting parameters such as cut-off length.

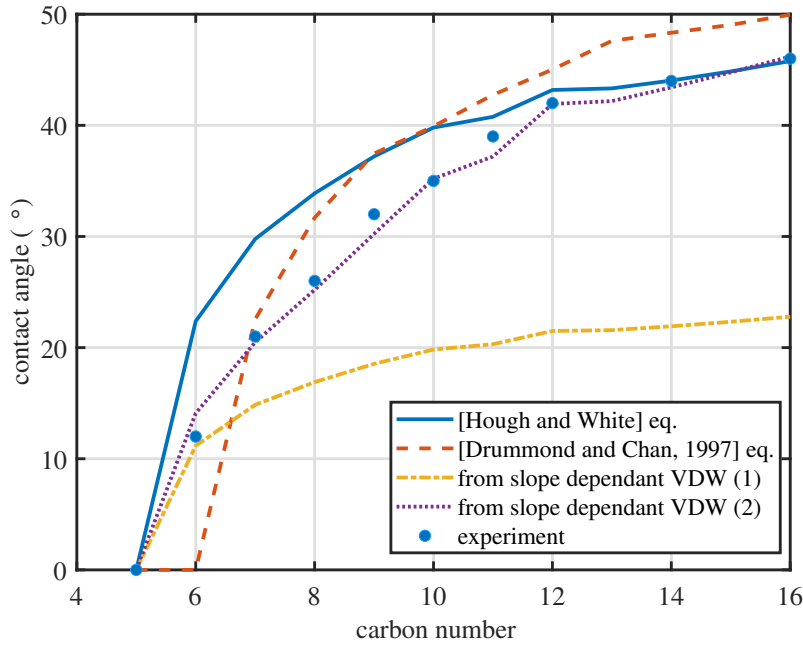


Figure 3.4: Comparison of theoretical and experimental [Fox and Zisman, 1950a] contact angle of the alkanes on PTFE substrate. The deviation of Hough and White [1980] from the experiment for lower contact angle can be explained by the effect of the slope of the interface.

The comparison of the calculated contact angle with the experiment on the FEP surface is shown in Fig. 3.5 and table 3.4. We see that in this case, all the predicted contact angles except for VDW potential for small slope (eq. 3.23) are in good agreement with the experimental measurements. However, for the two last points, which correspond to tetradecane and hexadecane, our generalized slope-dependant equation (eq. 3.24) gives better results, whereas for the first two, the cut-off modified equation based on parallel plate VDW interaction (eq. 3.21) are closer to the experiment. The experiment contact angle measurements tend to be lower for the first two n-alkanes (contact angle less than 45) and higher for the later two (contact angle higher than 45) (Fig.3.5).

Finally, the contact angles for the PDMS surface are shown in fig. 3.6 and table 3.5. In this case, the prediction from all the equations drastically differs from the experiments. The cut-off modified VDW interaction based on parallel interfaces (eq. 3.21) underestimates, and the generalized slope-dependant equation (eq. 3.24) overestimates the contact angle. This discrepancy could be because the adsorbed layer of n-alkanes on the PDMS surface can be significant to the point that it can drastically alter the

3.4. COMPARISON WITH EXPERIMENTAL DATA

Table 3.4: Hamaker constant and measured contact angle for spreading of Alkanes on FEP Teflon [Zisman, 1964]

Alkane Carbon Number	A_{svl} ($\times 10^{-20} J$)	cut-off length $h_{c svl}$ nm	θ with eq.3.20	θ with eq.3.21	θ with eq.3.23	θ with eq.3.24	$\theta_{experiment}$
11	4.17	0.16	44.57	41.55	22.18	44.31	42
12	4.24	0.16	46.77	43.89	23.27	47.61	45
14	4.26	0.159	47.55	47.29	23.65	48.66	49
16	4.32	0.159	49.16	48.95	24.44	50.67	51

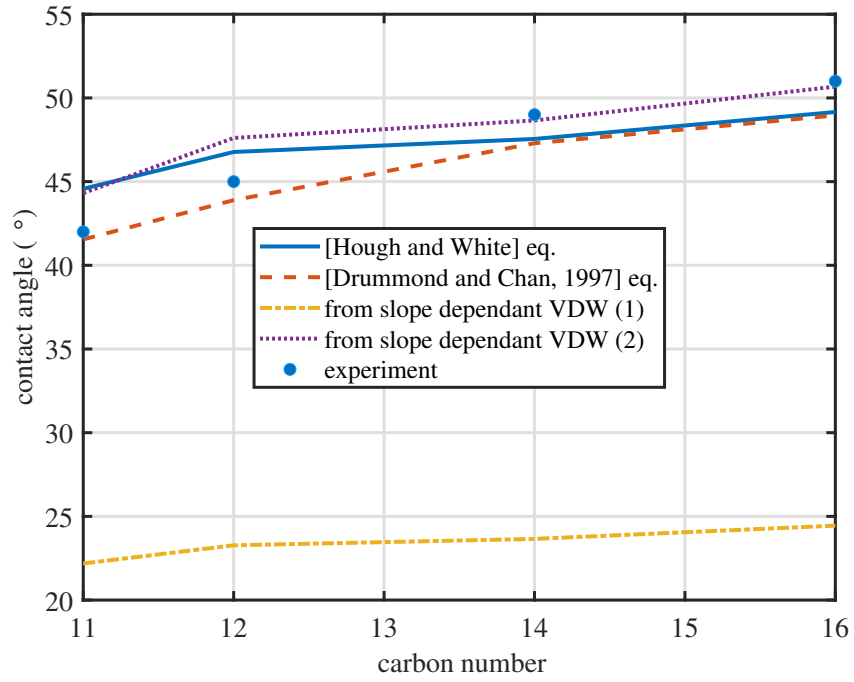


Figure 3.5: Comparison of theoretical and experimental [Zisman, 1964] contact angle of the alkanes on FEP substrate.

Table 3.5: Hamaker constant and measured contact angle for spreading of Alkanes on Polydimethylsiloxane (PDMS) [Baier and Meyer, 1992]

Alkane Carbon Number	A_{svl} ($\times 10^{-20} J$)	cut-off length $h_{c svl}$ nm	θ with eq.3.20	θ with eq.3.21	θ with eq.3.23	θ with eq.3.24	$\theta_{experiment}$
7	3.75	0.156	42.01	wetting	20.96	39.86	23
8	3.83	0.157	45.02	wetting	22.41	45.04	29
10	3.97	0.156	49.05	23.34	24.63	51.12	38
13	4.06	0.154	52.34	35.17	26.01	54.24	40
16	4.13	0.154	54.34	38.38	27	56.29	41

cut-off length for the interaction of solid-fluid-vapor. In other words, the correction due to the cut-off length should be considered in this case. Furthermore, the PDMS properties, surface energy, and the Hamaker constant could differ for the specific substrate used in the experiment.

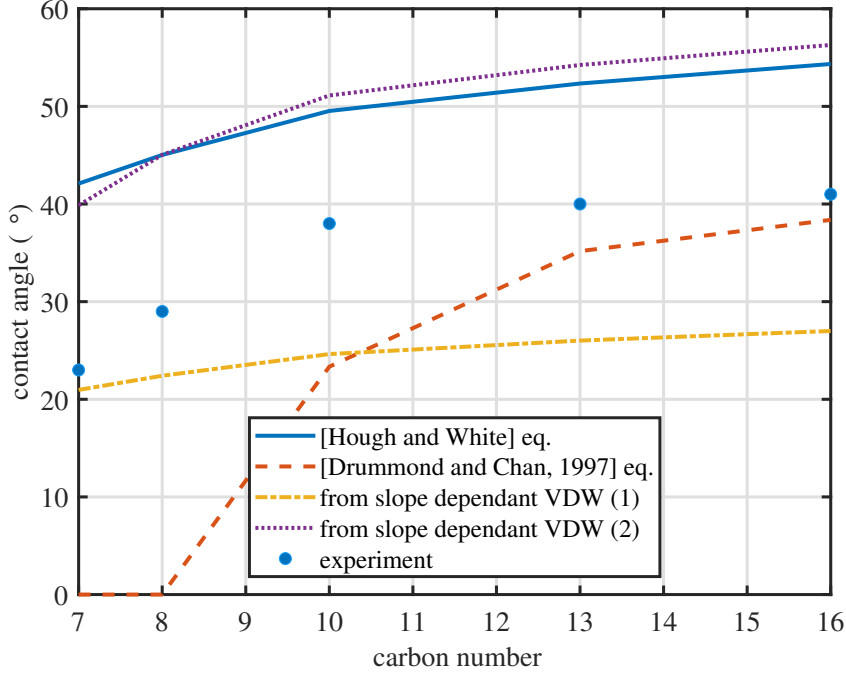


Figure 3.6: Comparison of theoretical (parallel plate) [Hough and White, 1980] and experimental [Fox and Zisman, 1950a] contact angle of the alkanes on PTFE substrate and Eq.3.23 (intersection plate). The deviation of Hough and White [1980] from the experiment for lower contact angle can be explained by the effect of the slope of the interface.

To summarize, we compared the contact angle measurements of n-alkanes on three different polymers with the value obtained from the equation eq .3.19. Although considering different cut-off lengths for the liquid/liquid interface and vapor/liquid/solid interface improved the prediction for the case of FEP, it worsened the predictions for PDMS and PTFE. The prediction of contact angle using the slope-dependant VDW potential was not accurate for the whole range of contact angles. However, the generalized slope-dependant VDW potential resulted in a better match for the case of PTFE and FEP surfaces.

3.5 Conclusions

In this chapter, we related the attractive VDW interaction with wettability and contact angle. Standard VDW models in the literature rely on the interaction between two parallel interfaces, which is not consistent with partial-wet systems. To circumvent this limitation, VDW interaction energy has been proposed for two intersecting plates in the limit of a small slope ($h_x \ll 1$). We derived the corresponding formula for the contact angle using such a VDW potential and assessed its range of validity. Importantly, we generalized these formulas for larger slopes. Finally, we compared the predictions of different models with reference experimental data from the literature. We conclude that:

- VDW attractive inter-molecular interaction can be used to describe the system wettability. The intermolecular forces assembled through disjoining pressure will be used in the lubrication model derived in Chapter 5.

- In order to remediate the non-additivity of the VDW interaction, the Hamaker constant should be calculated based on the Lifshitz theory of VDW, and the procedure written in Hough and White [1980] can be used.
- A meaningful discrepancy exists between the experimental value of the contact angle and those predicted via the VDW interaction. Furthermore, this discrepancy shows a trend with the contact angle itself, highlighting the dependency of the VDW potential on the contact angle, as suggested by different studies cited in this chapter.
- For partially wet systems with small contact angles, the form of VDW interaction that considers the slope of the interface gives better results than the model derived for parallel interfaces.

In future work, it will be crucial to perform different sets of systematic experiments with a broader range of fluids, similar to n-alkanes on polymer substrate, to avoid the contribution from other intermolecular forces and, at the same time, obtain a range of contact angle measurements up to 90 degrees. These experiments will help us to accurately discern the VDW potential's dependency on the contact angle. Performing measurements to obtain the fluid and substrate properties, *i.e.* surface tension energy and Hamaker constant, used in the experiment is also vital since there exists a range of different reported values in the literature for a system due to different conditions and purity and accuracy of the experiment.

In the next chapter, we investigate the slope-dependency of the repulsive electrical double layer potential.

Chapter 4

Two dimensional charge regulated electric double layer

Abstract

The electrostatic component is one of the main inter-molecular interactions typically known as the electric double layer (EDL) interaction in the spreading of the wetting phase. The accurate expression of EDL interaction is crucial for determining the spreading dynamics, such as stability. Standard EDL models rely on the solution of one-dimensional Poisson-Boltzmann (P-B) equation in between the fluid-fluid and the fluid-solid interface. During the spreading of a droplet, however, this assumption breaks down as the geometry of the wetting phase close to the contact lines correspond to intersecting interfaces. In addition, the charges' interaction on the domain surfaces is often neglected. In this study, we investigate the role of the wedge-shaped geometry near the three phase contact region by solving the Poisson-Boltzmann (P-B) equation in two dimensions. We use a surface complexation model to account for the interaction of the charges on the domain's boundaries. The coupled numerical scheme is validated using reference data. The model is then used to investigate the electrostatic interaction for a quartz/water/air systems. The results show the dependency of the electrostatic interaction on the contact angle and charge regulation that becomes important close to the contact. In addition, the results show a change in surface energy due to electrostatic while moving closer to the contact across the interface. This study is a step forward in better understanding the wetting properties of multi-phase systems.

Index terms— wettability, electric double layer, surface complexation models

4.1 Introduction

Wettability is essential in multiphase flow characterization in petroleum reservoirs (enhanced oil recovery) or aquifers (water resources) [Mansouri-Boroujeni et al., 2023, Soulaine et al., 2021a], environmental remediation [Shang et al., 2010], surface coating [Darhuber et al., 2000] and film deposition [Brinkmann and Lipowsky, 2002] and ink-jet printing quality [Wijshoff, 2010] where it controls the spreading of the wetting phase. The contact angle between the interfaces of wet and non-wet fluids and the solid surface can describe the wettability of a system at thermodynamic equilibrium [de Gennes, 1985]. However, contact angle measurement alone is not enough to understand the different phenomena that affect the spreading, typically leading to hysteresis, that could be the result of surface roughness, pressure in wetting film, and the movement of the contact line [Good, 1992]. The wettability can be described through the

interfacial energies of the wetting phase using the Young equation. This equation holds for the area away from the three-phase contact region, where the interfacial energy is constant, and the measured contact angle is a macro-scale quantity. The augmented Young equation (Derjaguin-Frumkin equation) describes the inter-molecular interactions with the interfaces of the wetting phase close to the contact point [Deryaguin et al., 1987]. This equation, which can also be derived by minimizing the free energy of a spreading droplet [Yeh et al., 1999], relates the macro-scale contact angle to the actual angle at the contact line, *i.e.* micro-scale contact angle (θ_μ) with the help of the inter-molecular interactions in this region. The inter-molecular interactions are expressed through the disjoining pressure, Π [Derjaguin, 1989]. In the literature, the thickness of the wetting phase in the region of interest for inter-molecular interaction is assumed to be approximately constant *i.e.* the approximation of parallel plate. However, for the partially wet condition, the wetting phase geometry at the three-phase contact region resembles a wedge geometry rather than a parallel plate [Tuller et al., 1999]. The dispersion component of the disjoining pressure was re-derived for a wedge geometry, and it shows the dependency of the results on the thickness of the wetting layer as well as the slope [Dai et al., 2008]. Furthermore, the new expression for the dispersion component suggests the change in surface tension across the interface close to the contact point [Alizadeh Pahlavan, 2018]. The variation in surface tension close to the contact can impact the dynamics of spreading of the wetting phase by imposing a local slip close to the contact point, eventually alleviating the singularity problem of moving contact line [Shikhmurzaev, 2007].

For the electrostatic component term, there were some tries in the literature to obtain the proper expression for the wedge geometry. The effect of contact angle on the EDL and vice versa has been studied in electrocapillarity by Chou [2001], Kang et al. [2003], Dörr and Hardt [2012], Das and Mitra [2013]. Kang et al. [2003] obtained the energy associated with wetting a surface due to EDL for a wedge geometry, using the electromechanical approach and Debye-Hückel approximation. They used the balance of electrostatic force on the volume and the electrostatic pressure force acting on the surface to obtain the mechanical equilibrium condition. Dörr and Hardt [2012], using a combination of analytical and numerical solutions, obtained the dependency of the electrostatic interaction with the contact angle. They pointed out that the electrostatic potential at the wet/non-wet interface is a function of the contact angle at the contact line. However, their results are applicable for a limited range of contact angles ($0.4\frac{\pi}{2} < \theta < 0.5\frac{\pi}{2}$), they neglected the charge on the wet/non-wet interface and they assumed a constant charge boundary condition on the wet/solid interface. However, the proper condition on the boundary is neither constant charge nor constant potential [Israelachvili, 2011, McCormack et al., 1995]. Therefore, further work is needed to obtain an equation for the electrostatic component of the disjoining pressure that covers a broad range of contact angles using realistic boundary conditions. The numerical solution is the preferable approach since it can also cover the effect of charge on the wet/non-wet interface, charge regulation, asymmetric electrolyte, and Stern layer since the inclusion of said factors complicates finding an analytical equation for EDL interaction [Israelachvili, 2011].

The electrostatic interaction is usually modeled by the Poisson-Boltzmann equation, which describes the charge distribution in the region of interest surrounded by the charged boundary. Devereux and De Bruyn [1963] derived the analytical expression for the electric double layer interaction between two parallel surfaces for constant electrostatic potential or charge and symmetrical electrolyte. A more physical boundary condition is introduced by Ninham and Parsegian [1971], which describes the accumulation of the charges on the surfaces with the help of ion-binding reactions on the surface-sites, also known as charge regulation [Trefalt et al., 2016]. A general approach based on the Debye-Hückel approximation for the charge regulation in one dimension was developed by Behrens and Borkovec [1999]. However, a more general approach can be implemented by modifying the surface complexation model (SCM) that describes

the ion-binding reactions at the reaction sites on the interface. The algorithm for SCM is developed by Westall [1980], which is the stepping stone for other SCMs such as the charge distribution multi-site complexation (CD-MUSIC) model and has been modified recently to implement the charge regulation on the surfaces [Gil-Díaz et al., 2021]. However, the mentioned approaches need modifications before being used readily for a wedge geometry that resembles the three-phase contact region.

This chapter aims to obtain an accurate description of electrostatic interaction for the wedge geometry at the three-phase contact region. This will provide us with an electrostatic potential that depends on the slope of the film. To do so, we solve the Poisson-Boltzmann equation coupled with a surface complexation model to evaluate the surface's boundary conditions. The P-B solution and the SCM are performed in two dimensions to capture the effect of the three-phase geometry.

The outline of the chapter is as follows: First, we explain the mathematical model to solve the Poisson-Boltzmann equation. Then, we introduce the surface complexation model used to obtain the boundary condition and enforce the charge regulation. Next, we explain the implementation of the coupled models. We show the validation of different components used in the model, followed by the results from modeling the quartz/water/air system in a thin film and wedge geometry. Finally, the conclusions are mentioned.

4.2 Mathematical model

This section explains the mathematical model we used to obtain the electrostatic force in the thin film of water on the quartz surface. The distribution of ions in the water film is described through the Poisson-Boltzmann equation. The surface complexation model describes the reactions of ions in the water film with the air/water and quartz/water interfaces.

4.2.1 Poisson-Boltzmann model

The electrostatic component of the disjoining pressure is due to the interaction of ion species in the thin film with the wetting fluid/solid and wetting fluid/non-wetting fluid interfaces [Pourakaberian et al., 2022]. Ions are adsorbed on the interface sites surrounding the film (counter-ions in excess, or repelled from them, co-ions in deficiency), which makes it electrostatically charged because the counter-charge of counter-ions is higher in magnitude than the co-charge of co-ions (Fig. 4.1). The counter-ions form a distribution in response to the charge of the surface [Leroy and Mainault, 2018]. The number density ρ_i of ion i in a location is related to the electrostatic potential ψ at that location. It can be computed via the Boltzmann distribution

$$\rho_i = \rho_{i\infty} e^{-\frac{z_i e}{k_B T} \psi}, \quad (4.1)$$

where ρ_{∞} is the number density of ion in the bulk phase equal to ion charge density (in $\frac{\text{mol}}{\text{liter}}$) multiplied by the $1000 \times \text{Avogadro}$ number, z_i is the valence of the ion, e is the electron charge (in C), k_B is the Boltzmann constant (in $\frac{\text{J}}{\text{K}}$) and T is the temperature (in K). Furthermore, the Poisson equation describes the relationship between charge and electrostatic potential

$$\nabla^2 \psi = \frac{-e}{\epsilon_0 \epsilon_r} \sum_i z_i \rho_i, \quad (4.2)$$

where ϵ_0 and ϵ_r are the permittivity of the vacuum (in $\frac{F}{m}$) and relative permittivity of the medium, respectively. Combining these two equations yields the Poisson-Boltzmann equation

$$\nabla^2 \psi = -\frac{e}{\epsilon_0 \epsilon_r} \sum_i z_i \rho_{i\infty} \exp\left(-\frac{ez_i}{k_B T} \psi\right). \quad (4.3)$$

The gradient in ion density will create an osmotic pressure, while the gradient of the electrostatic potential will create an electric field, $\mathbf{E} = -\nabla(\psi)$. The excess pressure of the electric field in a dielectric is obtained via the Maxwell stress tensor [Landau and Lifshitz, 1984]

$$\mathbb{T}_{ij} = P_0(\rho, T) \delta_{ik} - \frac{\epsilon}{8\pi} E^2 \delta_{ik} + \frac{\epsilon}{4\pi} E_i E_k \quad (4.4)$$

where P_0 is the osmotic pressure and δ_{ik} is the Kronecker symbol and the indices i, k denote different component of spatial direction. ϵ is the absolute permittivity in the medium. The range of EDL interac-

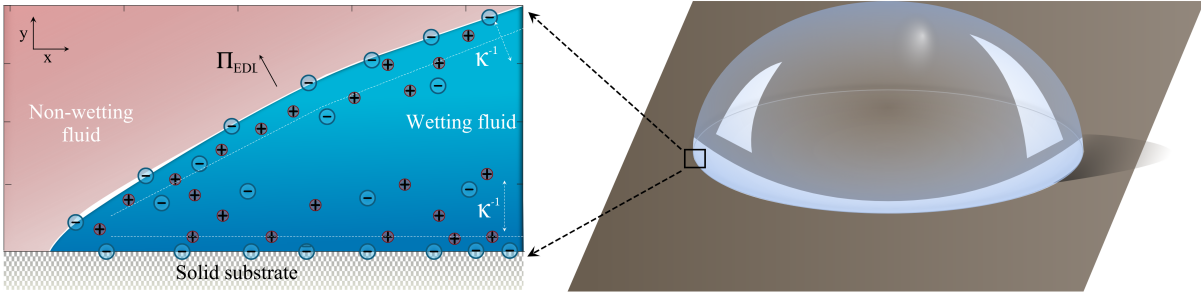


Figure 4.1: The counter-ions in the wetting film are adsorbed in the interfaces with the solid and non-wetting fluid. They form a distribution in response to charges on the surface. The zeta-potential ζ is defined as the electrostatic potential at the shear (or slipping) plane when there is flow on the surface and is assumed to be located at the beginning of the diffuse layer whose thickness is characterized by the Debye length [Leroy et al., 2012, 2022].

tion is characterized by the Debye-Hückel reciprocal length, κ , (or inverse of the Debye length) (in m^{-1}) defined as,

$$\kappa^2 = \frac{2000 I_b e^2}{\epsilon_r \epsilon_0 k_B T}, \quad (4.5)$$

where I_b is the ionic strength of the bulk wetting phase. In order to solve Eq. 4.3, the boundary condition on the domain should be specified. There are three types of boundary conditions typically used in the literature: a fixed electrostatic potential (corresponding to a Dirichlet condition), a fixed charge (corresponding to a Neumann condition), or a mixed condition of charge and electrostatic potential on the boundary of the domain [Bell and Peterson, 1972, Johnson et al., 2023].

However, for a general electrolyte of the bulk wetting phase, the boundary condition is neither constant-charge nor constant-potential, and the ionization of the surface groups determines the surface charge and potential [McCormack et al., 1995, Israelachvili, 2011]. The different choices in the boundary condition become significant when the distance between the different boundaries of the domain becomes comparable with the thickness of the diffuse layers (i.e., the Debye lengths [Israelachvili, 2011]). Ion adsorption or desorption on the domain's boundary influences charge and electrostatic potential. Therefore, to quantify the boundary conditions, we need to focus on the models that deal with surface speciation.

4.2.2 Surface complexation model - triple layer model (TLM)

The exchange of ions on the surface's reaction sites alters the surface's charge [Leroy et al., 2013]. The charge on the surface is balanced with the charge of the diffuse part of the EDL. The ion exchange reactions on the surface are expressed through chemical equilibrium reactions via surface complexation models (SCM). These surface complexation reactions are, e.g., protonation, deprotonation reactions, and metal ion adsorption reactions [Leroy et al., 2011]. A different SCM model deals with the locations where the mentioned reactions occur.

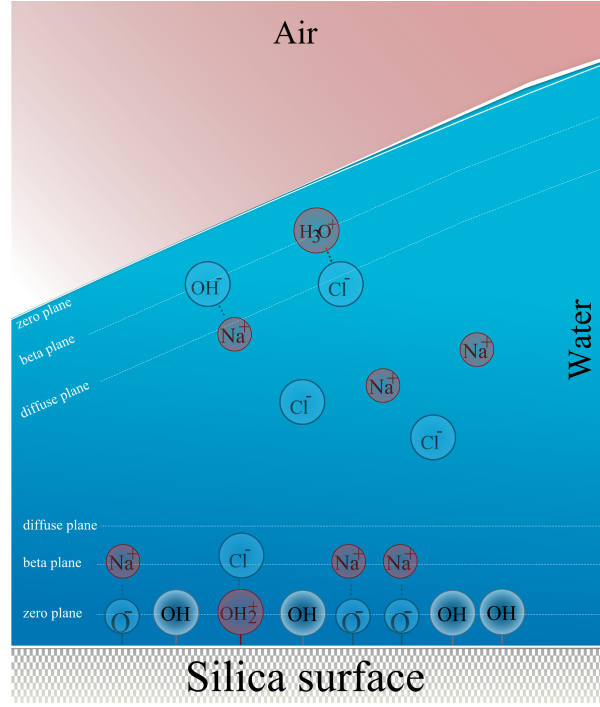
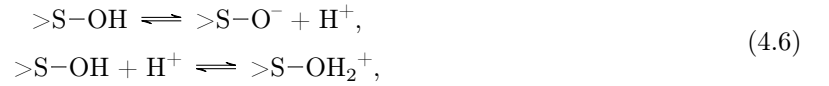
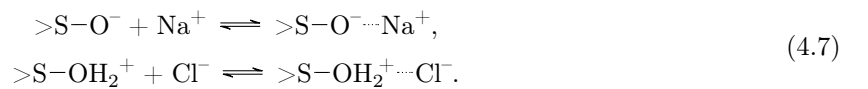


Figure 4.2: Sketch of surface speciation on the quartz/water and air/water interfaces and based on the SCM of Lützenkirchen et al. [2008], Leroy and Revil [2004]

Based on the triple-layer model, ion exchange takes place at different locations from the surface. At the surface *i.e.* zero plane, protonation and deprotonation of the surface take place (Fig. 4.2). The protonation/deprotonation at the zero-plane for quartz substrate can be generally expressed as



where $>\text{S}-\text{OH}$ is the silanol reaction site on the mineral surface. At a distance further away from the mineral surface (*i.e.* outer Helmholtz plane), the hydrated salt ion binding of the electrolytes in the solution takes place. The equilibrium reaction at the second layer is expressed as ion binding and speciation with the charged surface site. For example, for NaCl we have [Sverjensky, 2005]:



These two layers are usually assumed to be located at the Stern plane. The onset of the diffuse layer starts after the Stern layer, where the Poisson-Boltzmann equation is used to estimate the electrostatic

potential distribution.

The relationship between the concentration of different species for a reaction is expressed through the equilibrium constant; for example, for zero-plane on the quartz surface (Eq. 4.6), we have:

$$\begin{aligned} K_{deprotonation} &= \frac{[>\text{S-O}^-]\{\text{H}^+\}_0}{[>\text{S-OH}]}, \\ K_{protonation} &= \frac{[>\text{S-OH}_2^+]}{[>\text{S-OH}]\{\text{H}^+\}_0}. \end{aligned} \quad (4.8)$$

where $\{\text{H}^+\}_0 = \gamma[\text{H}^+]_0$ and γ is the activity coefficient. The activity coefficient of surface sites is assumed to be equal to one [Sverjensky, 2005]. Using the Boltzmann distribution, we can relate the concentration of species on the surface to the corresponding concentration in the bulk phase:

$$[\text{H}^+]_0 = [\text{H}^+] \exp\left(-z_i \frac{e}{k_B T} \psi\right) = [\text{H}^+] \exp\left(-\frac{e}{k_B T} \psi\right). \quad (4.9)$$

The charge balance at the different planes is obtained by summing all the charged species at that plane. The overall charge is equal to zero, therefore:

$$\sigma_0 + \sigma_\beta + \sigma_d = 0. \quad (4.10)$$

For each layer located between the "O-plane" and "beta-plane", and between the "beta-plane" and "d-plane", the Laplace equation describes the electrostatic potential distribution (Ohshima [2006]):

$$\frac{\partial^2 \psi}{\partial x^2} = 0, \quad (4.11)$$

where x is the distance from the mineral surface, with the boundary conditions (the continuity equations for the electrical potential):

$$\begin{aligned} \psi(0^-) &= \psi(0^+), \\ \psi(\beta^-) &= \psi(\beta^+), \\ \psi(d^-) &= \psi(d^+). \end{aligned} \quad (4.12)$$

In Eq. 4.11, we simplified the derivative in one direction, assuming that the planes are parallel to the surface. Simplifying further, we obtain the Gauss boundary conditions as:

$$\begin{aligned} -\epsilon_1 \frac{\partial \psi}{\partial x} \Big|_{x_0^+} &= \frac{\sigma_0}{\epsilon_0}, \\ \epsilon_1 \frac{\partial \psi}{\partial x} \Big|_{x_\beta^-} - \epsilon_2 \frac{\partial \psi}{\partial x} \Big|_{x_\beta^+} &= \frac{\sigma_\beta}{\epsilon_0}, \\ \epsilon_2 \frac{\partial \psi}{\partial x} \Big|_{x_d^-} - \epsilon_r \frac{\partial \psi}{\partial x} \Big|_{x_d^+} &= \frac{\sigma_d}{\epsilon_0}. \end{aligned} \quad (4.13)$$

Therefore, the relationship between electrostatic potential and surface charge densities at different

planes is obtained by integrating the left-hand side [Gil-Díaz et al., 2021]:

$$\begin{aligned}\sigma_0 &= -\epsilon_1\epsilon_0 \frac{d\psi}{dx}|_{0+} = C_1 (\psi_0 - \psi_\beta), \\ \sigma_\beta &= \epsilon_1\epsilon_0 \frac{d\psi}{dx}|_{\beta-} - \epsilon_2\epsilon_0 \frac{d\psi}{dx}|_{\beta+} = C_1 (\psi_\beta - \psi_0) + C_2 (\psi_\beta - \psi_d), \\ \sigma_d &= -\epsilon_2\epsilon_0 \frac{d\psi}{dx}|_{d-} - \epsilon_r\epsilon_0 \frac{d\psi}{dx}|_{d+} = C_2 (\psi_d - \psi_\beta) - \epsilon_r\epsilon_0 \frac{d\psi}{dx}|_{d+}.\end{aligned}\quad (4.14)$$

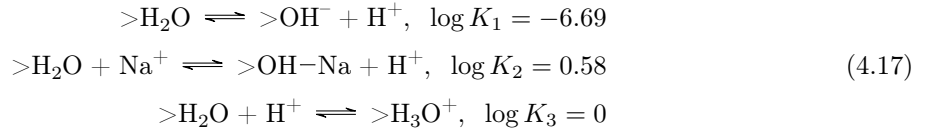
Here, C_i is called the capacitance of layer i equal to $\frac{\epsilon_i\epsilon_0}{h}$ and h is the thickness of the layer. The potential at zero, β and diffuse plane are denoted as ψ_0 , ψ_β and ψ_d respectively. The derivative of the potential at the beginning of the diffuse layer ($-\epsilon_r\epsilon_0 \frac{d\psi}{dx}|_{d+}$) is equal to the charge at the beginning of the diffuse layer. For an isolated planar wall, the charge on the beginning of the diffuse layer for a symmetrical electrolyte is [Hunter, 2013]:

$$\sigma_{dif} = \sqrt{\frac{2000}{\pi} I_0 \epsilon k_B T} \sinh\left(\frac{ze}{2k_B T} \psi_d\right), \quad (4.15)$$

however, for two interacting boundaries that are not parallel and asymmetrical electrolytes, the relationship between the charge at the diffuse layer plane ($-\epsilon_1\epsilon_0 \frac{d\psi}{dx}|_{d+}$) concerning its electrostatic potential is obtained numerically from Eq. 4.3. In addition, the surface charge densities of the zero and beta planes are given by

$$\begin{aligned}\sigma_0 &= [>\text{S-OH}_2^+] + [>\text{S-OH}_2^+ \cdots \text{Cl}^-] - [>\text{S-O}^-] - [>\text{S-O}^- \cdots \text{Na}^+], \\ \sigma_\beta &= [>\text{S-O}^- \cdots \text{Na}^+] - [>\text{S-OH}_2^+ \cdots \text{Cl}^-].\end{aligned}\quad (4.16)$$

The surface complexation model for the other interface, *i.e.*, water-air interface also needs to be specified in the same manner as the water-quartz interface. The reactions for air and water are taken from Lützenkirchen et al. [2008]:



The charge at zero-plane is assumed constant and equal to 0.003 C/m^2 . The values for capacitance are $C_1 = 0.22 \text{ F/m}^2$ and $C_2 = 1 \text{ F/m}^2$. In their model, they neglected the reaction with Cl^- , which we also did in this chapter.

According to these equations, the dimension of charge on the different planes is $\frac{\text{C}}{\text{m}^2}$. However, the dimension of charge for the mass and balance equation used in the following is mole/liter. Therefore, a conversion factor of $\frac{sa}{F}$ is required, where s is the specific area, a is the density, and F is the Faraday constant [Westall, 1980].

$$T_\sigma = \sigma \frac{sa}{F}. \quad (4.18)$$

4.3 Numerical implementation

This section explains the numerical technique to solve Eq. 4.3 in coupling with the SCM. We numerically solved the P-B equation with the finite element method. The boundary conditions for P-B come from

the SCM. Therefore, we implemented an iterative procedure to couple the P-B solver and the SCM. We discretized and numerically solved the P-B equation using the finite element method. The element is a line and triangle for one and two-dimensional cases, respectively. The weighting function is the linear interpolation between the vertices of the element. The system of equations to solve has the form:

$$A_{i,j}\psi_j = F_i(\psi), \quad (4.19)$$

where $A_{i,j}$ is the stiffness matrix and $F_i(\psi)$ is the integration of the non-linear term of the P-B equation over the element. Finally, using the Newton-Raphson method to deal with the non-linearity [Chen and Singh, 2002], we have the solution:

$$\psi^{it+1} = \psi^{it} - [A_T]^{-1} (A_{i,j}\psi^{it} - F(\psi^{it})), \quad (4.20)$$

where $A_T = A_{i,j} - \frac{\partial F_i}{\partial \psi_j}$ and 'it' is for the iteration. Once the error of electrostatic potential between two iterations becomes smaller than a threshold value (10^{-9}), the solution is obtained. Once we obtained the solution, we needed to calculate the gradient of the electrostatic potential on the domain's boundaries for later use in calculating the charge density and the stress on the domain.

4.3.1 Surface complexation modeling

In order to solve the Laplace and P-B equations for the equilibrium concentrations of ion species and the electrostatic potential at different planes, Westall [1980] used the following algorithm. First, the concentration of each surface species (c_i) is calculated by knowing the equilibrium constants, stoichiometric matrix (providing stoichiometric information about reactants and products in model reactions), and an initial guess for electrostatic potential:

$$\log c_i = \log K_i + \sum_j a_{i,j} \log (X_j \times \gamma_j), \quad (4.21)$$

and γ_j is the activity coefficient of species j , which is calculated based on Davis equation [Davies, 1962],

$$\log(\gamma_i) = -0.5092z_i^2 \left(\frac{\sqrt{I_0}}{1 + \sqrt{I_0}} - 0.3I_0 \right). \quad (4.22)$$

In the next step, the residual mass balance is calculated using the total concentration ($\mathcal{T}_j$) of each component (X_j):

$$Y_j = \sum_i a_{i,j} ((c_i - \log(\gamma_j)) - \mathcal{T}_j). \quad (4.23)$$

The goal is to minimize the mass balance residual, which is achieved through the Newton-Raphson iterative procedure by calculating the Jacobian of Y :

$$J_{j,k} = \frac{\partial Y_j}{\partial X_k} = \sum_i \left(a_{i,j} a_{i,k} \frac{c_i}{X_k} \right), \quad (4.24)$$

and $\Delta X = J_{j,k}^{-1} \times Y_j$, where $\Delta X = X_{original} - X_{improved}$. The Jacobian matrix for the electrostatic components requires modification:

$$\begin{aligned}
 J_{\psi_0, \psi_0} &= J_{\psi_0, \psi_0} + C_1 \frac{sa}{F} \frac{RT}{FX_{\psi_0}} \\
 J_{\psi_0, \psi_\beta} &= J_{\psi_0, \psi_\beta} - C_1 \frac{sa}{F} \frac{RT}{FX_{\psi_\beta}} \\
 J_{\psi_\beta, \psi_0} &= J_{\psi_\beta, \psi_0} - C_1 \frac{sa}{F} \frac{RT}{FX_{\psi_0}} \\
 J_{\psi_\beta, \psi_\beta} &= J_{\psi_\beta, \psi_\beta} + (C_1 + C_2) \frac{sa}{F} \frac{RT}{FX_{\psi_\beta}} \\
 J_{\psi_\beta, \psi_d} &= J_{\psi_\beta, \psi_d} - C_2 \frac{sa}{F} \frac{RT}{FX_{\psi_d}} \\
 J_{\psi_0, \psi_d} &= J_{\psi_d, \psi_0} = 0 \\
 J_{\psi_d, \psi_\beta} &= J_{\psi_d, \psi_\beta} + C_2 \frac{sa}{F} \frac{RT}{FX_{\psi_\beta}} \\
 J_{\psi_d, \psi_d} &= C_2 \frac{sa}{F} \frac{RT}{FX_{\psi_\beta}} + \frac{\partial}{\partial X_{\psi_\beta}} \left(\frac{\partial \psi_d}{\partial \psi_x} \right).
 \end{aligned} \tag{4.25}$$

In the last equation, we omitted the evaluation of the last part, $\frac{\partial}{\partial X_{\psi_\beta}} \left(\frac{\partial \psi_d}{\partial \psi_x} \right)$, since we did not have an explicit analytical equation for the two-dimensional case and obtaining the value numerically will require to solve PB model numerous times. Neglecting this term does not affect the results; however, it might affect the rate of convergence for the mass balance.

The stoichiometric matrix is obtained by formulating all the equilibrium equations, for example, for the case of NaCl as the salt:

$$\begin{aligned}
 X &= \begin{bmatrix} [\text{H}^+] & [\text{Na}^+] & [\text{Cl}^-] & [>\text{SOH}] & \exp\left(-\frac{e}{k_B T} \psi_0\right) & \exp\left(-\frac{e}{k_B T} \psi_\beta\right) & \exp\left(-\frac{e}{k_B T} \psi_d\right) \end{bmatrix} \\
 \mathcal{T} &= \begin{bmatrix} \mathcal{T}_{\text{H}^+} & \mathcal{T}_{\text{Na}^+} & \mathcal{T}_{\text{Cl}^-} & \mathcal{T}_{\text{SOH}} & \mathcal{T}_{\sigma_0} & \mathcal{T}_{\sigma_\beta} & \mathcal{T}_{\sigma_d} \end{bmatrix}
 \end{aligned} \tag{4.26}$$

The stoichiometric matrix for the case of two dimensions needs modification, as presented in Fig. 4.3.

4.3.2 Combination of P-B solver with SCM

The flowchart for coupling the P-B solver and SCM is shown in Fig. 4.4. The known variables are the total concentration of ions in the bulk wetting phase, equilibrium constants (K_i), total number of reaction sites on the quartz/water and air/water interfaces, and their respective capacitances.

1. Initialization

- guess ψ_0 , ψ_β , and ψ_d values for all the elements on the quartz/water and air/water interfaces and free concentration of ions (X_i) in the bulk wetting phase

2. Electrostatic calculation

- solve the Poisson-Boltzmann equation
- obtain the gradient of potential at the diffuse plane

3. Surface Complexation Model (SCM)

- obtain the concentration of the adsorbed and desorbed species: $\log(c_i) = \log(K_i) + \sum a_{ij} \log(X_j)$

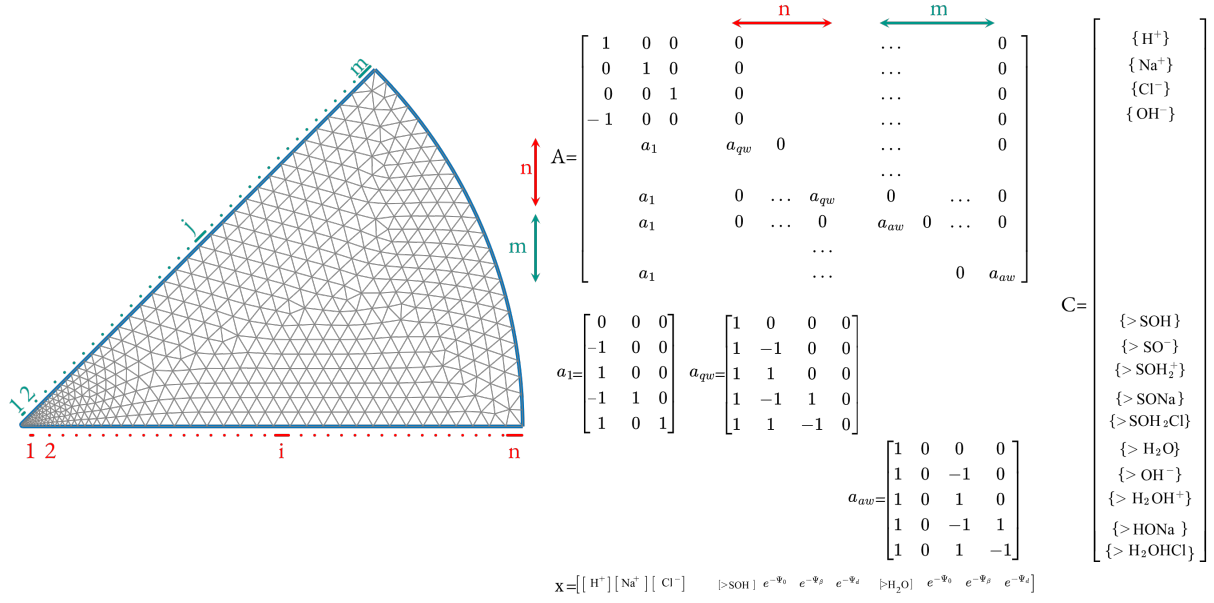


Figure 4.3: Enumeration of the stoichiometric matrix concerning the quartz/water and air/water interfaces.

- obtain the mass balance $Y_j = \sum a_{ij}c_i - \mathcal{T}_i$
- calculate the Jacobian matrix of mass balance (J)
- correct the initial guess: $X_{improved} = -(J)^{-1} \times Y + X_i$

4. Mass balance check

- update the electrostatic potential at the diffuse plane on the boundaries
- update the charge at the diffuse plane and go to step 1
- if the mass balance check is satisfied, go to step 5, otherwise go to step1

5. Output

- stress calculation

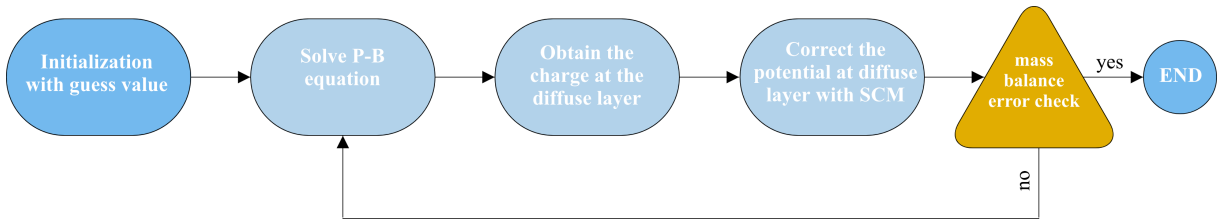


Figure 4.4: Charge regulation algorithm for 2-dimensional wedge

4.3.3 Stress calculation

We begin by writing the Maxwell stress tensor in fluid [Landau et al., 1984]:

$$\mathbb{T}_{ij} = -P_0(\rho, T)\delta_{ik} - \frac{\epsilon}{8\pi}E^2\delta_{ik} + \frac{\epsilon}{4\pi}E_iE_k \quad (4.27)$$

where P_0 is the pressure in the medium in the absence of the electric field, and E_i is the electric field in i direction. For the pressure, we can write the osmotic pressure equal to $i\rho RT$ where ρ is the ion density and i is the dimensionless van 't Hoff index. For a two-dimensional case, the stress tensor reads:

$$\mathbb{T} = \begin{bmatrix} -P_0 + \frac{\epsilon}{8\pi} (E_x^2 - E_y^2) & \frac{\epsilon}{4\pi} E_x E_y \\ \frac{\epsilon}{4\pi} E_x E_y & -P_0 + \frac{\epsilon}{8\pi} (E_y^2 - E_x^2) \end{bmatrix}. \quad (4.28)$$

In the case of a thin film (two parallel walls), the electric field in x direction is zero ($E_x = 0$), therefore:

$$\mathbb{T} = \begin{bmatrix} -P_0 - \frac{\epsilon}{8\pi} E_y^2 & 0 \\ 0 & -P_0 + \frac{\epsilon}{8\pi} E_y^2 \end{bmatrix}. \quad (4.29)$$

The stress tensor is projected on the boundary of the domain to obtain the stress vector,

$$\begin{bmatrix} \mathbb{T}_x \\ \mathbb{T}_y \end{bmatrix} = \begin{bmatrix} \mathbb{T}_{xx}n_x + \mathbb{T}_{xy}n_y \\ \mathbb{T}_{yx}n_x + \mathbb{T}_{yy}n_y \end{bmatrix}. \quad (4.30)$$

We project the stress vector on the boundary on the normal and tangential vector $t = [t_x, t_y]$ to the interface by:

$$\begin{bmatrix} \Pi \\ \tau \end{bmatrix} = \begin{bmatrix} \mathbb{T}_x n_x + \mathbb{T}_y n_y \\ \mathbb{T}_x t_x + \mathbb{T}_y t_y \end{bmatrix}. \quad (4.31)$$

In order to obtain the expression for the osmotic pressure, we write:

$$P_0 = k_b T \left(\sum \rho - \sum I_0 \right) = k_b T I_0 \sum (\beta_i e^{-z_i \Psi_i} - 1), \quad (4.32)$$

where $\beta_i = \frac{\rho_i}{I_0}$ and I_0 is the ionic strength. For the case of symmetrical electrolytes, we have:

$$P_0 = 2k_b T I_0 (\cosh(\Psi) - 1). \quad (4.33)$$

When the charge density is replaced by the Boltzmann distribution for the arbitrary electrolyte and the electric field is written as minus the gradient of electrostatic potential, we have:

$$\Pi = 2k_b T I_0 (\cosh(\Psi) - 1) - \frac{\epsilon \epsilon_0}{8\pi} \left(\frac{\partial \Psi}{\partial y} \right)^2 \quad (4.34)$$

and for a general electrolyte:

$$\Pi = k_b T N_A I_0 \sum (\beta_i e^{-z_i \Psi_i} - 1) - \frac{\epsilon_r \epsilon_0}{8\pi} \left(\frac{\partial \psi}{\partial y} \right)^2 \quad (4.35)$$

We obtain the energy per area associated with the tangential component:

$$W = \frac{1}{A_T} \int \tau A_i dl, \quad (4.36)$$

where A_i and A_t are the area of segment i and the total area of the interface, respectively. The integration is done over the boundary element, dl .

4.3.4 Gradient calculation

The calculation of the gradient of electrostatic potential is essential for the SCM as well as stress evaluation, especially at the boundaries. Therefore, we require a high order of accuracy for gradient calculation. For the one-dimensional case, we use a fourth order finite difference to calculate the gradient using the formula for the inside of the domain:

$$\frac{\partial \Psi}{\partial X_i} = \frac{-\Psi_{i+2} + 8\Psi_{i+1} - 8\Psi_{i-1} + \Psi_{i-2}}{12\Delta X} \quad (4.37)$$

and for the first node, which is located on the boundary, and the node just after it:

$$\begin{aligned} \frac{\partial \Psi}{\partial X_1} &= \frac{-25\Psi_1 + 48\Psi_2 - 36\Psi_3 + 16\Psi_4 - 3\Psi_5}{12\Delta X}, \\ \frac{\partial \Psi}{\partial X_2} &= \frac{-3\Psi_1 - 10\Psi_2 + 18\Psi_3 - 6\Psi_4 + \Psi_5}{12\Delta X}. \end{aligned} \quad (4.38)$$

Similarly, for the other boundary, we have:

$$\begin{aligned} \frac{\partial \Psi}{\partial X_n} &= \frac{25\Psi_n - 48\Psi_{n-1} + 36\Psi_{n-2} - 16\Psi_{n-3} + 3\Psi_{n-4}}{12\Delta X}, \\ \frac{\partial \Psi}{\partial X_{n-1}} &= \frac{3\Psi_n + 10\Psi_{n-1} - 18\Psi_{n-2} + 6\Psi_{n-3} - \Psi_{n-4}}{12\Delta X}. \end{aligned} \quad (4.39)$$

For the 2-dimensional case, the calculation of the gradient is more complex. In order to obtain an accurate estimation of the gradient, the same as the one-dimensional case, we change the geometry coordination from Cartesian to polar and used linear interpolation to obtain the value for electrostatic potential (Fig. 4.5). The gradient in polar coordinate is then calculated using $\nabla = (\frac{\partial}{\partial r}, \frac{1}{r} \frac{\partial}{\partial \theta})$. Now, we can use the same equation as in the one-dimensional case for each component of the gradient vector. Finally, to convert the gradient back from polar coordinate to Cartesian coordinate, we use the relationships:

$$\begin{aligned} \frac{\partial \Psi}{\partial X} &= \frac{\partial \Psi}{\partial r} \cos(\theta_i) - \frac{\partial \Psi}{\partial \theta} \sin(\theta_i) \\ \frac{\partial \Psi}{\partial Y} &= \frac{\partial \Psi}{\partial r} \sin(\theta_i) + \frac{\partial \Psi}{\partial \theta} \cos(\theta_i) \end{aligned} \quad (4.40)$$

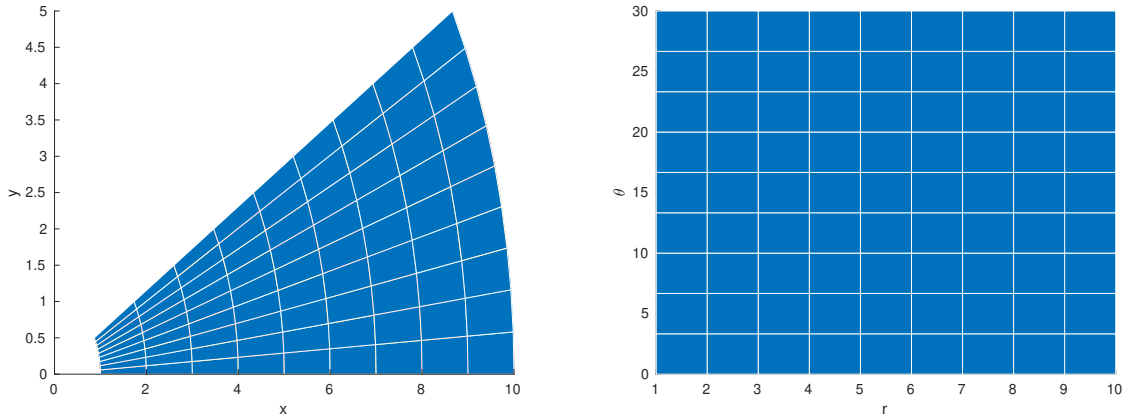


Figure 4.5: Illustration of transformation of Cartesian to polar coordinate

4.4 Results

The results comprised three main parts, (1) the validation of numerical scheme and the implementation of SCM for quartz/water and air/water interfaces, (2) the charge regulated electrostatic potential modeling for a thin film of water and (3) the charge regulated electrostatic potential modeling for the wedge of water. The latter is significant for electrostatic calculation in wettability characterization since the region where the electrostatic force becomes dominant resembles the wedge geometry rather than a thin film with uniform thickness.

4.4.1 Validation of P-B solver (one dimension)

To validate our numerical tool, we compared the predictions of the numerical solver for the EDL to analytical solutions of the P-B equation [Devereux and De Bruyn, 1963] for symmetrical electrolytes, using either Dirichlet or Neumann boundary conditions. The procedure to obtain the analytical solution is explained in McCormack et al. [1995]. The EDL pressure (obtained from Eq. 4.35) versus the thickness of the electrolyte solution is plotted in fig. 4.6a. We successfully compared our finite element method solver (FEM solver) with the BVP5C solver of MATLAB as well.

We also extended validation to imbalanced electrolytes. Here also, we compared our numerical method with the BVP5C method in MATLAB since the analytical solution does not exist. The electrolyte comprises two ion components with the concentration of 1 mol/L and 0.5 mol/L and the valence of +1 and -1, respectively. The EDL pressure is plotted versus the thickness of the electrolyte in Fig. 4.6b for the constant potential and charge boundary conditions. We also evaluated the relative root means

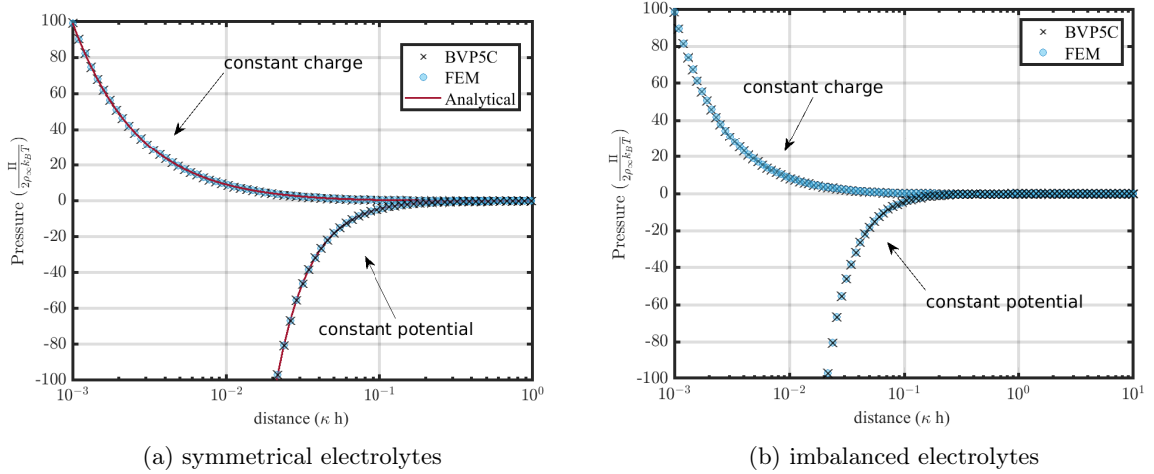


Figure 4.6: Comparison of EDL pressure calculated from the analytical equation, our FEM solver, MATLAB BVP5C solver for constant potential and constant charge boundary conditions. The boundary conditions are $\Psi_1 = -0.2$, $\Psi_2 = -0.1$, $S_1 = -0.2$, $S_2 = -0.1$ (dimensionless form). The electrolyte is (a) symmetrical with ionic strength of 1 mol/L (b) imbalanced with two components of 1 mol/L and 0.5 mol/L with the valence of +1 and -1 respectively.

square error of electrostatic potential obtained from our FEM solver and BVP5C solver in MATLAB and plotted in Fig. 4.7. The RRMSE is defined as $\sqrt{\frac{\frac{1}{n} \sum_{i=1}^n (\Psi_{iFEM} - \Psi_{iref})^2}{\sum_{i=1}^n \Psi_{iref}^2}}$. The overall RRMSE for the range of electrolyte thickness is below 10^{-6} .

Similarly, we plotted the RRMSE of electrostatic potential in fig. 4.8. In both cases of symmetrical

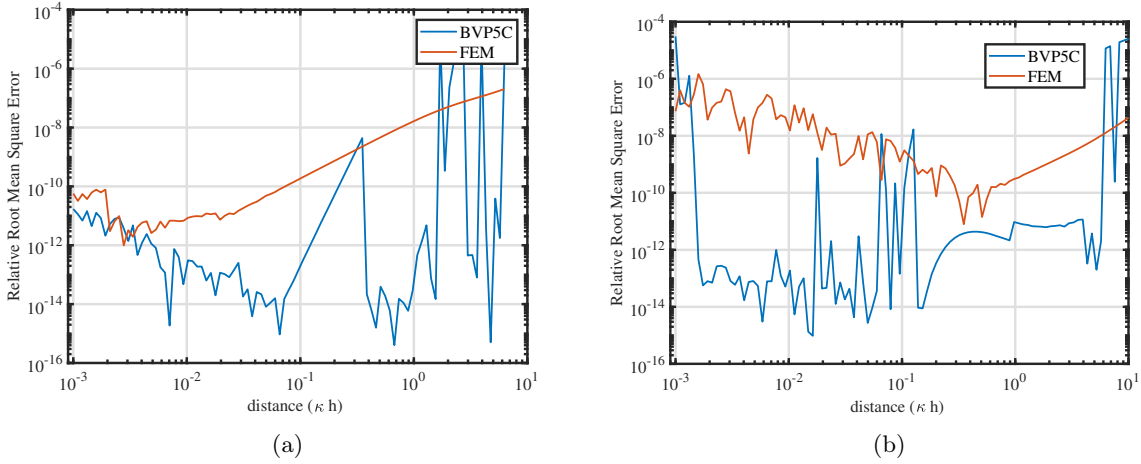


Figure 4.7: Comparison of relative root means square error of electrostatic potential calculated with our FEM solver and MATLAB BVP5C solver compared with the analytical equation for (a) constant potential and (b) constant charge boundary condition. The boundary conditions are $\Psi_1 = -0.2$, $\Psi_2 = -0.1$, $S_1 = -0.2$, $S_2 = -0.1$ (dimensionless form) and the electrolyte is symmetrical with ionic strength of 1 mol/L.

and imbalanced, our results exhibited excellent agreement with the reference solution.

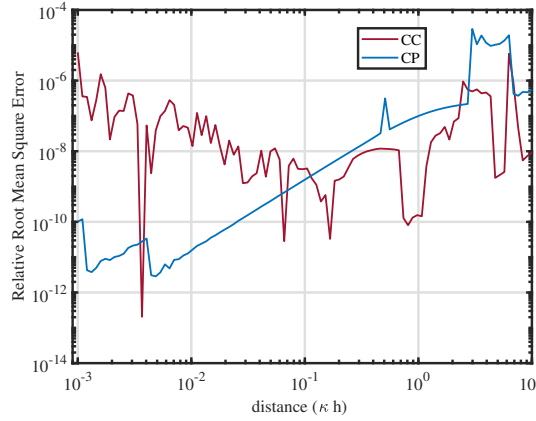


Figure 4.8: Relative root means square error of electrostatic potential calculated with our FEM solver compared with MATLAB BVP5C solver for constant potential and constant charge boundary conditions. The boundary conditions are $\Psi_1 = -0.2$, $\Psi_2 = -0.1$, $S_1 = -0.2$, $S_2 = -0.1$ and the electrolyte is imbalanced with two components of concentration 1 mol/L and 0.5 mol/L with the valence of +1 and -1 respectively.

4.4.2 Validation of coupling of P-B solver with SCM for quartz/water interface

In this section, we validated the coupling of the EDL solver and SCM, as well as SCM for the quartz/water interface for a film of water between two quartz surfaces in one dimension. The reference solution is from the benchmarking study done by Gil-Díaz et al. [2021] for a charge-regulated solid-liquid interface. The saltwater is composed of NaCl salt with 0.01 molar concentration at a pH ranging from 3-8. The total surface site density on the quartz surface is 4.6 sites per nm^{-2} (measured by thermogravimetry or tritium

exchange experiment [Hiemstra et al., 1989]). They solved the Poisson-Boltzmann equation using the collocation method and used the Newton-Raphson method for the non-linearity in the P-B equation. They used the same approach mentioned in Westall [1980] for SCM modeling. They numerically calculated the variation of potential with respect to charge density in the Jacobian of mass balance, while we neglected this term in our approach. This will not affect the results but it will slow down the rate of convergence. We plotted the electrostatic potential at the beginning of the diffuse layer (d-plane) and the surface charge density on the zero plane versus the thickness of the electrolyte between the two quartz surfaces in Fig. 4.9. The effect of charge regulation on the surface can be seen as the thickness of the saltwater decreases, and the surface charge density decreases while the electrostatic potential increases in magnitude.

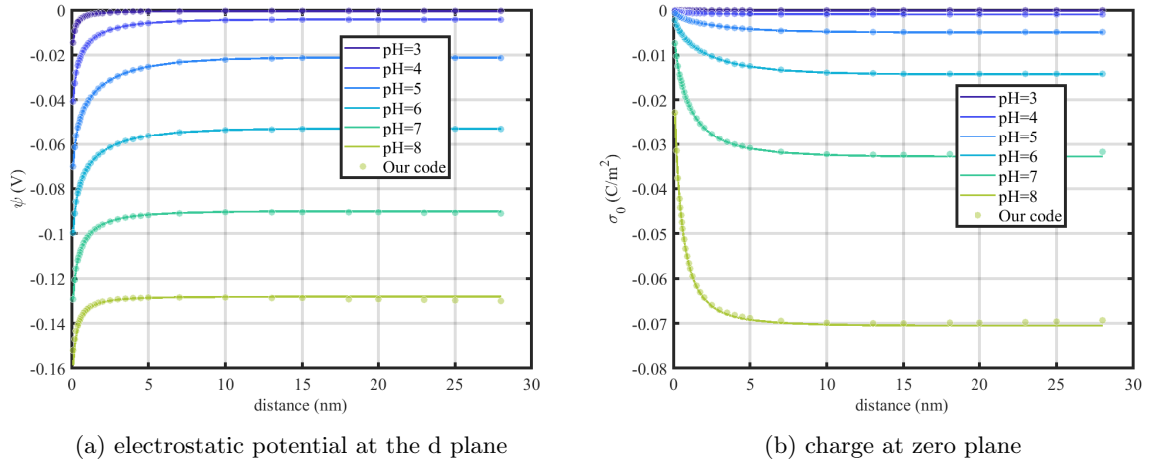


Figure 4.9: Comparison of our code with the reference code from Gil-Díaz et al. [2021], for 0.01 M NaCl and 4.6 sites nm⁻².

4.4.3 Validation of coupling of P-B solver with SCM for air/water interface

Similarly, we conducted validations for the SCM related to the air/salt-water interface. We implemented the model proposed by Lützenkirchen et al. [2008] for the air/water interface. Compared to the air/water interface SCM developed by [Leroy et al., 2012], the SCM of Lutzenkirchen et al. (2008) has the advantage of being applied to different types of hydrophobic media (air, ice, diamond, oil, Teflon). Similarly to their work, we compared the zeta potential from our model to the experimental measurements done by Yang et al. [2001], revealing a consistent trend. The experimental measurements of zeta potential were done by using the microelectrophoresis technique on fine bubbles dispersed in aqueous solution with sizes ranging from 10 to 70 μm . The gas bubbles were generated via passing current through a platinum wire at the bottom of the cell. The generated bubble rose upward while the cell was moving downward so that the camera captured the trajectory of the bubbles for a longer time (4-8 s), and then a voltage was applied to the cell. The zeta potential measurements were recorded on the "stationary plane" where the electroosmotic velocity was zero. Therefore, the measured velocity only corresponds to the effect of electrophoresis. Then, the zeta potential was obtained using the measured electrophoretic velocity with Smoluchowski equation. They also made the assumption of no slip on the surface of the gas bubble. The reported zeta potential value is the mean zeta potential value of 15 bubbles' zeta potential measurements at each solution condition.

Lützenkirchen et al. [2008] proposed a three layer model for the air/water interface, an ice-like layer, a liquid-like layer and the diffuse layer. The surface charge density at the zero plane, on the beginning of

the ice-like layer, is independent of the solution and equal to 0.003 C/m^2 . The zeta potential value results from the computed electrostatic potential at the distance of $0.67\kappa^{-1}$ from the beginning of the diffuse layer according to the Lützenkirchen et al. [2008] assumption. The comparison in Fig. 4.10 shows that the model can reproduce the trend observed by the experiment for different pH and salinities (NaCl).

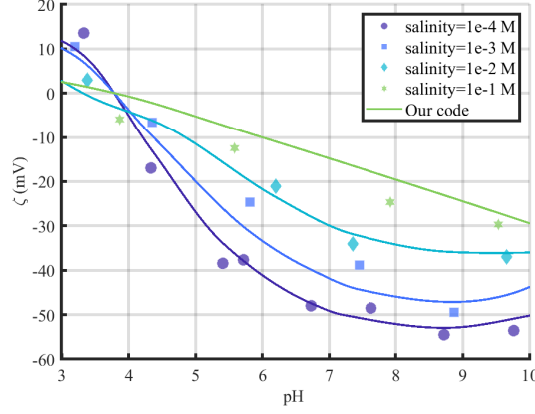


Figure 4.10: Comparison of our code zeta potential predictions with the experimental zeta potential data from Yang et al. [2001]. The zeta potential is calculated based on the electrostatic potential profile at the distance of $0.67\kappa^{-1}$ from the beginning of the diffuse layer.

4.4.4 Charge regulated electrostatic potential for a thin film of water between quartz and air

With our numerical tool validated, we ventured into modeling the Quartz/Water/Air system in a one-dimensional geometry. We obtained and plotted the electrostatic potential at the beginning of the diffuse layer, the surface charge density on the boundary, and the EDL pressure as the thickness of the water layer varies. The results are shown in Fig. 4.11. The electrostatic potential on the boundary for the two interfaces of air/water and quartz/water possess different values for the large thickness of water; however, as the thickness of the water layer decreases, the interaction of interfaces on each other influences the electrostatic potential, where at small thickness the electrostatic potential converges to the same value for both interfaces. The surface charge density on the zero plane for the quartz/water interface shows the effect of charge regulation. However, the surface charge density at the beginning of the air/water interface was fixed to 0.003 C/m^2 in the SCM. For a pH of 3, although the quartz/water interface possesses a negative and low electrostatic potential, with a lower water thickness, the value becomes positive. The EDL pressure shown in Fig. 4.11c increases as the pH of the water increases which is due to the increase in electrostatic potential magnitude on the boundaries.

4.4.5 Charge regulated electrostatic potential for the wedge of water/quartz/gas

Finally, we employed our coupled EDL model-SCM for a wedge geometry to describe the electrostatic intermolecular interactions comprehensively in the three-phase contact region. Here, we used the same parameters for the SCM models as in previous validation cases. We limited the water property to a pH of 4 and salinity of 0.01 molar. Our results, presented in Fig. 4.12, illustrate the modeled electrostatic potential on the air/water and water/quartz boundaries at the diffuse plane as a function of distance from the corner point for varying wedge angles. The trend is similar to a one-dimensional case, where the

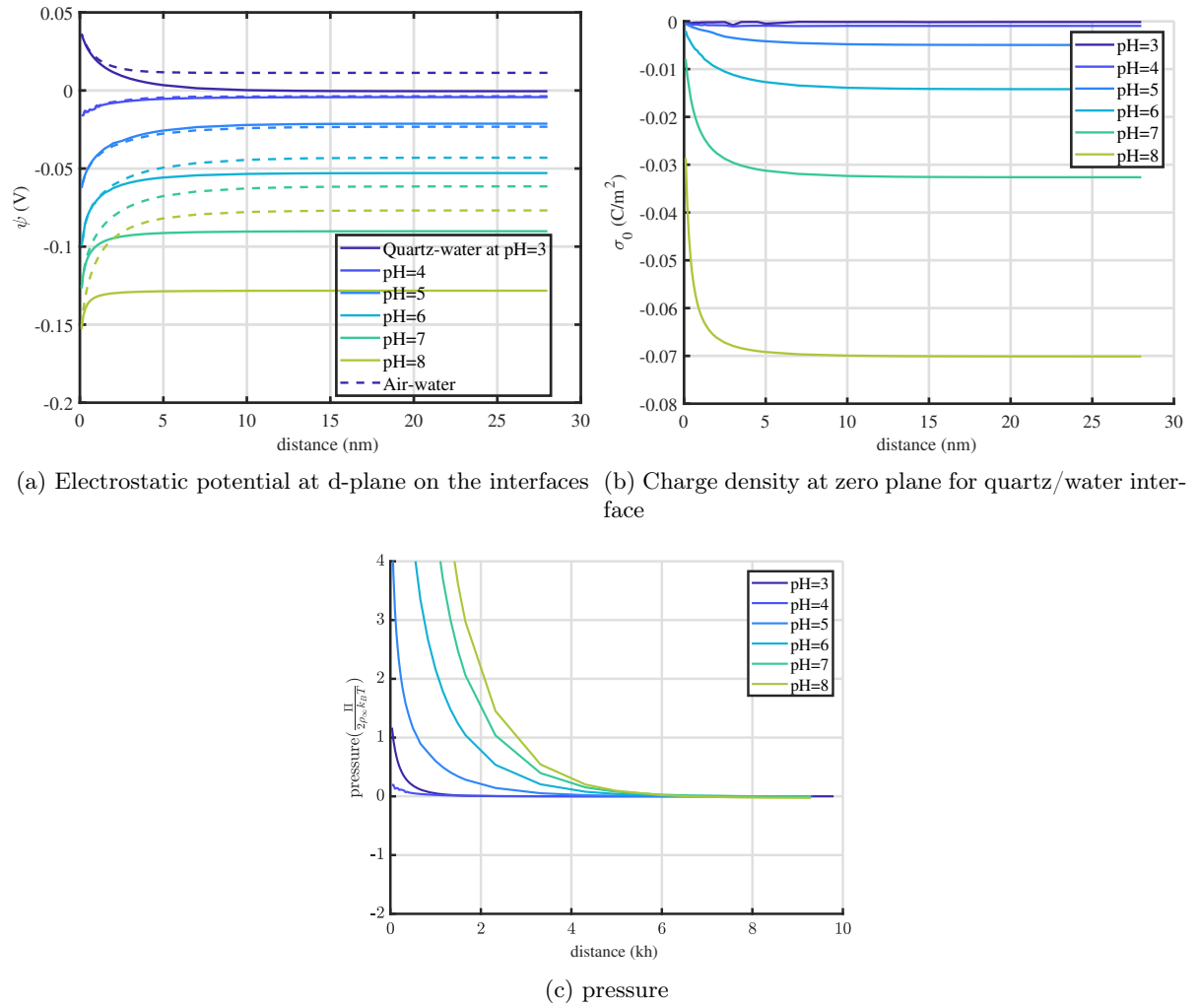


Figure 4.11: Results of our model for electrolyte of salinity 0.01 M NaCl for the salt-water film between quartz and air.

electrostatic potential on the two surfaces converges at the same value on the corner of the wedge. The range of effect of the wedge on the boundaries is bigger for smaller angles, e.g., $10 \kappa h$ for 10° , compared to higher angles, e.g., $5 \kappa h$ for 65° . The surface charge density at *beta* plane for air/water interface is more or less constant across the interface (Fig. 4.12b), since the SCM model assumes a fixed charge here. However, the magnitude of surface charge density on the water/quartz surface decreases more rapidly when the distance to the corner decreases due to the charge regulation. Additionally, we depicted the electrostatic potential at the corner point in relation to the wedge angle in fig. 4.13, which shows a non-linear trend, where the change in electrostatic potential increases for smaller angles (the electrostatic potential becomes more negative in this condition). To analyze the EDL pressure, the Maxwell stress

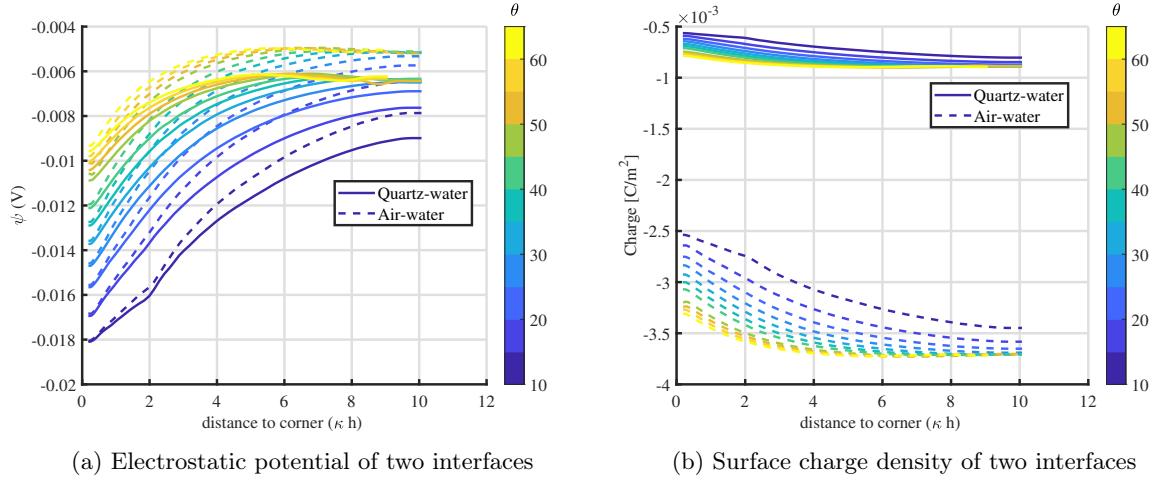


Figure 4.12: Results of our model for electrolyte of salinity 0.01 M NaCl for the wedge of water/quartz/gas. The properties of the surface are plotted as a function of the distance to the corner of the wedge.

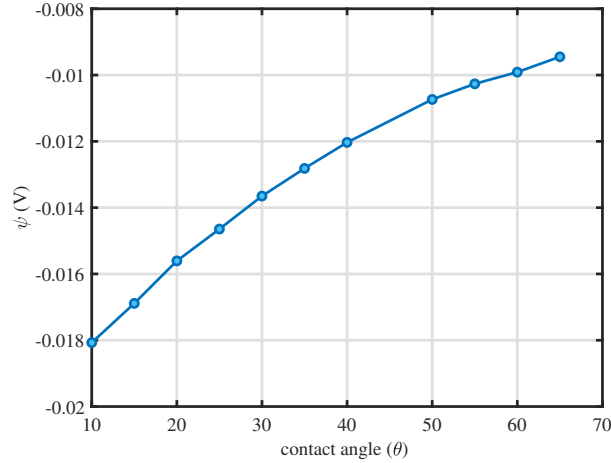


Figure 4.13: Electrostatic potential at the corner of the wedge for different contact angles.

tensor for the wedge is projected on the boundaries to obtain the stress vector (Eq. 4.31). The stress vector is again projected on the axis normal and tangent to the surface, which we call normal and tangent pressure. The normal component of the stress on the air/water and quartz/water interfaces for different values of wedge angle as a function of the distance to the corner of the wedge is shown in Fig. 4.14. The normal pressure on both surfaces has more or less the same magnitude and it increases non-linearly close to the wedge. The increase in pressure is higher for the smaller wedge angle, showing the dependence

of the normal component of EDL pressure to the angle of the wedge, as well as the distance between two interfaces. The tangent component of the pressure is analyzed in terms of energy by evaluating the

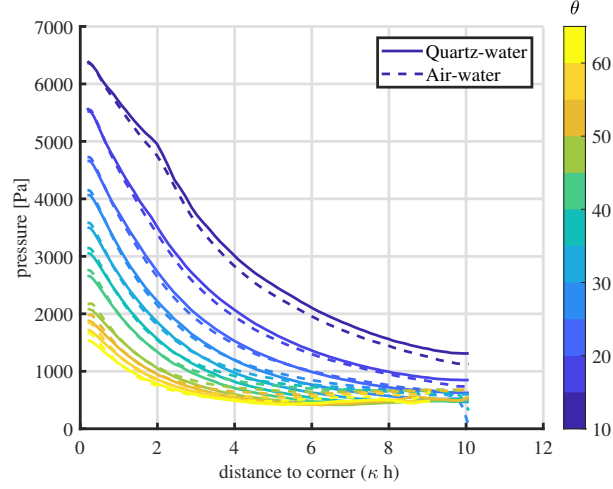


Figure 4.14: Pressure projected on normal vector on the boundary as a function of the distance to the corner of the wedge

force corresponding to the tangent pressure and integrating the force across the surface (Eq. 4.36). Since the tangent component of stress acts on the interface and in the same direction as the interfacial tension energy, the energy associated with it can be conceptualized as an interfacial tension energy modifier. Therefore, for the quartz/water interface, the energy per area caused by the electrostatic interaction will affect the quartz/water interfacial tension, and the same energy value on the air/water interface will modify the interfacial tension energy of air and water close to the contact region. The energy associated with the tangent stress on the two interfaces is shown in Fig. 4.15 as a function of the distance to the corner for different wedge angles. The tangent stress energy increases close to the wedge point, and converges to a finite value on the wedge. On the quartz/water interface, increasing the wedge angle has

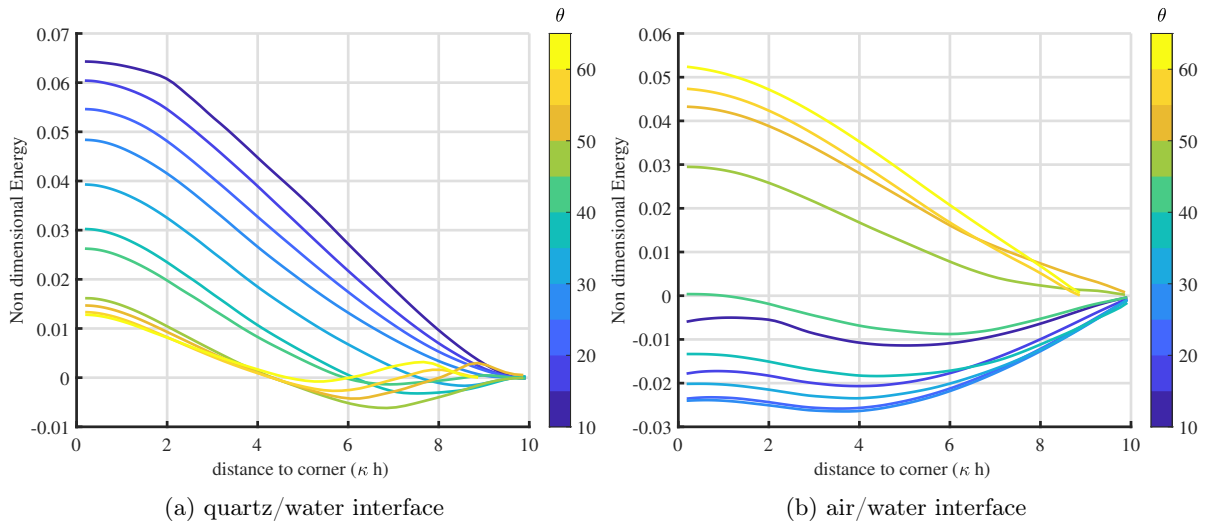


Figure 4.15: Wetting tension on tangential vector on the boundary as a function of the distance to the corner of the wedge

a monotonic behaviour on the energy. However, this is not the case for the air/water interface. In order

to illustrate this better, the total energy of tangent stress per area for each interface is shown in Fig. 4.16 for different wedge angles. The effect of the tangent component for the quartz/water interface increases as the wedge angle decreases and reaches a stable modification for a small wedge angle. Whereas, for the air/water interface, a wedge angle smaller than 40 tends to decrease the interfacial tension energy, and a wedge angle larger than 40 increases the interfacial energy. Studying different systems and cases can alter the significance of this observation. To show this, we presented the result for the system but at a pH of 7 in Fig.4.17, where the magnitude of energy is significantly higher.

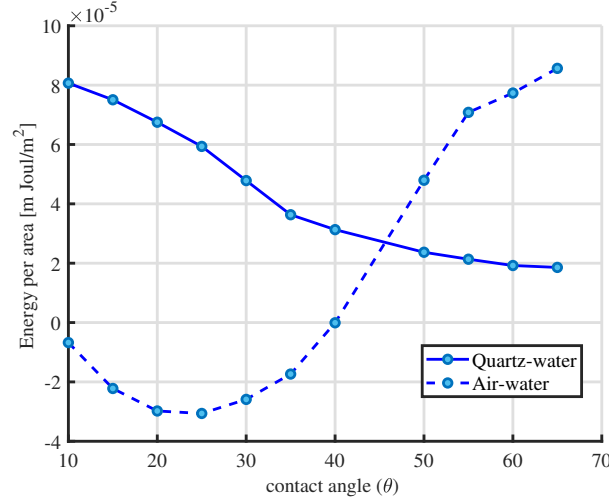


Figure 4.16: Tangent stress energy on the boundary as a function of the distance to the corner of the wedge for saltwater with pH of 4 and salinity of 0.01 molar.

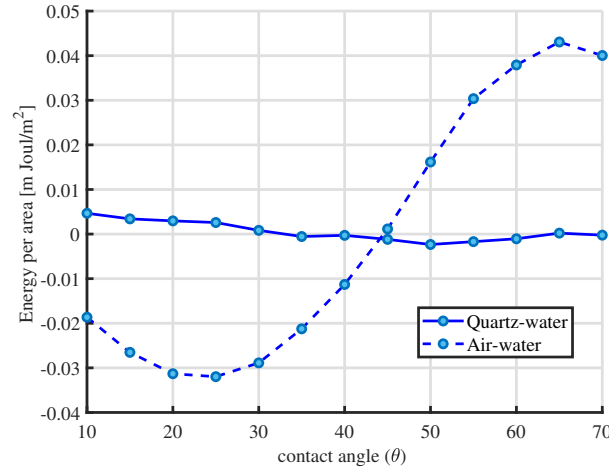


Figure 4.17: Tangent stress energy on the boundary as a function of the distance to the corner of the wedge for the saltwater with a pH of 7 and salinity of 0.01 molar.

4.5 Conclusion

We have developed a Poisson-Boltzmann (P-B) solver coupled with surface complexation models (SCMs) to describe the electrochemical properties of the electrical double layer (EDL) in two dimensions. We validated the P-B solver with the analytical and reference solutions, as well as the coupling with the SCM

for quartz/water and air/water interfaces. We utilized this tool to model the electrostatic interactions for a thin-film and a wedge geometry. The results from the later pertain to electrostatic force near the three-phase contact region. The boundary conditions are charge-regulated by coupling the P-B solver and SCM. We observed that the normal stress due to the electrostatic interaction depends on the wedge angle as well as the thickness of the wetting phase (or the distance to the contact point). We also observed and calculated the tangential component of the electrostatic pressure, whose value also depends on the wedge angle. This shows that the electrostatic interaction in the vicinity of the contact point depends on the contact angle and the distance to the contact point. Furthermore, the tangential component causes a change in surface tension close to the contact point.

For future work, the electrostatic interaction model obtained here can be combined with a lubrication model that utilizes a slope-dependent inter-molecular interaction to study the dynamics of the contact region.

Chapter 5

Lubrication model for wettability alteration

Abstract

We present the algorithm and the source code of our numerical model to characterize the wettability of a three-phase system. Wettability is imperative in describing two-phase flow in subsurface geo-environmental applications, including storage of carbon dioxide in deep saline aquifers and groundwater remediation. Although the concept of contact angle is widely used to characterize the affinity of a fluid pair with a solid substrate, it does not accurately describe wettability alteration due to changes in pH and salinity. The latter arises from inter-molecular interactions, which are dominant in the three-phase contact region where the solid, wetting, and non-wetting fluids meet each other. We developed a physically-rooted lubrication model for thin films to model wettability alteration and replace the concept of contact angle. The model accounts for inter-molecular forces, including van der Waals, electric double layer, and hydration potentials through a disjoining pressure term. Unlike other approaches, we introduce a slope-dependent disjoining pressure. We present the implementation algorithm and the source code. The model has been thoroughly verified and used to investigate the role of salinity and pH on wettability. We find out that the slope-dependent disjoining pressure and the precursor film thickness alter the stability of the spreading.

Index terms— wettability alteration, disjoining pressure, lubrication model, thin-film instability

5.1 Introduction

Multi-phase flow occurs in underground reservoirs such as petroleum reservoirs or aquifers. Understanding the flow inside these reservoirs helps us to maintain and develop the reservoirs more efficiently. One of the key parameters in studying multi-phase flows is wettability, which describes the interaction of the different flowing phases with the solid substrate [Mansouri-Boroujeni et al., 2023, Soullaine et al., 2021a, Zhao et al., 2016]. However, determining the system wettability is not a straightforward task as it varies with the different conditions of the system including interface velocity [Šikalo et al., 2005], pressure [Siemons et al., 2006], salinity [Jung and Wan, 2012, Jafari and Jung, 2018] and ion type [Chen et al., 2015], pH [Standnes and Austad, 2000], temperature [Tang and Firoozabadi, 2003] and droplet size [Deng et al., 2018]. In addition, some studies suggest that wettability alteration takes place in the reservoir during exploitation; *e.g.* low-salinity water injection for enhanced oil recovery [Abdi et al., 2022, Sheng,

2014], carbon capture and storage (CCS) in saline aquifers [Song and Zhang, 2013, Yang et al., 2005a, Chiquet et al., 2007], and groundwater remediation [Molnar et al., 2011].

Current approaches to measure wettability through the contact angle are limited because they can not account for the variations in pH, salinity, temperature, and pressure unless the measurement is done for each specific condition. At the *three-phase contact point* (TPCP), where the solid substrate and two immiscible fluid phases meet each other, inter-molecular forces become as important as larger scale effects including viscous, surface tension, and gravity forces [Chatzigiannakis et al., 2021]. These inter-molecular forces are not considered properly when using the "macroscopic" (continuum-scale) contact angle concept. Moreover, a precursor liquid film pre-wetting the solid surface after the TPCP has been observed experimentally [Ueno et al., 2012, Hardy, 1919], which is not considered in the classical contact angle concept. The precursor film thickness can grow from approximately 1nm up to 1 μ m [Teletzke et al., 1987, Hardy, 1919]. In this range of thickness, the effect of inter-molecular forces on the film becomes significant. These molecular interactions are described with the help of disjoining pressure, Π , that varies with the thickness of the film, h [Derjaguin and Churaev, 1978]. The disjoining pressure is due to the overall inter-molecular interaction of the two interfaces (*i.e.*, solid/fluid and fluid/fluid interfaces) of the thin film comprising dispersion, electrostatic, and structural components [Chatzigiannakis et al., 2021]. The dispersion force is usually referred to as *Van der Waals* (VDW) force since it makes up most of VDW force when at least one of the constituents of the interaction is non-polar [Israelachvili, 2011]. The dispersion forces arise from the fluctuation of the electromagnetic field in proximity to the interface [Derjaguin, 1989]. The electrostatic component of the disjoining pressure, also called the electric double layer (EDL) component, is due to the presence of ions locally in excess or deficiency in the film while having charged interfaces [Derjaguin, 1989]. The structural component of the disjoining pressure, also known as non-DLVO force, is due to the orientation and ordering of the molecules at the interfaces and several layers of molecules away.

The knowledge of inter-molecular interactions can lead to assessments of the static (or equilibrium) contact angle. Taheriotaghsara et al. [2021] studied the alteration in wettability of a brine-calcite-oil system when changing the salinity of the brine. They observed the change in contact angle due to a change in disjoining pressure curves. For a similar case, Pourakaberian et al. [2021] used Navier-Stokes equations in combination with the disjoining pressure quantity to obtain the time-scale of the transport of ions from the bulk to the contact region. This time scale corresponds to the time it can take for a change in wettability by changing the bulk salinity. In an experiment, Schwartz et al. [1964] measured the contact line force in a capillary tube with multiple air bubbles inside, and they showed that the solid surface roughness is not the sole cause for contact angle hysteresis. Kuchin and Starov [2015] developed a theory to model the effect of advancing and receding hysteresis by introducing in their model disjoining pressure curves with two local minima while not resolving any hydrodynamic equations.

Hydrodynamic of thin films can be resolved using diffuse-interface models [Seppecher, 1996], interface formation models [Shikhmurzaev, 2007], and *lubrication approximation* models [Reynolds, 1886, Oron et al., 1997, Craster and Matar, 2009]. The latter can be combined with disjoining pressures to include inter-molecular interactions on the thin film [Teletzke et al., 1987]. Huh and Scriven [1971] showed that assuming a pre-deposited film on the solid is necessary to uphold the lubrication assumption. Teletzke et al. [1987] categorized the films into thin-thin film (a few molecules diameter thickness) where the dynamic is mainly diffusive, thick-thin film (up to a few micrometers) where the effect of disjoining pressure is included in a lubrication model and thick film (bigger than a few micrometers) where the effect of disjoining pressure is negligible. They also showed that the hysteresis of the contact angle, *i.e.*, the difference in values of advancing and receding contact angle, does not only depend on the surface

roughness but also results from an equilibrium-seeking behavior of the film. This behavior was studied in the context of film stability and rupture [Oron et al., 1997, Burelbach et al., 1988, Alizadeh Pahlavan, 2018] through the linear stability analysis.

A common practice to track the spreading of a droplet using lubrication models is to use disjoining pressures for "flat" thin films [Yeh et al., 1999, Abu-Al-Saud et al., 2020]. For example, Wray et al. [2014] studied the deposition of coffee rings using disjoining pressure. They found that applying an external electric field enhances or diminishes the ring formation. Barrett and Ajaev [2022] developed a model for considering the evaporation of sessile drops spreading in which they highlight a relationship between disjoining pressure and evaporation rate by changing the contribution of the electrostatic component of the disjoining pressure. A comprehensive review of evaporation for sessile drops can be found in Wilson and D'Ambrosio [2023]. In such cases, the disjoining pressure only depends on the film thickness, $\Pi(h)$. The observation of non-zero contact angles at the nano-metric scale, however, contradicts this assumption [Chen et al., 2014]. This situation is particularly true for partially wet systems.

To overcome this limitation, researchers have derived disjoining pressure curves for wedge structures mimicking the angle formed by the fluid-fluid interface and the solid substrate [Wu and Wong, 2004, Dai et al., 2008, Dörr and Hardt, 2012] and for general curved interfaces [Wang et al., 2020]. It results in disjoining pressures that depend on higher-order derivatives of the film thickness, $\Pi(h, h_x, h_{xx})$. Alizadeh Pahlavan [2018] studied the effect of disjoining pressure with higher derivatives on droplet spreading. Their approach leads to a non-zero contact angle at TPCP. However, they used a Lennard-Jones potential type for the disjoining pressure to account for repulsive forces, including EDL and structural force. The use of appropriate models for the said repulsive forces, in addition to the slope-dependent dispersion component, is important since it can influence film stability. It can also provide the necessary tools to study the effect of fluid properties such as salinity and pH on the evolution of film.

In this chapter, we investigate the mechanisms occurring in the three-phase contact region, where inter-molecular interactions play a significant role. For that, we propose a comprehensive lubrication model for thin films that includes inter-molecular interactions through the concept of disjoining pressure. In the derivation, we included the dependency of inter-molecular force on the slope of the film to accurately model the non-zero slope of the film at the TPCP. This model can assess the wettability behavior of a three-phase system and its dependency on parameters such as salinity and pH.

The chapter is organized as follows. In Section 5.2, we introduce the mathematical model that we developed to investigate moving contact lines. In Section 5.3, we detail our numerical strategy to solve the lubrication model for thin film. In Section 5.4, we present simulations of the spreading of droplets. We start with two validation cases to verify the robustness of the numerical implementation. Then, we use the lubrication model combined with disjoining pressure model to investigate wettability alteration due to a change in pH and salinity. Finally, we close our manuscript with a summary and perspectives.

5.2 Mathematical model

In this section, we introduce our mathematical model to simulate the spreading of droplets. It consists of a lubrication model for thin films (Section 5.2.2) that includes inter-molecular interactions described with the help of disjoining pressure concept (Section 5.2.3) and discretized using the finite difference method (Section 5.3).

5.2.1 Free energy for thin film

Let's consider a two-dimensional (2D) film of thickness, $h(x)$, varying along the x direction as illustrated in Fig. 5.1. As the film is not a flat surface, we define the slope as the space derivative, $h_x = \frac{\partial h}{\partial x}$. The free energy of the film, $\mathbb{W}$ (J m^{-2}), includes the surface tension and gravity effects as well as the inter-molecular interaction effects,

$$\mathbb{W}(h, h_x) = \sigma \sqrt{1 + h_x^2} + \sigma_{SL} - \sigma_{SV} + \frac{1}{2} \rho g h^2 + W(h, h_x), \quad (5.1)$$

where $\sigma \sqrt{1 + h_x^2}$ is the surface tension energy of two fluid phases, σ_{SL} and σ_{SV} are the surface energies of solid with the two fluid phases, $\frac{1}{2} \rho g h^2$ is the gravitational energy, and W is the inter-molecular energy that is described in detail in the next section. Surface and gravitational energies represent macroscopic effects, while inter-molecular energy describes microscopic interactions. Note that in the long-wave approximation, the slope of the fluid-fluid interface is small ($h_x \ll 1$), and using Taylor series $\sqrt{1 + h_x^2} \approx 1 + \frac{h_x^2}{2}$.

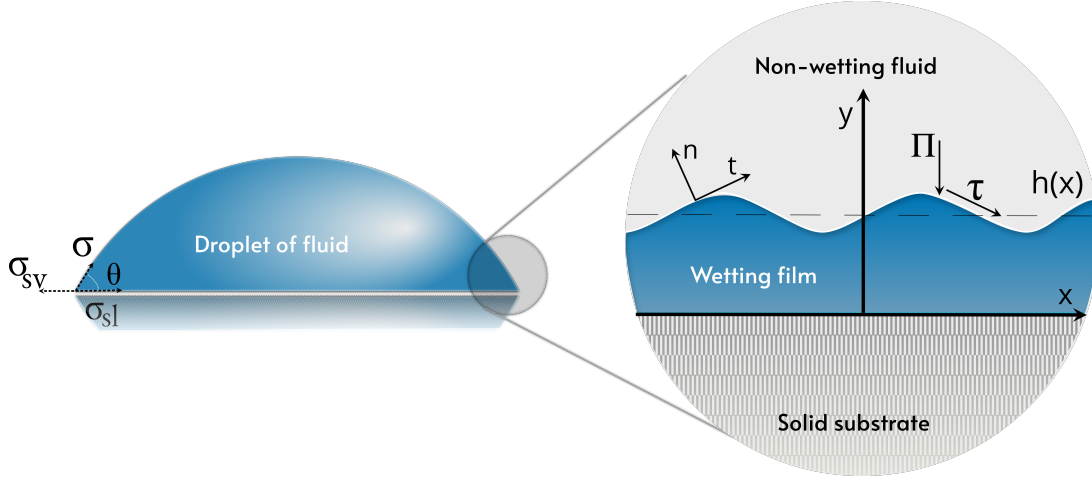


Figure 5.1: 2D sketch of the thin wetting film sandwiched in between the solid substrate and the non-wetting fluid. Both inter-molecular interactions and fluid flow exert an excess stress – with a normal (Π) and a tangential (τ) component – on the fluid-fluid interface. The inter-molecular interaction in the film can be expressed as a normal stress on the boundary of the film.

In practice, we define the energy potential, $\mathbb{P}(h, h_x, h_{xx})$, obtained using the variational derivative of the free energy with respect to height,

$$\mathbb{P}(h, h_x, h_{xx}) = \frac{\delta \mathbb{W}}{\delta h} = \left(\frac{\partial \mathbb{W}}{\partial h} - \frac{\partial}{\partial x} \left(\frac{\partial \mathbb{W}}{\partial h_x} \right) \right). \quad (5.2)$$

As the disjoining pressure, Π , is minus the variational derivative of the inter-molecular free energy, $\Pi(h, h_x, h_{xx}) = -\frac{\delta W}{\delta h}$, (see more details in Section 5.2.3) then the film potential,

$$\mathbb{P}(h, h_x, h_{xx}) = -\sigma \frac{\partial^2 h}{\partial x^2} + \rho g h - \Pi(h, h_x, h_{xx}), \quad (5.3)$$

depends on the surface tension force where $h_{xx} = \frac{\partial^2 h}{\partial x^2}$ is the interface curvature, on the gravity potential, and on the inter-molecular forces.

5.2.2 Lubrication model for thin films

Our model relies on the lubrication approximation to simulate the spreading of a droplet. Lubrication approximation is a reduced-order model of Navier-Stokes equations in which one dimension – the film thickness – is smaller than the other two (see Fig. 5.1). The evolution equation for the film thickness, h , is obtained by integrating the Navier-Stokes equations over the film thickness [Reynolds, 1886]. In this chapter, we consider a two-dimensional system that reduces into a one-dimensional (1D) evolution equation. Extrapolation to three-dimensional systems follows similar developments. The integration of the mass balance equation reads,

$$\frac{\partial h}{\partial t} + \frac{\partial q_s}{\partial x} = 0, \quad (5.4)$$

where $h(x)$ is the film thickness (in m), $q_s = hv_s$ is flow rate within the film (in m^2/s), and v_s is the depth-averaged film velocity (in m/s). The latter is obtained by integrating the Stokes momentum equation between two parallel interfaces and using the long-wave approximation (*i.e.*, the wavy aspect of the fluid-fluid interface is negligible with respect to the size of the system). The driving force magnitude is a pressure-like gradient, $\partial\mathbb{P}/\partial x$, that accounts for gravity, interface curvature, and inter-molecular forces, as we will see later on. The final form of v_s strongly depends on the fluid-solid (*e.g.*, no-slip or partial slip, λ) and fluid-fluid boundary conditions (*e.g.*, free surface or mutual shear-stress, τ). A generic form of the resulting mass flow rate reads,

$$q_s = -M(h)\frac{\partial\mathbb{P}}{\partial x} + \mathbb{T}(h), \quad (5.5)$$

where $M(h)$ is the fluid mobility (in $\frac{\text{m}^3}{\text{Pa}\cdot\text{s}}$), $\mathbb{T}(h)$ (in m^2/s) accounts for mutual shear stress at the fluid-fluid interface, and for space variations of the surface tension, and $\mathbb{P}$ is the pressure (in Pa) within the film. Expressions of $M(h)$ and $\mathbb{T}(h)$ are provided in Table 5.1 for various fluid-fluid and fluid-solid conditions. The mobility term, M , depends on the fluid-solid boundaries. The standard formula, $M(h) = \frac{h^3}{3\mu}$, corresponds to cases in which the wetting fluid has a no-slip behavior at the solid surface. Such a mobility expression, however, tends towards zero if the film thickness is zero, leading to an ill-posed equation, and requires to account for a precursor film – artificial or real – that always wets the solid surface [Diez et al., 2000]. A Navier slip describing the fluid-solid boundary condition can circumvent this issue where $u|_{y=0} = \lambda \frac{\partial u}{\partial y}|_{y=0}$. The mobility is, then, modified to account for the Navier slip length, λ . When considering free surfaces, *e.g.*, a droplet of oil surrounded by air, the hydrodynamic of the fluids is decoupled, and the shear stress in $\mathbb{T}(h)$ is $\tau = 0$. Note that this hypothesis is no longer true for fluid pairs of moderate viscosity ratio [Roman et al., 2020]. In this case, it is necessary to couple the lubrication model with a Navier-Stokes based solver that computes the hydrodynamics within the non-wetting phase, and, therefore, the mutual shear-stress, τ [Abu-Al-Saud et al., 2020].

Table 5.1: Mobility for fluid-solid interface and the stress boundary condition for fluid-fluid interface term in the lubrication model

	Mobility, $M(h)$	$\mathbb{T}(h)$
No slip	$\frac{h^3}{3\mu}$	$\frac{h^2}{2\mu} \left(\frac{\partial\sigma}{\partial x} + \tau \right)$
Navier slip	$\frac{1}{\mu} \left(\frac{h^3}{3} + \lambda h^2 \right)$	$\frac{1}{\mu} \left(\frac{h^2}{2} + \lambda h \right) \left(\frac{\partial\sigma}{\partial x} + \tau \right)$

Finally, combining the mass balance (Eq. 5.4) with the mass flow rate in the film (Eq. 5.5) and the energy potential equation (Eq. 5.3), the evolution equation of the film thickness reads [Oron et al., 1997,

Alizadeh Pahlavan, 2018, Mitlin, 1993]:

$$\frac{\partial h}{\partial t} = \frac{\partial}{\partial x} \left(M(h) \frac{\partial}{\partial x} \left(-\sigma \frac{\partial^2 h}{\partial x^2} + \rho g h - \Pi(h, h_x, h_{xx}) \right) - \mathbb{T}(h) \right). \quad (5.6)$$

This is the equation that is solved numerically in this chapter (see Section 5.3). The challenge is two-fold: first, the bi-Laplacian operator associated with the interface curvature is a fourth-order space derivative that necessitates dedicated treatment, and second, the equation is non-linear. The derivation in full details is done in section. A.4.

5.2.3 Inter-molecular interactions and disjoining pressure

In thin films and at the vicinity of the three-phase contact region, the thickness of the wetting fluid becomes comparable with the range of inter-molecular interactions described through the concept of disjoining pressure (Π). The latter is evaluated through the knowledge of the dispersion (Van der Waals, Π_{VDW}), electrostatic (Electric Double Layer, Π_{EDL}), and structural (Π_{str}) components [Derjaguin et al., 1987]:

$$\Pi = \Pi_{VDW} + \Pi_{EDL} + \Pi_{str}. \quad (5.7)$$

The combination of Van der Waals and Electric Double Layer interactions is also known as the DLVO interaction (short for Derjaguin, Landau, Verwey and Overbeek [Derjaguin and Landau, 1941, Verwey et al., 1948]). The structural or steric component of the disjoining pressure is related to the structure and the molecules' orientation close to the interface. All types of interactions mentioned previously are long-range interactions, *i.e.* their amplitude varies with the film thickness, h . Because films are not always parallel to the solid substrate, we will see that the inter-molecular forces can be slope-dependent (*i.e.*, they vary with h_x as well). In practice, we use the inter-molecular free energy, W , instead of the disjoining pressure to provide a more general equation. We have,

$$W = W_{VDW} + W_{EDL} + W_{str}. \quad (5.8)$$

The disjoining pressure is obtained from energy (W) using the variational derivative,

$$\Pi(h, h_x, h_{xx}) = -\frac{\delta W(h, h_x)}{\delta h} = -\left(\frac{\partial W}{\partial h} - \frac{\partial}{\partial x} \left(\frac{\partial W}{\partial h_x} \right) \right). \quad (5.9)$$

In the following, we introduce the different components used in this chapter to model the spreading of a droplet.

Van der Waals

The dispersion component of the disjoining pressure is due to the polarization of atoms and molecules and exists for even non-polar molecules. It is described by the Van der Waals (VDW) energy. The VDW potential is often obtained for parallel interfaces and depends only on the film thickness. For non-uniform films with arbitrary surfaces, including wavy films, however, it also depends on higher derivatives of the film thickness, including slope and interface curvature [Wang et al., 2020]. The same is true for partially wet systems and small contact angles. Based on the work of Wu and Wong [2004], Dai et al. [2008] derived a VDW interaction energy that depends not only on the film thickness but also on the slope of

the interface. It reads,

$$W_{VDW} = -A_{123} \left(\frac{1}{12\pi h^2} + \frac{h_x^2}{16\pi h^2} \right), \quad (5.10)$$

where $A_{123} = A_{22} - A_{12} - A_{23} + A_{13}$ is the Hamaker constant. The indices 1, 2, 3 refer respectively to solid, wetting, and non-wetting fluid. Hamaker constant encompasses the polarizability and number density of the constituents. In the limit of thin films ($h_x \rightarrow 0$), Eq. 5.10 tends toward the classical form of Van der Waals energy, $W_{VDW} = \frac{-A_{123}}{12\pi h^2}$, that is derived formally for parallel interfaces of a thin film in contact with the vapor [Israelachvili, 2011]. The corresponding disjoining pressure obtained with the variational derivative is, $\Pi_{VDW}(h, h_x) = -\frac{A_{123}(4-3h_x^2+3hh_{xx})}{24\pi h^3}$, that tends towards $\Pi_{VDW}(h) = \frac{-A_{123}}{6\pi h^3}$ for negligible slope.

Electric Double Layer

The electrostatic component of the disjoining pressure is due to the interaction of ion species in the thin film with the fluid-solid and fluid-fluid interfaces. Ions are adsorbed on the interface surrounding the film (or repelled from it), which makes it electrostatically charged (Fig. 5.2). The counter-ions form a distribution in response to the charge of the interface. The distribution of counter-ions in the film, in addition to the interaction of the interfaces themselves with each other, creates an excess pressure that is called the electric double layer (EDL) pressure. Actually, there are two electric double layers – one for each interface bounding the wetting film – characterized by the electrostatic potential, ψ_i (in Volt), often assimilated to the zeta-potential, ζ_i that is defined as the electrostatic potential at the shear (or slipping) plane when wetting fluid flow occurs on the substrate. The range of interaction of EDL is characterized

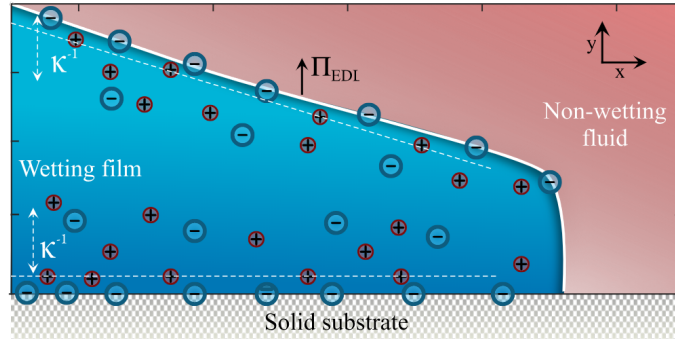


Figure 5.2: The ions in the wetting film will get adsorbed on the interfaces with the solid and non-wetting fluid, and the counter-ions form a distribution in response to charges on the interface. The zeta-potential ζ is the electrostatic potential measured at a distance away from the interface (Stern layer thickness), illustrated by the white dashed line.

by the Debye-Hückel reciprocal length (in m^{-1}),

$$\kappa^2 = \frac{\rho_\infty e^2}{\epsilon \epsilon_0 k_B T}, \quad (5.11)$$

where ρ_∞ is the ionic strength in the bulk times the Avogadro number (in $\frac{\text{mol}}{\text{liter}}$), k_B is the Boltzmann constant (in $\frac{\text{J}}{\text{K}}$), T is temperature (in K), e is unit charge (in C), ϵ is relative permittivity of the fluid and ϵ_0 is the permittivity of vacuum (in $\frac{\text{F}}{\text{m}}$).

The EDL variation with respect to the film thickness is obtained by first specifying how the adsorbed charges on the interface are affected by the thin film thickness. For an oil-brine-calcite system, Taheri-

otaghsara et al. [2021] by comparison of experimental measurements of contact angle and their results obtained with the disjoining pressure calculation, concluded that the assumption of constant charge on the oil-brine interface and constant electrostatic potential on the brine-calcite interface, as the thickness of the film of brine changes provides the best match. Here, we consider constant charge in the film as the thickness of the film varies. Gregory [1975] derived the EDL potential free energy for two parallel plates with constant charge in the film:

$$W_{EDL} = \frac{2\rho_{\infty}k_BT}{\kappa} \left[2\bar{\Psi} \ln \frac{B + \bar{\Psi} \coth \kappa h/2}{1 + \bar{\Psi}} - \ln (\bar{\Psi}^2 + \cosh \kappa h + B \sinh \kappa h) + \kappa h \right], \quad (5.12)$$

where $\Psi_i = \frac{e\psi_i}{k_BT}$ is the reduced electrostatic potential of the interface with solid ($i = 1$) and with the non-wetting fluid ($i = 2$), $\bar{\Psi} = \frac{\Psi_1 + \Psi_2}{2}$ is the average potential, and $B = \sqrt{1 + \bar{\Psi}^2 \operatorname{csch}^2 \kappa h/2}$. The corresponding disjoining pressure EDL component is

$$\Pi_{EDL}(h) = \rho_{\infty}k_BT \left[2B - \frac{(\Psi_1 - \Psi_2)^2 \exp(-\kappa h)}{B^2} - 2 \right]. \quad (5.13)$$

Other EDL potentials can be derived by integrating the Poisson-Boltzmann equation with boundary conditions including constant charge, constant potential, and mixed-conditions [Pourakabarian et al., 2021]. The lubrication model for thin films that we introduce in this chapter is generic, and all kinds of EDL potential can be used.

Structural component

In this chapter, the structural – or steric – component considers a repulsive hydration force that decays monotonically with distance from the surface. We have,

$$W_{str}(h) = w_0 e^{-\frac{h}{\lambda_0}}, \quad (5.14)$$

where w_0 is the amplitude of the hydration in the order of $3 - 30 \times 10^{-3} \text{Jm}^{-2}$, and λ_0 is the decay length-scale in the order of $0.6 - 1.1 \text{nm}$ [Israelachvili, 2011]. Note that the hydration force changes with different types of cations solved in the water [Israelachvili, 2011]. The corresponding disjoining pressure component is, $\Pi_{st}(h) = \frac{w_0}{\lambda_0} e^{-\frac{h}{\lambda_0}}$.

5.2.4 Film stability criteria

Films can destabilised and rupture. A stability criterion for the lubrication equation, Eq. 5.6, is obtained using a linear stability analysis along the same lines as the work of Oron et al. [1997]. It is achieved by applying a perturbation to a uniform solution,

$$h = h_0 + h'_0 e^{ikx + st}, \quad (5.15)$$

where k is the wave number of the perturbation, and s is the perturbation frequency. By substituting into Eq. 5.6, while neglecting $\mathbb{T}(h)$, we have:

$$\begin{aligned} \mu s h'_0 e^{ikx+st} = & -\frac{1}{3} \frac{\partial}{\partial x} \left(-ik^3 h'_0 e^{ikx+st} (h_0 + h'_0 e^{ikx+st})^3 \left(\sigma - \frac{\partial \Pi}{\partial h_{xx}} \right) \right) \\ & + \frac{1}{3} \rho g \frac{\partial}{\partial x} \left(ik h'_0 e^{ikx+st} (h_0 + h'_0 e^{ikx+st})^3 \right) \\ & + \frac{1}{3} \frac{\partial}{\partial x} \left((h_0 + h'_0 e^{ikx+st})^3 \left(-ik h'_0 e^{ikx+st} \frac{\partial \Pi}{\partial h} + k^2 h'_0 e^{ikx+st} \frac{\partial \Pi}{\partial h_x} \right) \right). \end{aligned} \quad (5.16)$$

By carrying out the derivative and $h' \rightarrow 0$, we have:

$$\mu s = -\frac{1}{3} h_0^3 k^2 \left[k^2 \left(\sigma - \frac{\partial \Pi}{\partial h_{xx}} \right) + \rho g - \left(\frac{\partial \Pi}{\partial h} + ik \frac{\partial \Pi}{\partial h_x} \right) \right]. \quad (5.17)$$

The growth rate is $Re(s) = -\frac{1}{3} h_0^3 k^2 \left[k^2 \left(\sigma - \frac{\partial \Pi}{\partial h_{xx}} \right) + \rho g - \frac{\partial \Pi}{\partial h} \right]$ and the phase speed is $Im\left(\frac{s}{k}\right) = \frac{1}{3} h_0^3 k^2 \frac{\partial \Pi}{\partial h_x}$. If $Re(s) < 0$ then the perturbation decays and the film is stable:

$$k^2 \left(\sigma - \frac{\partial \Pi}{\partial h_{xx}} \right) + \rho g - \frac{\partial \Pi}{\partial h} > 0 \quad (5.18)$$

This criterion means that the stability depends on the wave number of the perturbation. If the disjoining pressure is only a function of h , meaning the contact angle is close to zero, we recover the film stability condition derived by Oron et al. [1997]:

$$\rho g - \frac{\partial \Pi}{\partial h} > 0. \quad (5.19)$$

A uniform deposited film can be the result of the adsorption of the wet phase on the solid surface before the spreading of the droplet and is dynamically stable. However, the rupture of the film discussed in this chapter is mainly due to the perturbation at the contact point when a droplet is placed on the film. Based on this criterion and unless specified otherwise, the simulations of a spreading droplet will be set up with a precursor film that wets the solid substrate during the droplet spreading and whose thickness, b , is large enough to avoid thinning of the film leading to premature rupture. However, as the spreading continues, the thickness of the film might change at TPCP and fall in the unstable region.

5.3 Numerical implementation

The lubrication equation for thin films is solved in a one-dimensional horizontal solid surface to investigate the spreading of a droplet and the impact of wettability conditions. This is achieved by discretizing a non-dimensionalized lubrication equation with the Finite-Difference Method and solving it with an in-house MATLAB program.

5.3.1 Non-dimensionalization of the lubrication model for thin films

Expanding the disjoining pressure terms and using the chain rule, $\frac{\partial \Pi_{VDW}(h, h_x, h_{xx})}{\partial x} = \left(\frac{\partial \Pi_{VDW}}{\partial h} \right) \frac{\partial h}{\partial x} + \left(\frac{\partial \Pi_{VDW}}{\partial h_x} \right) \frac{\partial^2 h}{\partial x^2} + \left(\frac{\partial \Pi_{VDW}}{\partial h_{xx}} \right) \frac{\partial^3 h}{\partial x^3} = -\frac{A_{123}}{2\pi h^4} \left(1 - \frac{3}{4} h_x^2 - h h_{xx} \right) h_x + \frac{A_{123}}{8\pi h^2} h_{xxx}$, the lubrication equation (Eq. 5.6) is recast into,

$$\frac{\partial h}{\partial t} = \frac{\partial}{\partial x} \left[\mathbb{M}(h) \frac{\partial^3 h}{\partial x^3} \right] + \frac{\partial}{\partial x} \left[\mathcal{M}(h) \frac{\partial h}{\partial x} \right] - \frac{\partial \mathbb{T}(h)}{\partial x}, \quad (5.20)$$

where the pseudo-mobility terms for the bi-Laplacian and Laplacian are,

$$\begin{aligned}\mathbb{M}(h) &= -M(h) \left[\sigma - \frac{A_{123}}{8\pi h^2} \right], \\ \mathcal{M}(h) &= M(h) \left[\rho g - \frac{A_{123}}{2\pi h^4} \left(1 - \frac{3}{4} h_x^2 + h h_{xx} \right) - \frac{\partial \Pi_{EDL}}{\partial h} - \frac{\partial \Pi_{st}}{\partial h} \right].\end{aligned}\quad (5.21)$$

The dimensionless evolution equation for the film thickness is obtained by introducing the scaling length and time, x_* , h_* , and t_* . We substitute $h = \tilde{h} h_*$, $x = \tilde{x} x_*$ and $t = \tilde{t} t_*$ into Eqs. 5.20-5.21 where $\sim$ denotes the non-dimensional variables. Using the characteristic time-scale $t_* = \frac{3\mu x_0^4}{\sigma h_0^3}$, we obtain,

$$\frac{\partial \tilde{h}}{\partial \tilde{t}} = \frac{\partial}{\partial \tilde{x}} \left[\tilde{\mathbb{M}}(\tilde{h}) \frac{\partial^3 \tilde{h}}{\partial \tilde{x}^3} \right] + \frac{\partial}{\partial \tilde{x}} \left[\tilde{\mathcal{M}}(\tilde{h}) \frac{\partial \tilde{h}}{\partial \tilde{x}} \right] - C_T \frac{\partial \tilde{\mathbb{T}}(\tilde{h})}{\partial \tilde{x}}, \quad (5.22)$$

and the dimensionless pseudo-mobility terms are:

$$\begin{aligned}\tilde{\mathbb{M}}(\tilde{h}) &= -M(\tilde{h}) \left[1 - \frac{C_{VDW} \varepsilon^2}{4\tilde{h}^2} \right] \\ \tilde{\mathcal{M}}(\tilde{h}) &= M(\tilde{h}) \left[B_o - \frac{C_{VDW}}{\tilde{h}^4} \left(1 - \frac{3}{4} \varepsilon^2 \tilde{h}_x^2 + \varepsilon^2 \tilde{h} \tilde{h}_{\tilde{x}\tilde{x}} \right) - C_{EDL} \frac{\partial \tilde{\Pi}_{EDL}}{\partial \tilde{h}} - C_{st} \frac{\partial \tilde{\Pi}_{st}}{\partial \tilde{h}} \right],\end{aligned}\quad (5.23)$$

where the Bond number is $B_o = \frac{\rho g x_*^2}{\sigma}$, the dimensionless coefficients for the disjoining pressure potentials are $C_{st} = \frac{\omega_0 x_*^2}{\lambda_0^2 \sigma}$, $C_{EDL} = \frac{\rho_\infty k_B T \kappa x_*^2}{\sigma}$, and $C_{VDW} = \frac{A_{123} x_*^2}{2\pi h_*^4 \sigma}$ and the coefficient for shear stress term corresponds to the viscosity ratio between the non-wetting and the wetting fluids, $C_T = \frac{\mu_{nw}}{\mu_w}$. The size aspect ratio is $\varepsilon = \frac{h_*}{x_*}$. The dimensionless mobility is found in Table 5.2.

Table 5.2: Dimensionless mobility and the stress boundary condition term in the lubrication model

Fluid-solid boundary	$M(\tilde{h})$	$\mathbb{T}(\tilde{h})$
No-slip	$\tilde{h}^3$	$\frac{\tilde{h}^2}{2} (\tilde{\sigma}_{\tilde{x}} + \tau)$
Navier slip	$\tilde{h}^3 + 3\tilde{\lambda} \tilde{h}^2$	$\left(\frac{\tilde{h}^2}{2} + \tilde{\lambda} \tilde{h} \right) (\tilde{\sigma}_{\tilde{x}} + \tau)$

5.3.2 Discretization

We obtain a system of linear equations using finite difference discretization for each point of the domain between two successive time-steps. The set of equations to be solved has the form:

$$\frac{h_i^{t+1} - h_i^t}{\Delta t} + \theta \left(\sum_{n=-2}^{n=2} a_n h_{i+n} \right)^{t+1} + (1 - \theta) \left(\sum_{n=-2}^{n=2} a_n h_{i+n} \right)^t = 0. \quad (5.24)$$

This discretization is second-order in space (central difference) and second-order in time because we use the Crank–Nicolson method with $\theta = \frac{1}{2}$. The evolution equation for the film thickness comprised a second-order differentiation for the gravity and height-dependent inter-molecular potential and a fourth-order differentiation for the curvature and slope-dependent inter-molecular potential. The discretization of the fourth-order differential term in Eq. 5.20 for a uniform mesh spacing is:

$$\frac{\partial}{\partial x} \left[\mathbb{M}(h) \frac{\partial^3 h}{\partial x^3} \right] = \mathbb{M}_{i+1/2} \frac{h_{i+2} - 3h_{i+1} + 3h_{i-1} - h_{i-2}}{(\Delta x)^4} - \mathbb{M}_{i-1/2} \frac{h_{i+1} - 3h_i + 3h_{i-1} - h_{i-2}}{(\Delta x)^4}, \quad (5.25)$$

and discretization of the second-order differential term in Eq. 5.20 using finite-difference method (FDM) with a central difference is:

$$\frac{\partial}{\partial x} \left[\mathcal{M}(h) \frac{\partial h}{\partial x} \right] = \mathcal{M}_{i+1/2} \frac{h_{i+1} - h_i}{(\Delta x)^2} - \mathcal{M}_{i-1/2} \frac{h_i - h_{i-1}}{(\Delta x)^2}, \quad (5.26)$$

Here, we only mention the expressions for the uniform spacing one-dimension mesh. However, the equation can be rewritten for any arbitrary spacing. This is what we have done to implement Adaptive Mesh Refinement techniques.

To ensure the positivity of the solution for all film thicknesses and the convergence of the scheme, we used the modification introduced in Zhornitskaya and Bertozzi [1999], Diez et al. [2000] as the regularization of the mobility term. The regularization comprised of imposing a precursor film on the domain $h(x, 0) \rightarrow h(x, 0) + b$ and a modification for mobility term. This film is initially perceived as a numerical artifact to perform the simulation since a film thickness of zero will impose problems for the simulation by rendering the mobility term zero at the TPCP. However, when we are performing the simulation considering the inter-molecular forces, then the film thickness gains physical meaning, and the value is inferred by the disjoining pressure curve and its derivative. After lifting up the initial solution, the mobility term for the fourth-order differentiation undergoes a regularization [Diez et al., 2000]:

$$\mathbb{M}^*(h) = \frac{\mathbb{M}(h)h^4}{b^a\mathbb{M}(h) + h^4}. \quad (5.27)$$

Interpolation of the mobility term on the cell faces for the fourth-order differentiation is done as:

$$\mathbb{M}_{i+1/2} = \begin{cases} \frac{h_{i+1}-h_i}{g_{i+1}-g_i} & h_{i+1} \neq h_i \\ \mathbb{M}(h_i) & h_{i+1} = h_i \end{cases} \quad \text{and} \quad g = \int \frac{dh}{\mathbb{M}(h)}, \quad (5.28)$$

meanwhile, the interpolation of mobility for the second-order differential terms is the arithmetic mean:

$$\mathcal{M}_{i+1/2} = \frac{\mathcal{M}(h_i) + \mathcal{M}(h_{i+1})}{2}. \quad (5.29)$$

5.3.3 Mesh and Adaptive Mesh Refinement

In order to obtain accurate results, the mesh size in the vicinity of TPCP should be in the same order of magnitude as the precursor film thickness. This is because the film thickness used in the mobility term becomes small and comparable with the precursor film. Therefore, we used a non-uniform mesh, which is coarse in most parts of the domain and gets finer close to the TPCP. In addition, non-uniform grid greatly reduces the runtime.

As the TPCP location changes with the film spreading, we implemented an adaptive mesh refinement (AMR) scheme to follow the movement of TPCP and dynamically refine the mesh close to the contact point. It uses the gradient of the film thickness in combination with the higher order derivative as an indicator of the TPCP. Once we obtain the location of TPCP, we can use a uniform expansion method to perform a grading on the mesh. Typically an equation of the form $\Delta x_i = \Delta x_0 f^i$ is used, where f is the expansion coefficient (< 1). This equation gives a linear behavior for grid spacing versus distance, as shown in Fig. 5.3. The spacing based on this equation is not smooth at the TPCP, therefore we also tried a parabolic distribution. Using a parabolic distribution will result in a more smooth profile at TPCP, however, it requires more number of points. One can use a combination of linear and parabolic (mixed distribution in the Fig. 5.3) to remedy this.

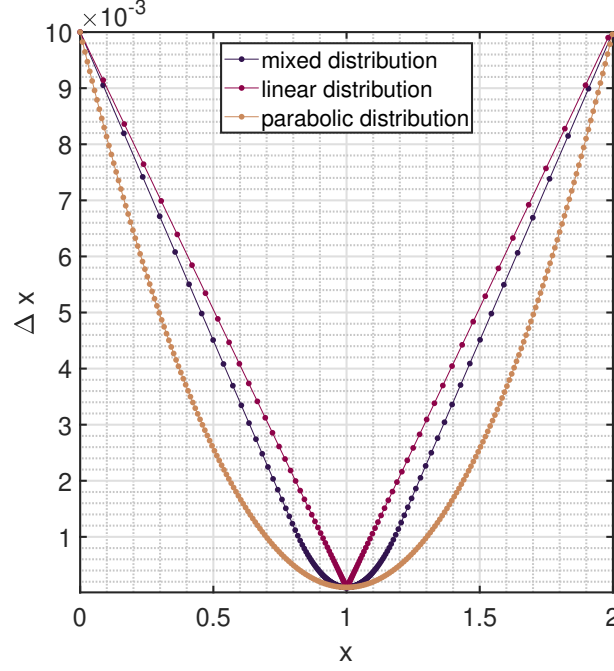


Figure 5.3: The behavior of grid spacing versus distance for a domain where TPCP is located at $x = 1$. The grid spacing decreases as it gets closer to the TPCP to reach a required threshold.

When the mesh is modified, new nodes are created with unknown values for the thickness. We use linear interpolation to find the value for the film thickness on these points. It should be noted that the choice of interpolation for new points could ultimately alter time required for the convergence of the solver.

5.3.4 Solution algorithm

The simulation starts with creating a mesh over the initial droplet profile. We set a symmetric condition for the center of the droplet, and we specify $\frac{\partial h}{\partial x} = 0$ and $\frac{\partial^3 h}{\partial x^3} = 0$ at the other end of the 1D domain to describe an infinite boundary. Then, the coefficient matrix of the linear system is populated using the mobility values.

The calculation of the inter-molecular terms in the mobility terms in Eq. 5.20 is done explicitly since they contain nonlinear terms. Therefore, we imposed a loop for each time step to make sure the error caused by this implementation is smaller than a set criterion (10^{-8}). If the criteria can't be reached within a finite number of iterations, the time-stepping is reduced. In order to speed up the simulation, the time interval increases as the simulation progress, and it is constrained by maintaining $\max(error_i) < 10^{-2}$ calculated by

$$error \approx \frac{2\Delta^t}{\Delta^{t-1}} \frac{\Delta^{t-1}h^{t+1} + \Delta^t h^{t-1} - (\Delta^{t-1} + \Delta^t)h^t}{(\Delta^{t-1} + \Delta^t)h^t}, \quad (5.30)$$

where Δ^i is the time-step at time i .

The flowchart of the algorithm written in MATLAB is illustrated in Fig. 5.4. It contains an inner loop for the convergence of the mobility interpolation terms and an outer loop for the advancement of time. The time-stepping is dynamic and is controlled by different criteria mentioned earlier. The simulation will stop if it reaches the designated end time or if the time-stepping becomes too small.

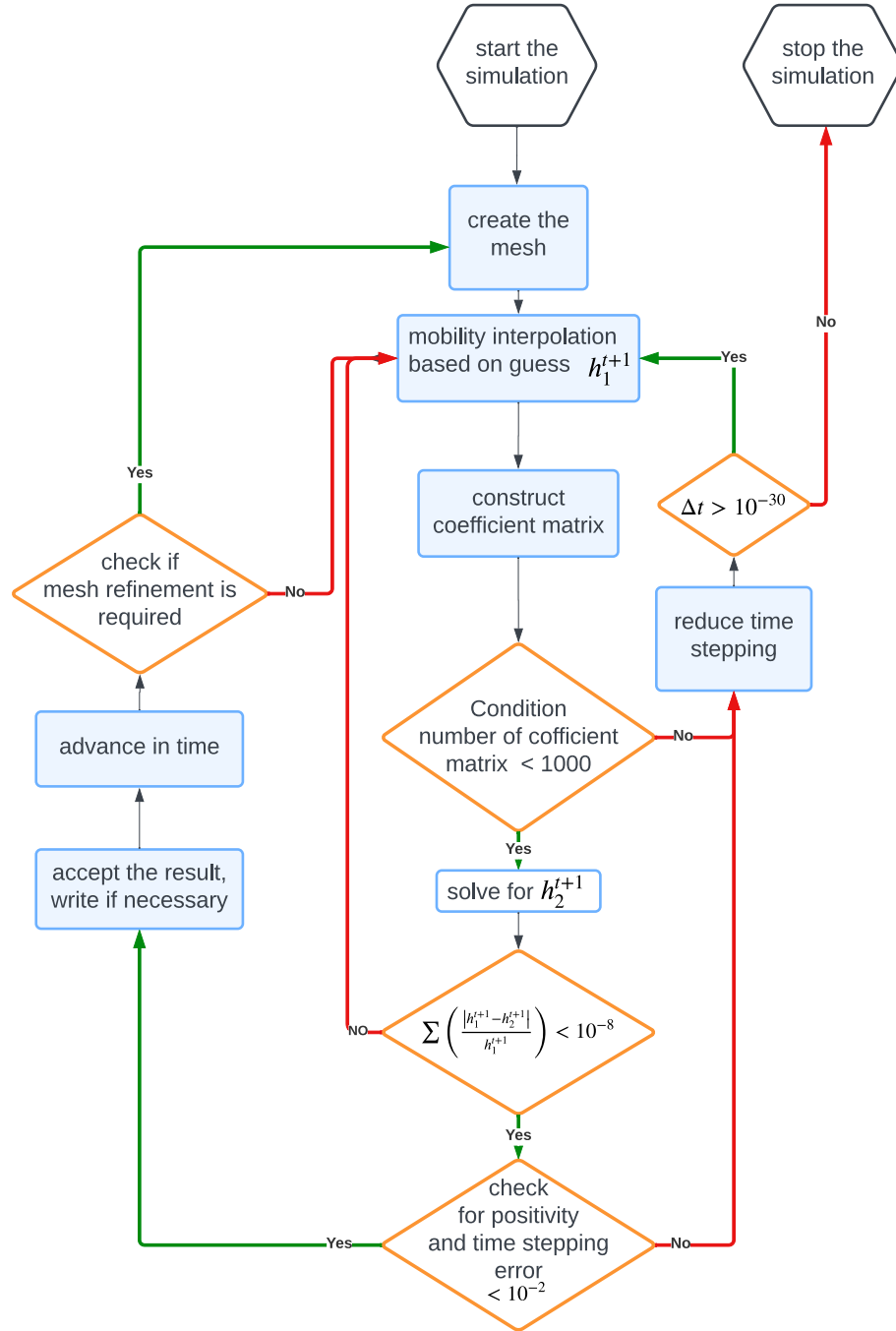


Figure 5.4: The flowchart for the algorithm written in MATLAB to numerically solve the film thickness evolution equation.

5.4 Results

In this section, we present and discuss the simulation of the spreading of a droplet using our lubrication model for thin film combined with disjoining pressure model. The two first cases (Sections 5.4.1 and 5.4.2) compare our model with reference solutions of an oil droplet surrounded by air spreading on a solid substrate to verify the robustness of the numerical implementation. Then, we investigate the effect of wettability alteration on the spreading of a film with different salinity and pH (Section 5.4.3), where we study the spreading of water on carbonate surface in presence of oil.

5.4.1 Evolution of films driven by curvature

The objective of this case is to verify the fourth-order derivative discretization with adaptive mesh refinement (AMR) in the lubrication equation and its numerical implementation. One-dimensional spreading of a droplet only driven by surface tension effects is compared with a self-similar analytical solution. This solution exists for a mobility term $M(h) = h$, and the curvature as the only driving force, [Diez et al., 2000], hence this solution is for the free energy density of the system

$$\mathbb{W} = \sigma \left(1 + \frac{1}{2} h_x^2 \right). \quad (5.31)$$

For a (dimensionless) droplet of height $h = 1$ and radius $x = 1$, centered on the coordinate $x = 0$, and whose initial shape is given by,

$$h(x, t = 0) = \begin{cases} [1 - x^2]^2 & \text{if } |x| \leq 1, \\ 0 & \text{elsewhere,} \end{cases} \quad (5.32)$$

the self-similar evolution is

$$h(x, t) = \begin{cases} (1 + 120t)^{-1/5} \left[1 - \left(\frac{x}{x_f(t)} \right)^2 \right]^2 & \text{if } |x| \leq x_f(t), \\ 0 & \text{elsewhere,} \end{cases} \quad (5.33)$$

and $x_f(t) = (1 + 120t)^{1/5}$ is the radius of the droplet versus time.

The numerical model consists of a $x = 8$ cm long 1D domain. The droplet is deposited on top of a precursor film of thickness b to ensure positive values of the film thickness. The droplet boundaries are at $x = \pm 2$ cm and the initial condition for the film in the lubrication model is given by Eq. 5.32 by setting the dimensionless length and height as $x_* = 10h_* = 2$ cm. In all the numerical simulations, the time stepping is dynamic and ensures the criteria in Eq. (5.30), while the maximum dimensionless time-stepping is set to 10^{-6} .

In Fig. 5.5a, we compare the spreading of the droplet obtained using the lubrication simulation for $b = 0.001 \times h_*$ and AMR with the self-similar solution. The droplet spreads under the action of the surface tension. The droplet radius and the maximum height of the droplet are plotted in Fig. 5.5b. In Fig. 5.5c, we compare the mean square error (given by $\frac{1}{n} \sum_{i=1}^n (h_{analytical} - h_{simulation})^2$) for a uniform mesh with spacing as small as b and the AMR mesh. The mean square error becomes smaller as b decreases. In addition, the error ceases to increase at later times (> 10 s) for small enough values of b (around $0.001 \times h_*$). The advantage of using AMR with respect to a uniform grid is the fewer grid points and faster simulation. For example, in the case where $b = 0.001 \times h_*$, a uniform grid has five times more

points than the AMR. Meanwhile, the simulation took 22 times longer.

The results are in very good agreement with the reference solution, which confirms the strength of the bi-Laplacian discretization with AMR.

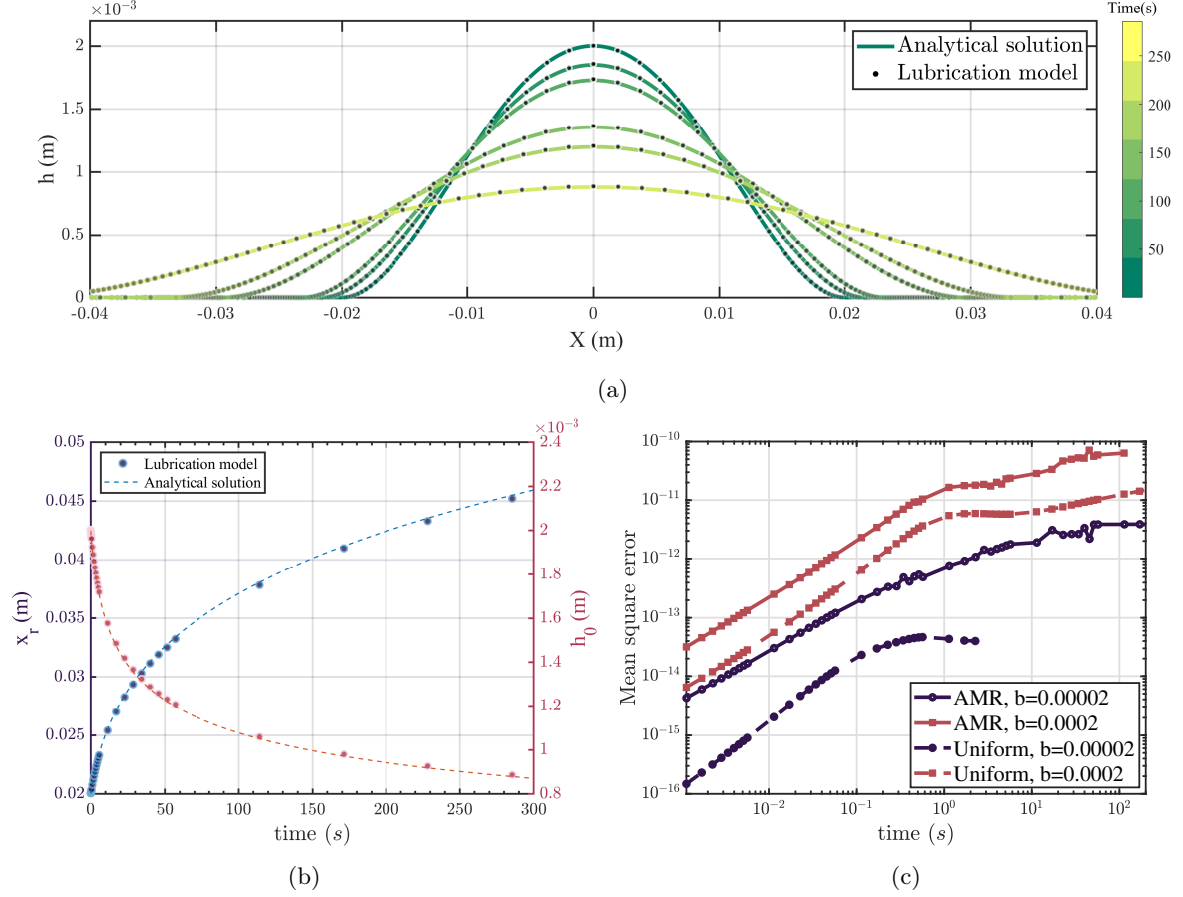


Figure 5.5: Spreading of the droplet driven by the curvature, (a) lubrication model prediction versus analytical solution for the evolution of the droplet. The time is indicated by the color map on the right. The numerical results are in good agreement with the analytical solution. (b) The droplet radius and maximum thickness obtained from the lubrication model are compared with the analytical solution. (c) The mean square error of the lubrication model compared with the analytical solution for uniform and AMR mesh with different values of b .

5.4.2 Spreading of a droplet driven by curvature and gravity

The objective of this case is to verify the implementation of both gravity and curvature in the lubrication model. As there is no analytical solution for such a case [Diez et al., 2000], the verification is achieved by comparing the spreading of droplets obtained with the lubrication model and a Volume of Fluid approach. The latter is a Navier-Stokes-based interface capturing approach that is used as a reference solution to verify the relevance of the reduced-order lubrication model.

We consider a droplet of silicon oil surrounded by air. Fluid properties are summarized in Table 5.3. The initial shape of the droplet is a semi-ellipsoid described by $\left(\frac{x}{x_*}\right)^2 + \left(\frac{y}{h_*}\right)^2 = 1$ where $x_* = 2\text{cm}$, $y_* = 0.2\text{ cm}$. The aspect ratio of the initial shape is consistent with the hypothesis of the lubrication model – *i.e.*, the film thickness is much smaller than the other dimension – which allows for a fair comparison between the two approaches. To focus on the effect of curvature and gravity avoiding challenges associated

with the three-phase contact line, we consider a 20 μm ($0.01h_*$) thick silicon oil film at the surface of the solid substrate. At the time $t = 0$, the droplet spreads under the action of gravity and surface tension. Navier-Stokes simulation provides a two-dimensional mapping of the fluid evolution onto the computational domain. This mapping is then depth-averaged to form a reference film thickness profile that is compared with the solution of the lubrication model.

Table 5.3: Fluid properties used in Section 5.4.2 to simulate the spreading of a droplet driven by curvature and gravity.

phase	density kg m^{-3}	viscosity Pa s	surface tension N m^{-1}
silicon oil	968	0.2	0.021
air	1	1×10^{-6}	

In the lubrication model, the free energy density is

$$\mathbb{W} = \sigma \left(1 + \frac{1}{2} h_x^2 \right) + \frac{\rho g h^2}{2}, \quad (5.34)$$

and the mobility is $M(h) = \frac{h^3}{3\mu}$. The fluid-fluid interface is considered a free surface because the shear stress of air onto the oil droplet is negligible, and we have $\mathbb{T}(h) = 0$. The Bond number and the time scale used in the simulation are $B_o = 180$, and $t_0 = 1/580$. This corresponds to a one-dimensional domain of 4 cm and a gravity field, $g = 9.8 \text{ m s}^{-2}$. The domain is discretized with non-uniform grid blocks, and AMR is used during the simulation at the tip of the droplet.

The Navier-Stokes reference solution is obtained using the Volume of Fluid solver of the Computational Fluid Dynamics open-source package OpenFOAM (<https://www.openfoam.org>), namely *interFoam* solver. The Volume of Fluid solves for the Navier-Stokes mass balance and momentum equations in both fluid phases as well as the evolution of the fluid distribution, α [Hirt and Nichols, 1981]. Surface tension effects due to interface curvature are described using Brackbill’s force [Brackbill et al., 1992]. The computational domain consists in a two-dimensional 100 mm $\times$ 5 mm box meshed with a uniform grid whose spacing in x and y direction is $\Delta x = \Delta y = 0.02$ mm. The phase field, α , is initialized using the droplet shape used in the lubrication model with $x_* = 10y_* = 2$ cm, which corresponds to the same Bond number as in the lubrication simulation. A 0.02 mm thick film prewets the bottom boundary. The bottom edge is a no-slip condition. The top and right boundaries are set as zero-gradient for velocity, pressure, and phase field. The left side is set as symmetry. The simulation is run for 20s with a constant time-step $\Delta t = 3 \times 10^{-7}$ s that satisfies Brackbill’s time-stepping criteria [Brackbill et al., 1992]. In order to obtain the film thickness along the horizontal direction from the Volume of Fluid simulation, the resulting two-dimensional phase field, α , is integrated over the vertical axis. The evolution of the droplet radius is obtained by integrating the phase field along the bottom boundary.

A comparison between the lubrication model and OpenFOAM Volume of Fluid results is seen in Fig. 5.6. We observe a very good agreement between the two approaches for the evolution of the droplet (Fig. 5.6a), the thickness of the droplet at the center, as well as the movement of the TPCP with respect to time (Fig. 5.6b). The overall difference between the lubrication model and the VOF approach predictions is shown in Fig. 5.6c. These results give confidence in the robustness of the numerical implementation of the lubrication model. In the following, we investigate the spreading of a droplet with gravity, surface tension, and disjoining pressure.

We also investigated the effect of the droplet size on the spreading. Two oil droplets of $x_* = 2$ mm; $y_* = 0.2$ mm and $x_* = 10$ mm; $y_* = 1$ mm are considered. They correspond to Bond numbers of 1.8 and

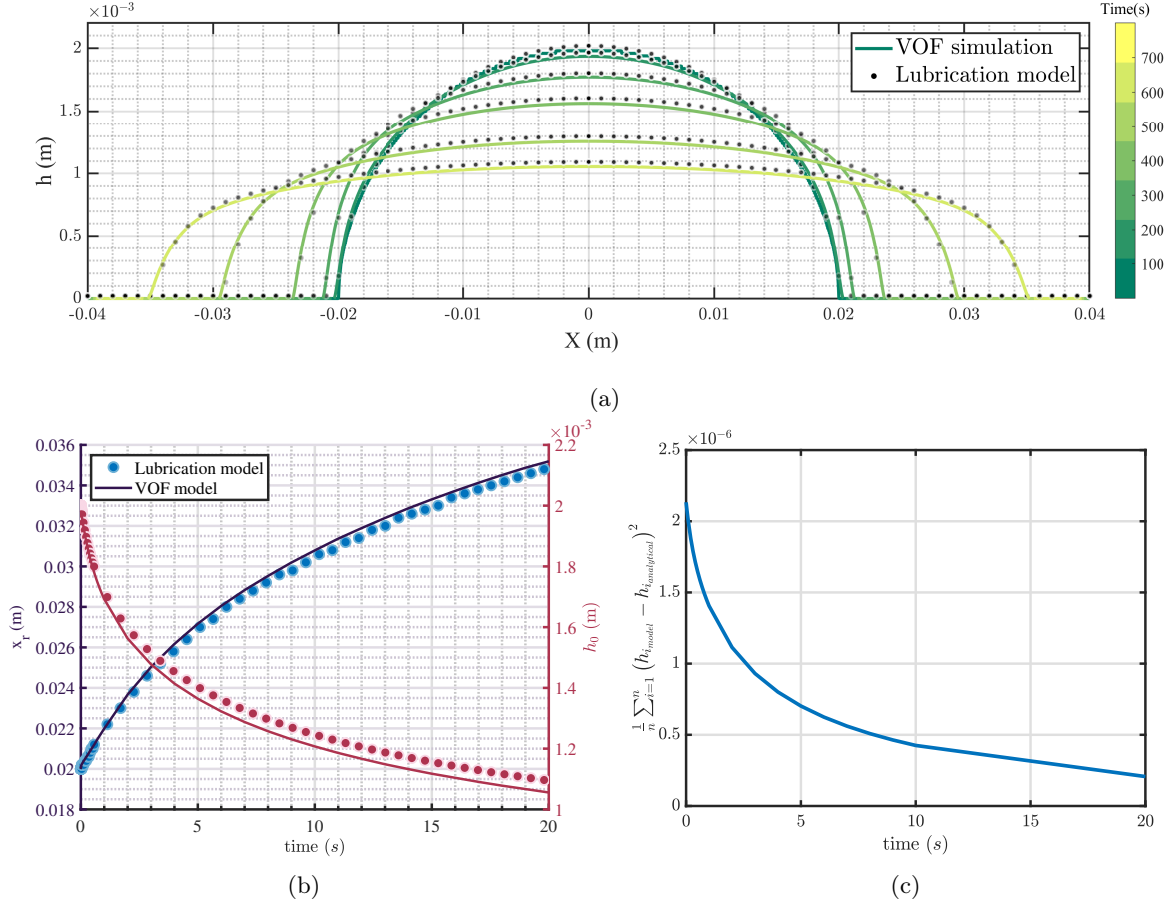


Figure 5.6: Comparison of our lubrication model and a two-phase flow solver of *OpenFOAM* for the spreading of silicon oil against air. (a) Profile of spreading of the droplet (gravity and curvature), time(s) scale on the right. The lubrication model shows good agreement with the two-phase flow solver of *OpenFOAM*. (b) Comparison of lubrication model with VOF for droplet radius and height of the droplet at the center. (c) Mean square difference between lubrication model and VOF film thickness predictions versus time.

180, respectively. At late time, the bigger droplet profile is close to a pancake shape, while the smaller droplet is closer to a lens shape. In Fig. 5.7, the advancing contact angle is plotted against the capillary number for the velocity at the TPCP for times $> 10^{-1}$ s. We notice that both Ca - θ results fit Tanner's law (i.e., $Ca \propto \theta^3$ which suggests that the lubrication model captures the apparent contact angle due to hydrodynamic viscous bending).

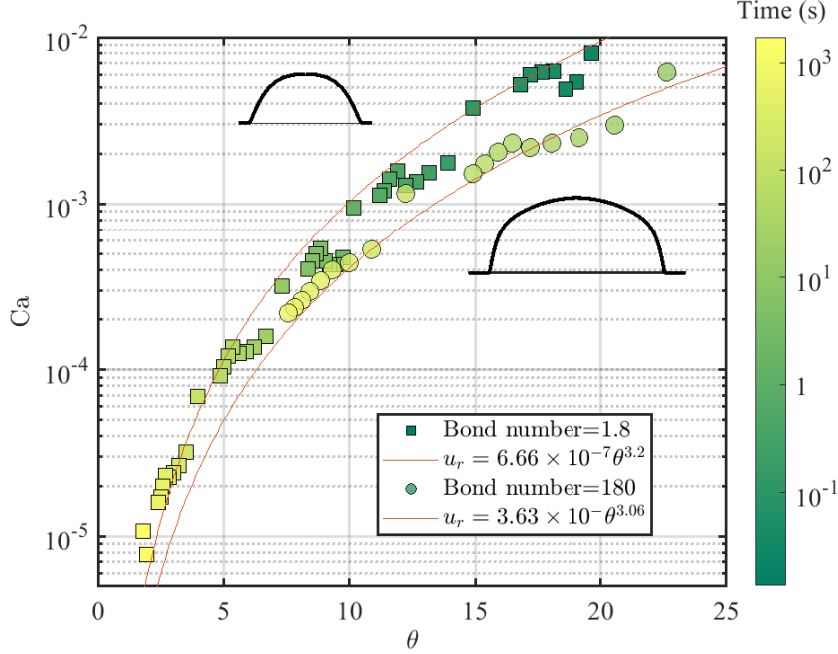


Figure 5.7: Capillary number versus advancing contact angle for different Bond numbers. The fitted curves are based on Tanner's equation.

5.4.3 Spreading of a droplet driven by curvature, gravity, and disjoining pressure

In this section, we investigate the spreading of water against oil on a calcite surface while changing the water's properties, including its salinity. This kind of simulation requires accounting for the effect of inter-molecular interactions in addition to surface tension and gravity potentials.

To model wettability alteration due to a change of salinity and pH, the free energy density of the film includes the curvature, gravity, and inter-molecular (Van der Waals, EDL, and hydration) interaction energy:

$$\mathbb{W} = \sigma \left(1 + \frac{1}{2} h_x^2 \right) + \frac{\rho g h^2}{2} + \sigma_{SL} - \sigma_{SV} + W_{VDW} + W_{EDL} + W_{Str}. \quad (5.35)$$

We assume a no-slip boundary condition on the calcite surface, and the mobility term is $M(h) = \frac{h^3}{3\mu}$. We also neglect the effect of stress on the water-oil interface, $\mathbb{T}(h) = 0$.

Disjoining pressure for high- and low-salinity waters

We consider three different water solutions that differ by their salinity, namely a high-salinity water and two low-salinity waters with different pH in accordance with the work of Mahani et al. [2015]. The high-salinity water is the formation water of a hydrocarbon reservoir, and the low-salinity water corresponds

to diluted seawater by 25 times. Mahani's experiment was carried out to relate the wettability alteration in low-salinity water flooding to electrostatic measurements on the interfaces. Here, we used their measurements to evaluate the EDL potential for the three water solutions. Inter-molecular interaction parameters are obtained using the values in Table 5.4. For both solutions, the Hamaker constant comes from Hough and White [1980], and the hydration potential parameters come from Israelachvili [2011]. For EDL calculation, the electric potential of the interface, ψ_i , is assumed to be equal to the zeta-potential of the interface, ζ_i .

The resulting disjoining pressures and their corresponding derivative versus thickness for the case of low- and high-salinity waters are plotted in Fig. 5.8. The first row (Fig. 5.8a, Fig. 5.8b) corresponds to a flat thin film whereas the second row (Fig. 5.8c, Fig. 5.8d) corresponds to a wedge with an angle of 45° . The film of low-salinity water (1) and (2) in the wedge case with an angle of 45° is stable for all the thicknesses since the derivative of disjoining pressure is positive, while for the high-salinity case, the stable thickness is below around 3 nm (Fig. 5.8d). However, by decreasing the angle, the range in which the film is stable changes. For the flat film, *i.e.*, zero angle, the derivative of the disjoining pressure is negative from very large thickness up until the thickness close to 2 nm for the high-salinity case. Whereas for the low-salinity (1) and (2), there is a mid-range thickness around 10 nm where the disjoining pressure and its derivative are positive, resulting in a thicker stable film compared to the high-salinity case. We consider the flat thin film curves for the stability analysis since it represents the lower value of film thickness for the film stability and the worst-case scenario.

Table 5.4: Parameters used for simulation of spreading droplets considering curvature, gravity, and inter-molecular force

VDW [Hough and White, 1980]					
Hamaker constant (A) J				1.3×10^{-20}	
EDL [Mahani et al., 2015]					
water	ζ_1/ζ_2 [mV]	ionic strength (ρ_∞)	pH	ϵ	T [K]
High-salinity	+5/-3	3.66	7	78.54	300
Low-salinity (1)	-15/-25	0.035	7		
Low-salinity (2)	+5/-20	0.035	12		
Hydration potential [Israelachvili, 2011]					
Hydration amplitude (w_0) Jm ⁻²				30×10^{-3}	
Hydration length-scale (λ_0) nm				0.8	
Fluid properties					
water		density	viscosity	surface tension	
		[kg/m ³]	[Pa × s]	[N/m]	
high-salinity		1000	10 ⁻³	0.0118	
low-salinity		1000	10 ⁻³	0.0131	

Impact of salinity and pH on wettability properties

The initial shape of the droplet is a semi-ellipsoid described by $\left(\frac{x}{x_*}\right)^2 + \left(\frac{y}{h_*}\right)^2 = 1$, where $x_* = 0.1$ mm; $y_* = 0.01$ mm corresponding to a Bond number of 0.0166. The computational domain is a 1D segment

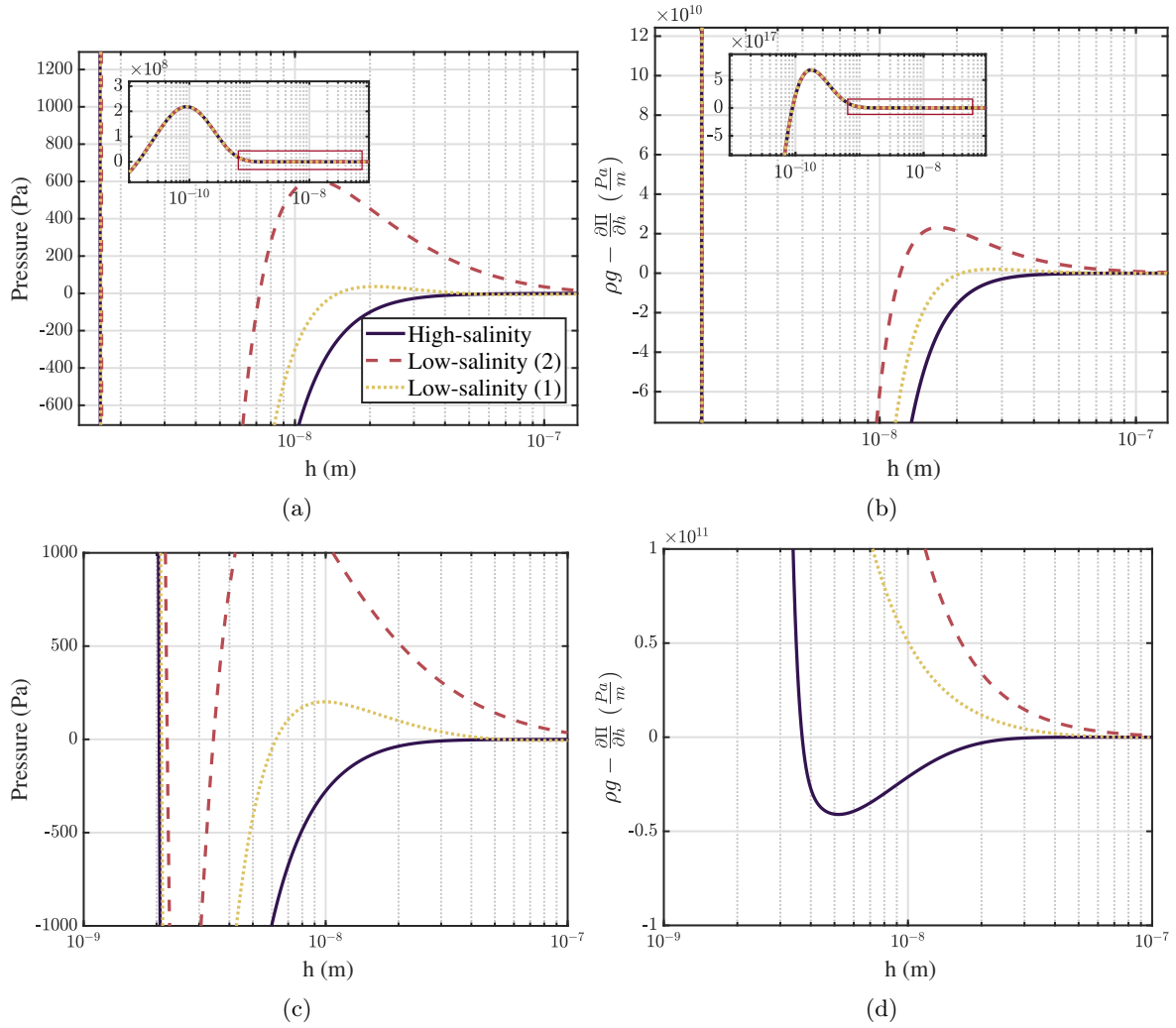


Figure 5.8: Inter-molecular property for the thin film of water in the system of water/oil/carbonate. (a,b) Disjoining pressure and its derivative for a flat film. The inset represent the overall range for the film thickness and showing the current range in the red rectangle. (c,d) Disjoining pressure and its derivative for a wedge film with the contact angle of 45 °.

of length $4 \times x_*$, discretized non-uniformly with $\Delta x_{max} = 0.05 \times y_*$ and $\Delta x_{min} = 0.5 \times b$. The droplet is deposited on a precursor film of thickness, $b = 10\text{nm}$, that is thick enough to avoid premature unstable films during spreading according to the stability criterion.

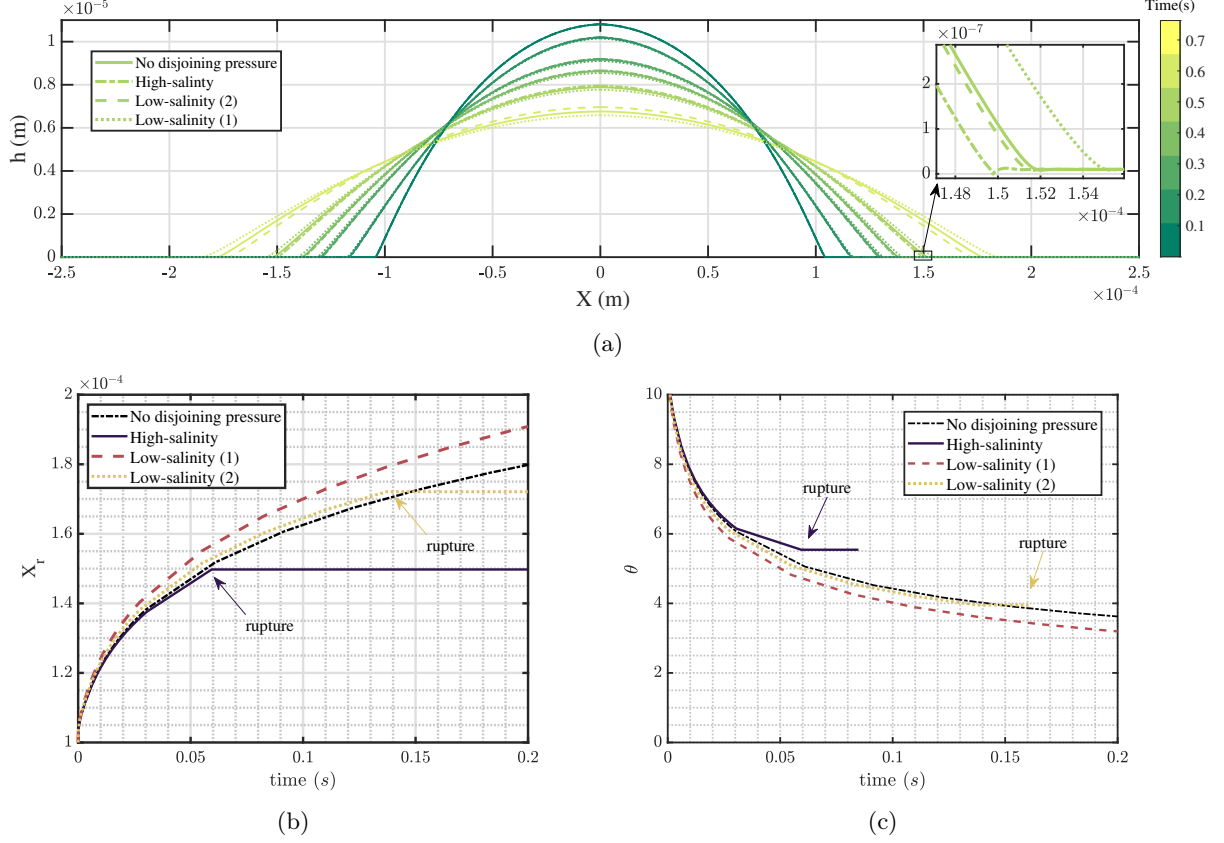


Figure 5.9: Spreading of water in the system of water/oil/carbonate considering curvature, gravity, and disjoining pressure with the Bond number of 0.0166. (a) The plot of the water droplet profile for three different water types. Time is indicated by the color bar. In the inset plot, the profile of the film close to TCP is shown at the time of rupture for high-salinity. The high-salinity water advances slower in comparison with the low-salinity cases and undergoes a rupture eventually. The transition of low-salinity (1) water to the precursor thickness occurs more smoothly compared to the high-salinity case. (b) Evolution of droplet radius. The spreading of high-salinity and low-salinity (2) water is halted at around 0.05 and 0.15 seconds, respectively, due to thinning of the precursor film at TCP. (c) Variation of the contact angle at the inflection point with respect to time.

Simulations are run for 1 second or until the film ruptures. The evolution of the droplet spreading with the Bond number of 0.0166 is shown in Fig. 5.9a for the three different cases as well as the case without disjoining pressure. We also plot the evolution of the wetting area in Fig. 5.9b as well as the contact angle variation with respect to time (Fig. 5.9c). The latter is obtained by computing the slope of the interface at the inflection point. We observe different spreading patterns for the two types of water. On the one hand, the high-salinity water spreads for around 0.05 seconds until the precursor film gets ruptured, which stops the spreading. The equilibrium state corresponds to a contact angle $\theta \approx 6$. On the other hand, low-salinity (1) water droplet spreads faster, wetting the whole solid substrate, in agreement with the disjoining pressure curve (see Fig. 5.8a). The spreading of low-salinity water (2) follows a similar behavior to the high-salinity water, but the film rupture happens later. This situation corresponds to a contact angle, $\theta \approx 4$.

In Fig. 5.10, the contact angle is plotted against the capillary number for the velocity of the TPCP during the spreading of the thin film for the time $> 10^{-3}$ s. The capillary number is defined as $Ca = \frac{\mu u}{\sigma}$. Interestingly, the intermediate-time data points fit into an equation of $Ca = a \times \theta^3$, similar to Tanner's law [Tanner, 1979] or Cox-Voinov dynamic contact angle [Voinov, 1976, Cox, 1986].

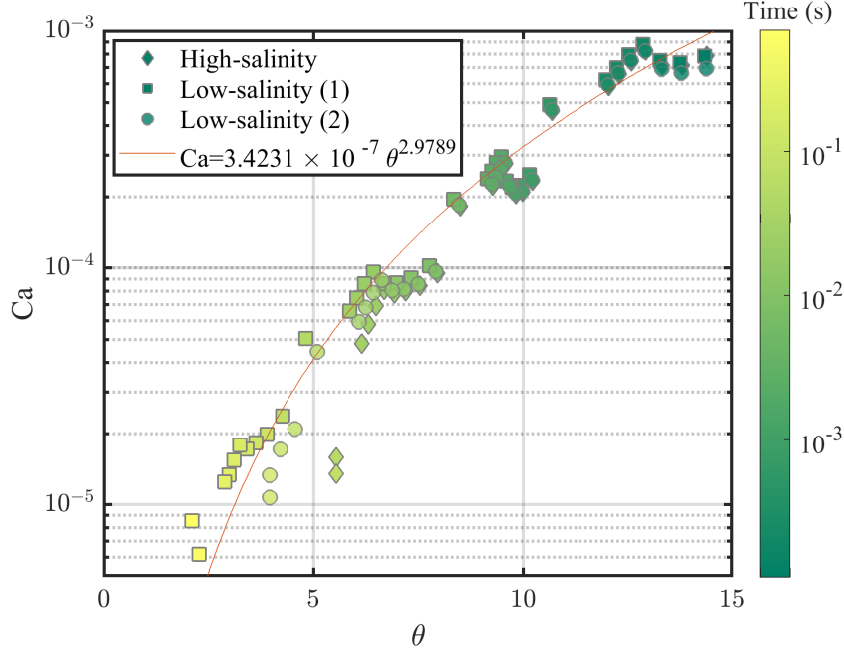


Figure 5.10: Capillary number versus contact angle for spreading of the thin film with different water salinity in the system of water/oil/carbonate considering curvature, gravity, and disjoining pressure. The fitted curves are based on Tanner's equation for contact angle.

The different behaviors observed for the three waters are explained using the disjoining pressure derivative: a film with a thickness higher than ~ 10 nm is stable for low-salinity cases, whereas for the high-salinity water, films thicker than around 1 nm are unstable and will eventually rupture by introducing a perturbation. To analyze further the mechanisms leading to rupture, we plot the evolution of the minimum film thickness at the vicinity of the TPCP (see Fig. 5.11). We see an oscillatory behavior of the film thickness at TPCP versus time. This oscillation exists even in the absence of disjoining pressure (curvature is the only driving mechanism for the spreading), suggesting that instabilities are initiated by curvature effects. The oscillation can be enhanced or dampened based on the disjoining pressure. For the low-salinity water (1), the oscillation is dampened around a constant thickness corresponding to a stable film. Therefore, the TPCP spreads until complete wetting. For the low-salinity (2) and high-salinity waters, the minimum thickness decreases down to values for which the disjoining pressure corresponds to unstable films that eventually break up. For high-salinity water, the oscillations diverge, leading to a premature film rupture.

Effect of the precursor film thickness

In this part, we investigate the effect of the precursor film thickness on the droplet spreading for only the high-salinity water case because we are mainly interested in determining the effect of the initial precursor. We consider a precursor thickness b ranging from 0.5 to 80 nm. Different spreading behaviors are expected because the disjoining pressure derivative (see Fig. 5.8b) is negative for $b > 1$ nm (unstable film) and

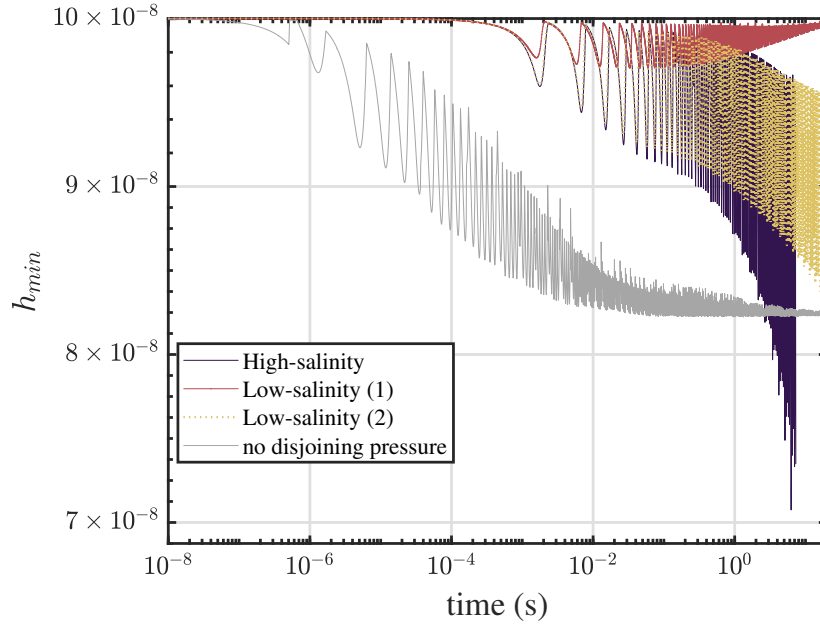


Figure 5.11: The oscillation of TPCP thickness versus time for spreading of water with different properties. The oscillation in the case of low-salinity (1) gets dampened in late times, whereas for high-salinity, it grows until the rupture of the film. For low-salinity (2), the growth of amplitude of oscillation becomes steady in late times.

tends toward a positive asymptote for $0.2 \text{ nm} < b < 1 \text{ nm}$. The effect of the precursor film thickness on the droplet radius evolution and the time-to-rupture is seen in Fig. 5.12. We observe two spreading patterns leading to stationary droplets that depend on the initial precursor film thickness, b : *i*) film rupture, and *ii*) TPCP equilibrium.

On the one hand, for precursor films larger than 1 nm , the droplet spreading comes to a halt after some time due to film rupture. This is expected as the disjoining pressure derivative is negative for $b > 1 \text{ nm}$ (see Fig. 5.8). The smaller the precursor films, the earlier the film rupture, and the smaller the droplet radius. Note that if the droplet radius evolves almost linearly with b , the time-to-rupture response is not linear.

On the other hand, for precursor films smaller than 1 nm , we observe an increase in the precursor film stability, for which the spreading stops not because of film rupture but because the TPCP slows down until it reaches an equilibrium state. This is expected because the disjoining pressure curve is strongly repulsive for $0.2 \text{ nm} < b < 1 \text{ nm}$.

These simulations highlight two different behavior due to the initial precursor film. It means that for TPCP advancing on a dry surface, the film is stable, whereas, in advancing on a pre-wet solid, the film at TPCP will be unstable and causes rupture. Simulation results for the ultra-thin film should be interpreted cautiously because the continuum mechanics hypothesis breaks down for films below $\sim 1 \text{ nm}$ since the Knudsen number (ratio between mean free path over the length scale) at this thickness is around 0.1 corresponding to the transition between continuum scale and molecular scale [Gad-el Hak, 1999].

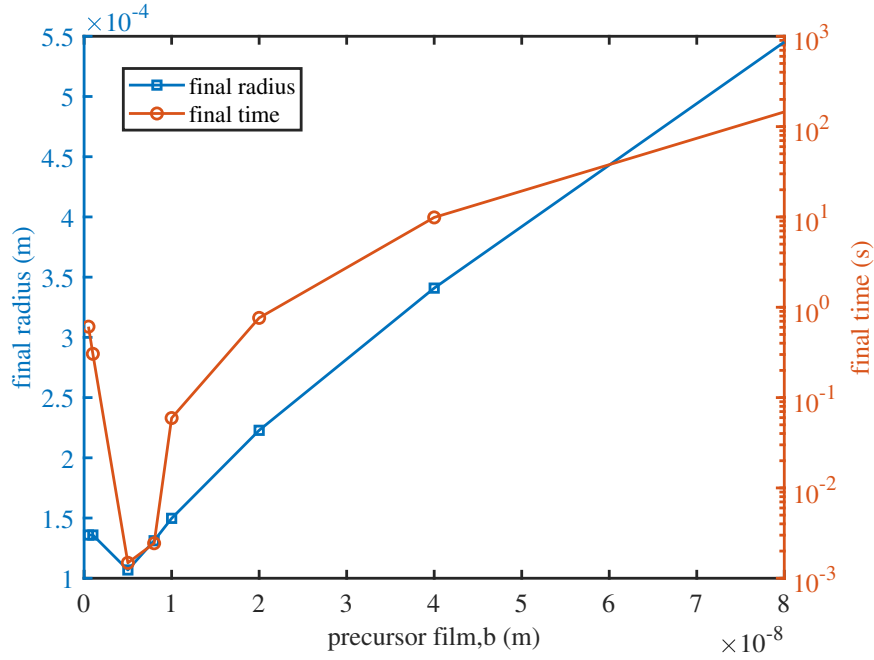


Figure 5.12: The final radius of the droplet of high-salinity water spreading on the calcite surface in the presence of oil for different precursor water film thicknesses and its corresponding rupture time.

5.5 Conclusion

We developed a lubrication model that accounts for inter-molecular interactions to model the wettability behavior of a three-phase system. The model is physically rooted and does not rely on the concept of contact angle. Instead, inter-molecular interactions are described using disjoining pressure concept, including Van der Waals, Electric Double Layer, and hydration interactions. This approach can predict wettability alteration due to the effect of fluid composition, salinity, and pH. Therefore, our lubrication model with slope-dependent disjoining pressure can be used to characterize contact angles for different chemical and physical parameters.

The numerical implementation of the model was verified using cases for which reference – analytical and numerical – solutions exist. The Adaptive Mesh Refinement feature is key to resolving the contact line dynamics in acceptable simulation times. A similar procedure can be used to extend our one-dimensional lubrication model to 2D.

The low- versus high-salinity water examples presented in this chapter highlight the capabilities of our lubrication model for thin films to simulate wettability alteration due to a change in salinity conditions. Indeed, changing pH and salinity alters the EDL and, to some extent, the hydration force, which influences the precursor film stability and eventually leads to three spreading behaviors: spreading with complete wetting, droplet immobilization by film rupture, and immobilization without rupture by force equilibrium. We have also shown that the initial thickness of the precursor film strongly impacts the spreading of a droplet.

Future work will focus on the inclusion of slope-dependent EDL models obtained in section 4 in the lubrication model for thin-film. Furthermore, the model can be modified to address spreading on the surface with roughness, as well as studying the chemical non-equilibrium system where the salinity/pH of the wetting phase changes as the film spreads. The dynamics of the non-wetting fluid has been neglected

in this work. Future lines of research concern the coupling of our lubrication model with a Navier-Stokes-based solver to account for larger-scale hydrodynamics and the mutual shear stress at the fluid-fluid interface.

Chapter 6

Conclusion and perspective

In this thesis, we studied the physico-chemical phenomena close to the contact of a wetting phase on the solid substrate to describe the wettability behavior in multiphase systems. In doing so, we focused first on the molecular scale, where we obtained the effect of the disjoining pressure on the wettability.

- We used Van der Waals (VDW) inter-molecular interaction to describe the wettability of a system comprised of non-polar constituents. We observed that considering the geometry of the wetting phase close to that contact region influences the VDW interaction, providing a better agreement with the experimental data, especially for a partially wetting system with a small contact angle (smaller than 30°).
- We investigated the role of the wetting phase geometry close to the contact region on the electrostatic component of the disjoining pressure. In addition, we considered a more physical boundary condition that arises from the interaction of ions in the wetting phase and the sites on the solid substrate. It will result in a charge accumulation on the interface. We observed that the geometry influences the electrical double layer (EDL) interaction. The normal pressure of EDL, which is typically associated with the EDL component of disjoining pressure, depends on the contact angle as well as the thickness of the wetting phase. Furthermore, having a wedge-shaped geometry gives rise to the tangential component of the electrostatic pressure, whose value also depends on the wedge angle. Furthermore, the tangential component causes a change in surface tension close to the contact point, which leads to a local slip.
- The accurate representation of the wetting phase close to that contact will result in a disjoining pressure that depends not only on the wetting phase's thickness but also on its slope. In order to include the effect of disjoining pressure, in the larger scale model, we used the lubrication theory. We included a slope-dependent disjoining pressure into the lubrication model and investigated the dynamics of the wetting phase. From modeling the spreading of water with different salinities against oil on carbonate rock, we obtained different spreading behaviors corresponding to different wettability properties.
- The film stability is greatly influenced by the inter-molecular forces, which consequently affects the spreading of the wetting phase. In addition, the inter-molecular force obtained from an accurate representation of wetting phase geometry at the contact results in tangential stress, which acts as a slip boundary condition close to the contact.

The future work of this thesis can be categorized into two branches. The first focuses on including other components in the surface complexation model, while the second path is coupling the lubrication model with other up-scale hydrodynamic modeling tools.

- The dissolution of CO_2 into the water and its effect on the inter-molecular force can be studied readily by adding the appropriate surface speciation into our coupled Poisson-Boltzmann-surface complexation model (PB-SCM) solver. Considering other pairs of fluids is also possible by considering the corresponding surface speciation in the SCM model, *e.g.* the oil/brine/carbonate system. Furthermore, through the lubrication model, the dynamic effect on wettability can also be observed for such systems.
- The results of film spreading obtained from the lubrication model can be compared with experimental data acquired from electron microscopy. The electron microscopy method is able to provide *in situ* measurements at molecular scale. These measurements can be used as validation of the model and calibration of inter-molecular interactions.
- The coupling of the lubrication model with a two-phase flow simulator is essential since we can investigate other effects, such as shear stress due to the non-wetting phase. In addition, the effect of disjoining pressure can be observed on a larger scale, such as a network of interconnected pores and throats.

Appendix A

Appendices

A.1 Volume of fluid simulation of two-phase flow

Finding analytical solutions to these sets of differential equations for even simple geometries is difficult. Therefore, we can find the solution numerically through discretization in time and space. The choice of discretization method depends on the geometry and the set of differential equations. *Computational* fluid dynamics (CFD), Lattice Boltzmann methods (LBM), and smoothed particle hydrodynamics (SPH) are known as direct methods, while pore network modeling is an example of the indirect method [Soulaine et al., 2021b]. CFD usually relies on *finite volume method* (FVM) to discretize the Navier-Stokes and mass balance since it preserves the conservation of mass in its formulation. Here, we used the Volume of fluid for the two-phase flow simulation. *Volume of fluid* (VOF) technique can be used to integrate the differential equation for the domain and develop one set of differential equations for both phases. Other techniques that deal with two-phase flow are *level-set* [Abu-Al-Saud et al.] and phase field (diffuse interface method).

A.1.1 Integration of mass and momentum equation

In the VOF method, one momentum and mass balance set is solved for both phases with a modification term in the governing equations. The coloring function is introduced to identify each phases of a, b (Fig.A.1):

$$\begin{cases} \alpha = 1 & \text{phase } a \\ 0 < \alpha < 1 & \text{region between phases} \\ \alpha = 0 & \text{phase } b. \end{cases} \quad (\text{A.1})$$

The density and viscosity can be written as:

$$\begin{aligned} \rho &= \alpha \rho_a + (1 - \alpha) \rho_b, \\ \mu &= \alpha \mu_a + (1 - \alpha) \mu_b. \end{aligned} \quad (\text{A.2})$$

By volume averaging the mass balance equation (eq.2.1) and using the boundary condition at the interface, we can derive the phase continuity [Carrillo et al., 2020]:

$$\frac{\partial \alpha}{\partial t} + \nabla \cdot (\alpha \langle \mathbf{u}_a \rangle) = 0, \quad (\text{A.3})$$

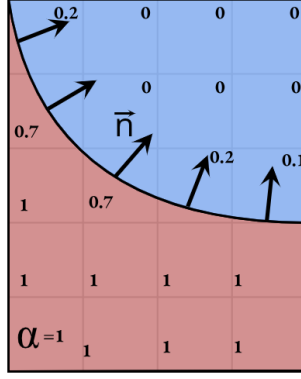


Figure A.1: Real sharp interface and the color function representation of the interface for the VOF

Which $\langle \rangle$ refers to the average over the control volume. The phase continuity equation for the second phase can be written similarly. We add and subtract the following terms in order to write the phase continuity equation with respect to the velocity of the control volume rather than the velocity of one phase [Rusche, 2003]:

$$\frac{\partial \alpha}{\partial t} + \nabla \cdot [\alpha \langle \mathbf{u}_a \rangle + \alpha \langle \mathbf{u}_a \rangle - \alpha \langle \mathbf{u}_a \rangle + (1 - \alpha) \langle \mathbf{u}_b \rangle - (1 - \alpha) \langle \mathbf{u}_b \rangle] = 0, \quad (\text{A.4})$$

which simplifies as:

$$\frac{\partial \alpha}{\partial t} + \nabla \cdot (\alpha \langle \mathbf{U} \rangle) + \nabla \cdot [\mathbf{U}_r \alpha (1 - \alpha)] = 0, \quad (\text{A.5})$$

where, $\langle \mathbf{U} \rangle = (\alpha \langle \mathbf{u}_a \rangle + (1 - \alpha) \langle \mathbf{u}_b \rangle)$ and compression velocity, $\mathbf{U}_r = \langle \mathbf{u}_a \rangle - \langle \mathbf{u}_b \rangle$. Adding continuity equation for both phases will give:

$$\nabla \cdot (\langle \mathbf{U} \rangle) = 0, \quad (\text{A.6})$$

The one-field formulation of the NS equations for multi-phase flows is [Hirt and Nichols, 1981, Brackbill et al., 1992, Tryggvason et al., 1998]:

$$\frac{\partial (\rho \langle \mathbf{U} \rangle)}{\partial t} + \nabla \cdot (\rho \langle \mathbf{U} \rangle \langle \mathbf{U} \rangle) = -\nabla p + \nabla \cdot \mu (\nabla \langle \mathbf{U} \rangle + \nabla \langle \mathbf{U}^T \rangle) + \mathbf{F}_{body} + \mathbf{F}_s, \quad (\text{A.7})$$

where the last term on the right side of the equation is surface tension forces and is calculated on the interface in the next section.

A.1.2 Surface force

The problem that arises here is the discontinuity (of *e.g.* density or α) across the interface. Brackbill et al. [1992] proposed a continuum surface force (CSF) model as a solution for this problem, in which they used a delta function to volume integrate the surface force into volume force:

$$\mathbf{F}_s = \sigma \kappa \nabla \alpha, \quad (\text{A.8})$$

where κ is the curvature of the interface and is calculated as:

$$\kappa = -\nabla \cdot \frac{\nabla \alpha}{|\nabla \alpha|}. \quad (\text{A.9})$$

The surface tension force is calculated using the gradient of the coloring function, which means numerical fluctuations in the color function can produce erroneous surface forces and cause an unreal velocity field, which is also known as spurious current [Pavuluri et al., 2018]. To rectify this problem, Raeini et al. [2012] proposed a sharp surface force model (SSF), where they modified the color function that is used for the surface tension force calculation as:

$$\alpha_{sharp} = \frac{1}{1-2C}[\min(\max(\alpha, C), a-C) - C], \quad (\text{A.10})$$

where C is in the range of $[0, 0.5]$. This function renders the value for the color function smaller than C to zero for the calculation of surface force.

A.1.3 Time stepping criteria

Since the treatment of capillary force is done explicitly, criteria for the time stepping should be imposed to ensure the stability of the solution. Brackbill et al. [1992] derived the following criteria for the time step limit:

$$\Delta t_{max} = \sqrt{\frac{\rho_{ave} \Delta x^3}{2\pi\sigma}}, \quad (\text{A.11})$$

where $\rho_{ave} = \frac{\rho_a + \rho_b}{2}$.

A.1.4 Simulation results and discussion

We used *OpenFOAM* as the numerical tool to simulate the flow in pore-scale. *OpenFOAM* is an open-source toolbox written in C++ that supports various numerical solvers for continuum mechanics problems, notably for fluid flow problems. We compare the results from the simulation of two-phase in pore-scale with one experiment and another numerical model run by *COMSOL*. This simulation aims to understand the capabilities and limitations of the currently used model to model wettability in two-phase flow. We performed another simulation corresponding to a micro-PIV experiment of spreading the wetting phase in a capillary tube. This simulation aims to compare the velocity profile close to the three-phase region with the experiment.

Two-phase flow in porous media

Here, the objective is to investigate the effect of wettability on the two-phase pore-scale simulation. Initially, we used a generic 2-D pore and throat network that resembles the porous media (fig.A.2).

The meshing is performed by constructing a 2-D rectangular mesh of $0.18 \mu\text{m} \times 0.112 \mu\text{m}$ for each grid. Then, the grain was removed from the mesh, and a refining step was performed on the surface of the grain (fig.A.3). The grids on the surface were smoothed to obtain the profile of the solid. Finally, a refined layer was added to the surface of the grain to improve the numerical accuracy.

Single-phase simulation

We wanted to obtain the corresponding permeability of the domain. Therefore, we performed a single-phase simulation first. We used a SIMPLE solver of *OpenFOAM* to simulate the single flow in a network of pores and throats. SIMPLE (semi-implicit method for pressure linked equation) algorithm is used for the steady-state flow and is an iterative method. The momentum equation is solved based on an initial guess for velocity and pressure. The results are corrected by the pressure correction equation for the

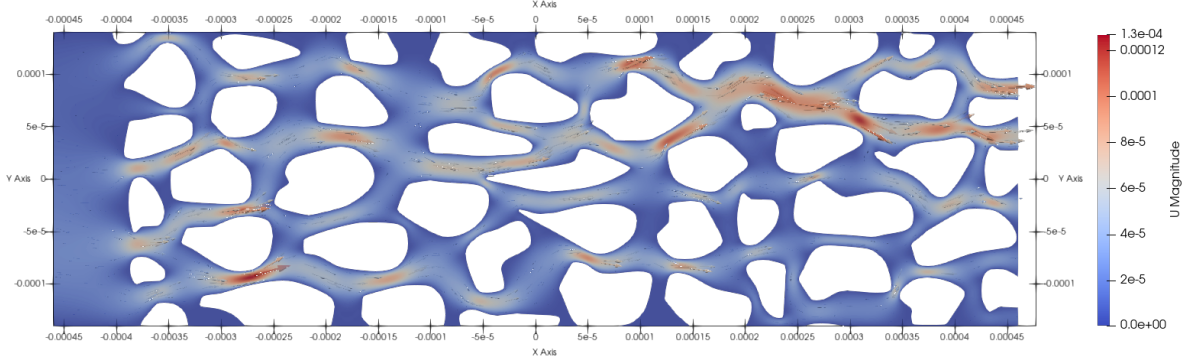


Figure A.2: Single phase flow in porous media [Geometry courtesy of Cyprien Soulaïne]. The white indicates the matrix of the porous medium. The pressure gradient of 0.0001 Pa was imposed for the flow, and the permeability ($K_x = 12.45$) for a single phase was obtained.

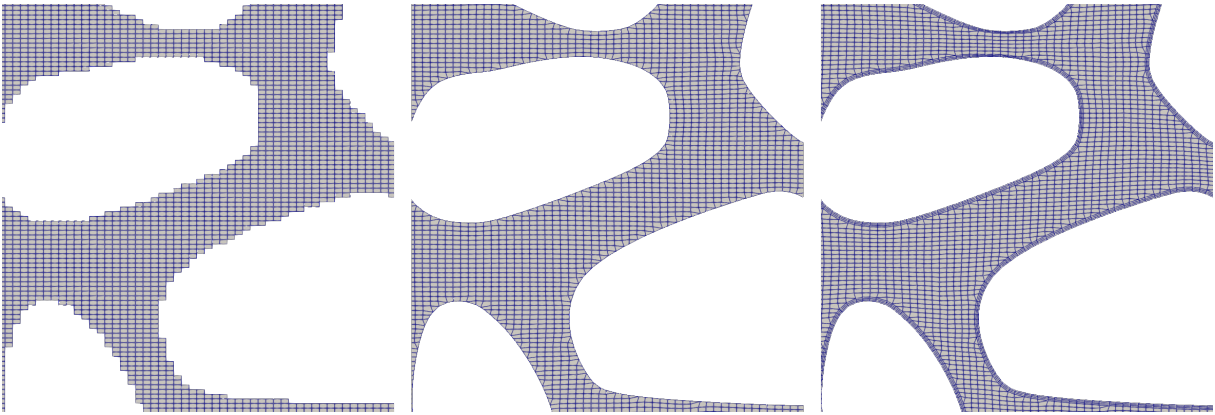


Figure A.3: Meshing for the domain. The left image is the result of removing the grain from the block of rectangular mesh. The middle image is the result of smoothing the mesh on the surface of the grain. The refined layer is added to the solid surface for the right image.

mass flux, and the pressure is updated. The iteration continues until the velocity and pressure accuracy meet the required criteria.

We imposed a pressure gradient of 0.0001 Pa on the geometry, and the velocity is calculated. In order to obtain the permeability, we used the following equation obtained from 1.1:

$$K_X = \mu \frac{L}{\Delta P} \frac{1}{V} \int_V u_x dv. \quad (\text{A.12})$$

We obtain $K_x = 12.45$ Darcy, and the porosity is 56.5% .

Wettability effect

We performed two-phase simulations to observe the effect of wettability and contact angle on the flow. The initial distribution of phases is seen in Fig.A.4, where the injecting fluid is shown with red, and the blue represents the displaced fluid. We used the *InterFOAM* solver of the OpenFOAM package. *InterFOAM* solves the VOF equations introduced earlier in this chapter. The computational domain is set to be initially saturated with one fluid (blue), and the invading fluid is injected from the left. The invading phase has a $\mu = 6 \text{ cp}$ and $\rho = 1000 \frac{\text{kg}}{\text{m}^3}$. The displaced phase has a $\mu = 1 \text{ cp}$ and $\rho = 726 \frac{\text{kg}}{\text{m}^3}$. The interfacial tension is 51 dyn/cm , and the contact angle is set. The results of the two-phase pore-scale

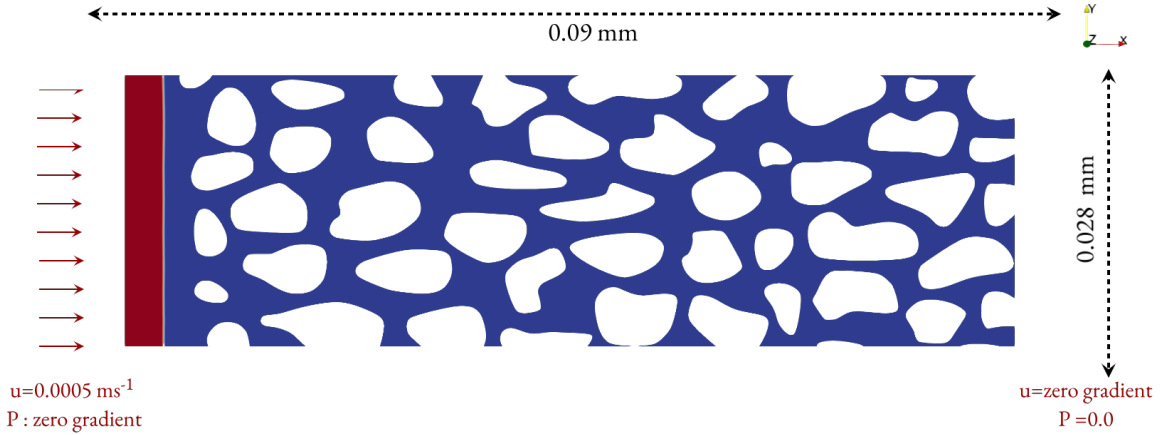


Figure A.4: Simulation case geometry, red and blue are invading and displaced phases, respectively, and the grain is depicted by white.

simulation can be seen in the table A.1. The results indicate how changing the contact angle, which is only applied on the three-phase contact line, affects the residual displaced saturation and the relative permeability. In order to investigate further the reliability of this two-phase simulation, we look at the fluid distribution and compare it with some related experiments in the literature in the next section.

Table A.1: The result of two-phase pore-scale simulation with different wettability conditions with respect to the residual saturation and relative permeability. The simulation is done with the *InterFOAM* solver of *OpenFOAM*. For the invading phase and the displaced phase, $\mu = 6 \text{ cp}$, $\rho = 1000 \frac{\text{kg}}{\text{m}^3}$ and $\mu = 1 \text{ cp}$ and $\rho = 726 \frac{\text{kg}}{\text{m}^3}$ respectively. The interfacial tension is 51 dyn/cm .

Contact angle	displace-phase residual saturation	relative permeability of invading phase
30	0.0055	0.316
90	0.056	0.318
120	0.09	0.26

Discussion

The fluid distribution on one of the simulation cases shows the result for the drainage flow, where the non-wetting phase displaces the wetting phase, as shown in Fig.A.5.

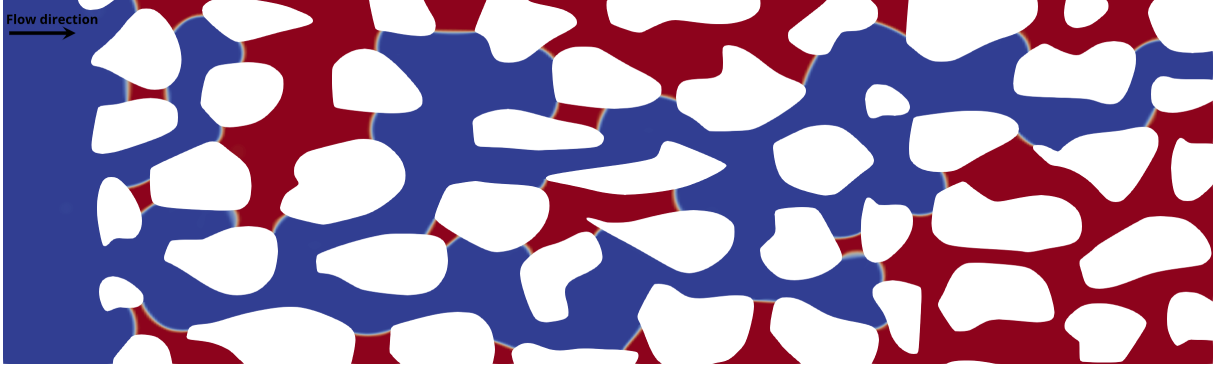


Figure A.5: Distribution of different phases in the pores. The process is the drainage of the wetting phase (red) by the non-wetting phase (blue) with *OpenFOAM*

However, for the case of displacement of the non-wetting phase by the wetting phase, we noticed some trapped phase on the boundary of the solid (fig.A.6). The non-wetting phase will get trapped on the solid surface, producing droplets.

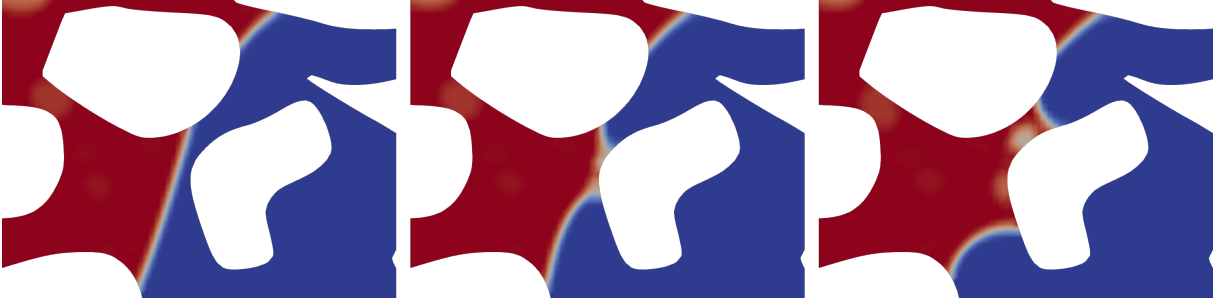


Figure A.6: Movement of interface from left to right. The droplet appears after the interface spreads on the solid surface, where the wetting phase (red) displaces the non-wetting phase (blue). CSF method is used for surface force.

We simulated both no slip and partial slip boundary conditions on the solid surface. In order to minimize the effect of the interface on the formation of this trapped droplet, we changed the calculation of the surface force in the solver from the default method in the *InterFOAM*, which is CSF, and implemented the SSF method. However, there was a slight improvement regarding the droplet formation (fig.A.7).

In order to find out if the formation of this trapped phase is not because of the irregularities in the surface of the grain, we simplified the geometry of the solid phase by considering only one circular grain in the middle of the domain. The grain and mesh geometry is shown in fig.A.8. We noticed that the same droplet is created just behind the grain.

In order to confirm if this trapped phase is physical or not, we compared the result with a similar micro-model experiment by Lee et al. [2015]. In their experiment, the flow goes through a network of circular grains in a domain with the dimensions of $50\mu m \times 1000\mu m \times 18mm$. Based on their images, the velocity of the interface is $U_{interface} \approx 2 \times 10^{-3} m/s$. The fluid properties they used in their experiments can be found in the table A.2.

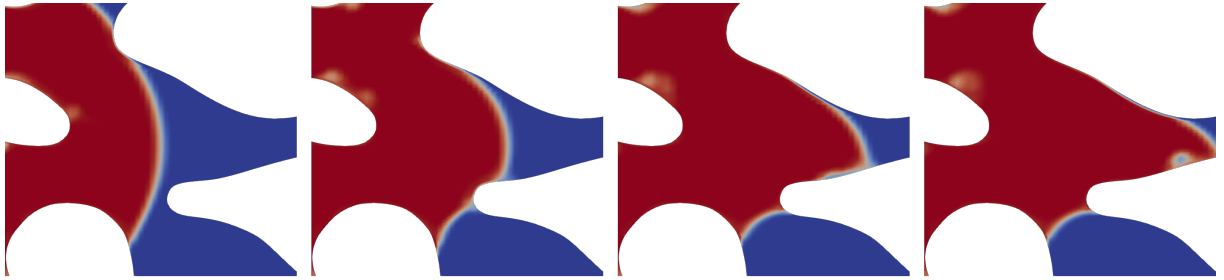


Figure A.7: Movement of interface from left to right. The droplet appears after the interface spreads on the solid surface, where the wetting phase (red) displaces the non-wetting phase (blue). SSF method for the surface force

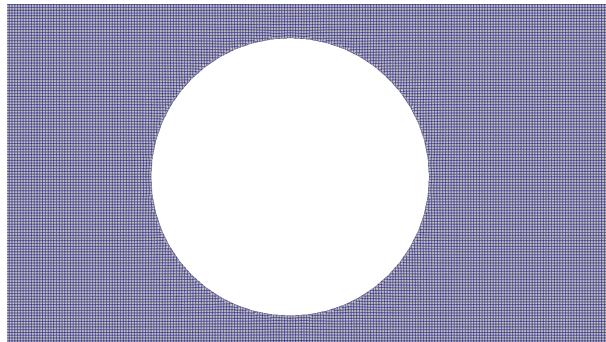


Figure A.8: Mesh of the circular grain

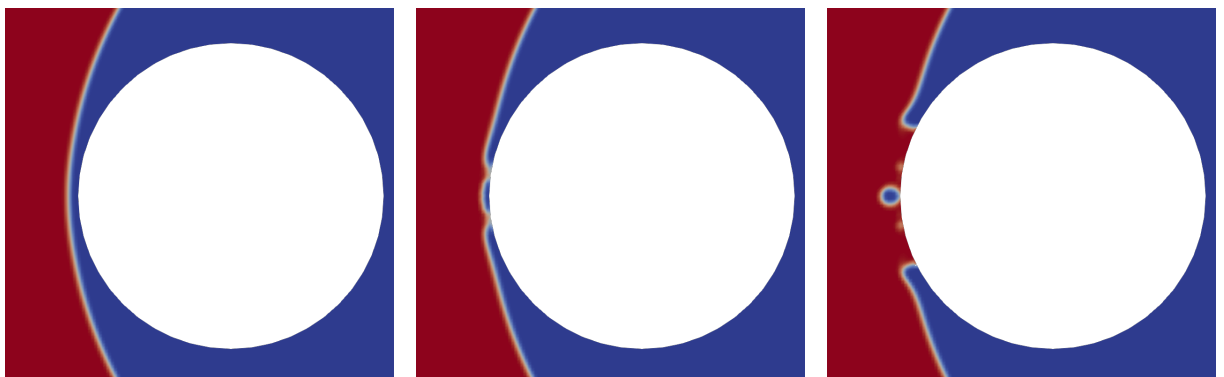


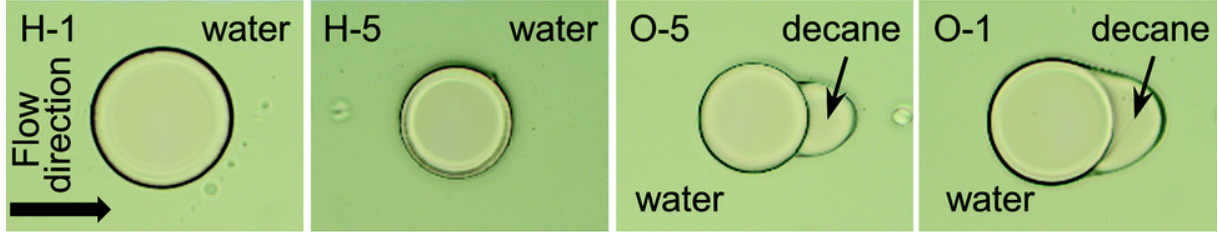
Figure A.9: Movement of interface from left to right for the circular grain. The droplet appears after the interface spreads on the solid surface.

They injected water in the micro model filled with decane (A in Fig.A.10), where the wettability of the circular grain changes from highly water-wet (H-1) to highly oil-wet (O-1). They also injected decane in the micro-model, initially filled with water (B in Fig.A.10). The droplet formation is seen in the micro model experiment but not for the same simulation case as our study which corresponds to the A-H-1 case in the fig.A.10. Furthermore, the trapped bubble is formed after the grain, as shown in Fig.A.10.

phase	density (kg/m^3)	viscosity (cp)	surface tension $dyne/cm$	reference
water	1000	1	51	[Lee et al., 2015]
decane	726	0.85		
water	1000	1	72.86	[Jahanbakhsh et al., 2021]
air	1.2	1.8×10^{-2}		

Table A.2: Fluid properties for the experiment of Lee et al. [2015] and simulation of Jahanbakhsh et al. [2021]

A Water displaces decane



B Decane displaces water

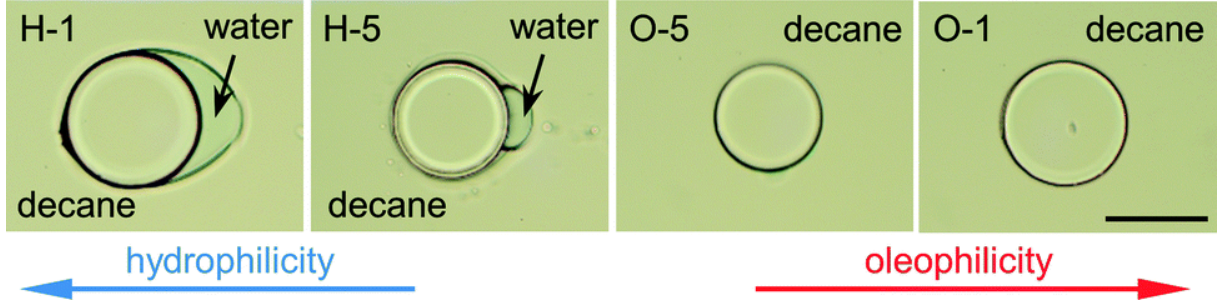


Figure A.10: Flow of water and decane and the formation of droplet [Lee et al., 2015]. The wettability of the circular grain changes from highly water-wet (H-1) to highly oil-wet (O-1).

We found another numerical study in which they study the effect of wettability in two-phase flow by Jahanbakhsh et al. [2021]. They simulated the two-phase flow in a network of circular grains with *COMSOL*. The dimension of their simulation is $3mm \times 4.33mm$. The flow condition for their simulation was $\bar{U}_{max} \approx 0.78m/s$ with the Reynolds number of 0.01-1 and Capillary number of $1e-4$. The properties of the fluids in their simulation can be found in the table A.2.

They reported the trapped phase and formation of the trapped droplets, but the same as our simulation, it seems that the droplet forms before the grain (fig.A.11). A possible explanation is that the film on the grain breaks after contact with the invading phase on the left side of the grain; the film contracts toward the right side and then shapes a droplet. This points out the lack of a proper expression on the boundary condition for the grain that can represent this contraction and the discrepancy between the simulation result and the experiment. In this scenario, we suggest that modeling the thin film thickness

with our lubrication model can represent the boundary condition on the solid surface better than the contact angle.

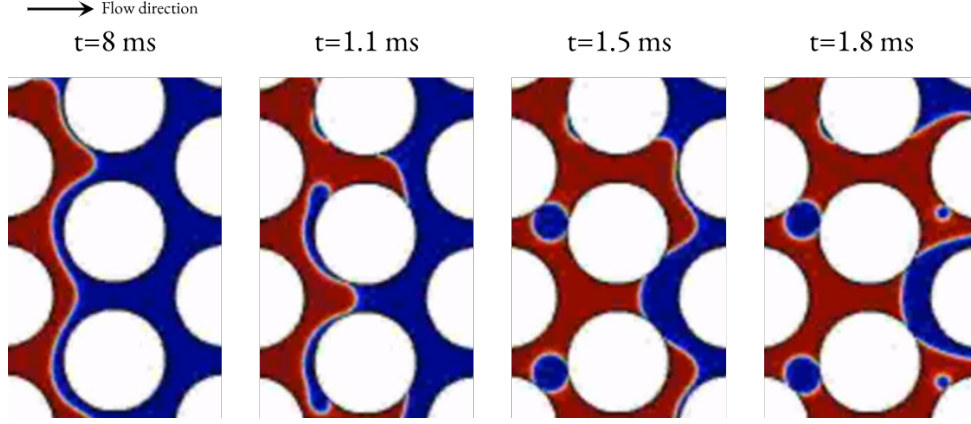


Figure A.11: Movement of interface from left to right for the circular grain, where the wetting phase (red) is displacing the non-wetting phase (blue). The droplet appears as the interface spreads on the solid surface before the grains [Jahanbakhsh et al., 2021].

Spreading of the thin film

This section presents the simulation of the wetting phase's spreading in a capillary channel. The objective is to clarify the accuracy and reliability of the currently used two-phase simulation tools in the limit of three-phase contact region. We compare the simulation result with a micro-PIV experiment in the literature.

The experimental case

Zimmerman [2011] performed a high-resolution micro-PIV near a moving contact line to spread a thin film. They used three channels with a square cross-section (fig.A.12) and the dimensions of $30\mu m \times 300\mu m \times 5cm$, $50\mu m \times 500\mu m \times 5cm$ and $100\mu m \times 1000\mu m \times 5cm$. They used two fluids for their experiment: spreading glycerol/water against air and a sugar solution (glucose/fructose solution, GFS) against air. They studied the spreading at very small velocity, $U_{interface} : 1.7 - 33\mu m/s$, with the dimensionless numbers of $Ca = 1.6 \times 10^{-4} - 6.2 \times 10^{-4}$, $Re = 8.7 \times 10^{-8} - 5.7 \times 10^{-6}$, $Bo = 10^{-3}$. Re-circulation is apparent in some of their measurements (fig.A.13) just before the three-phase contact line.

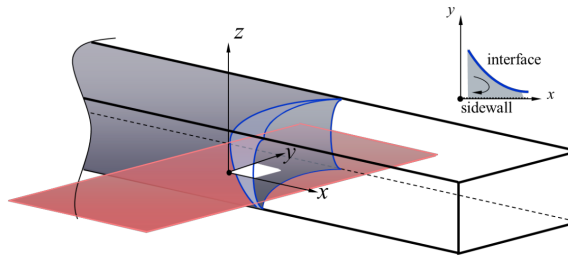


Figure A.12: Schematic of capillary channel used by Zimmerman [2011]

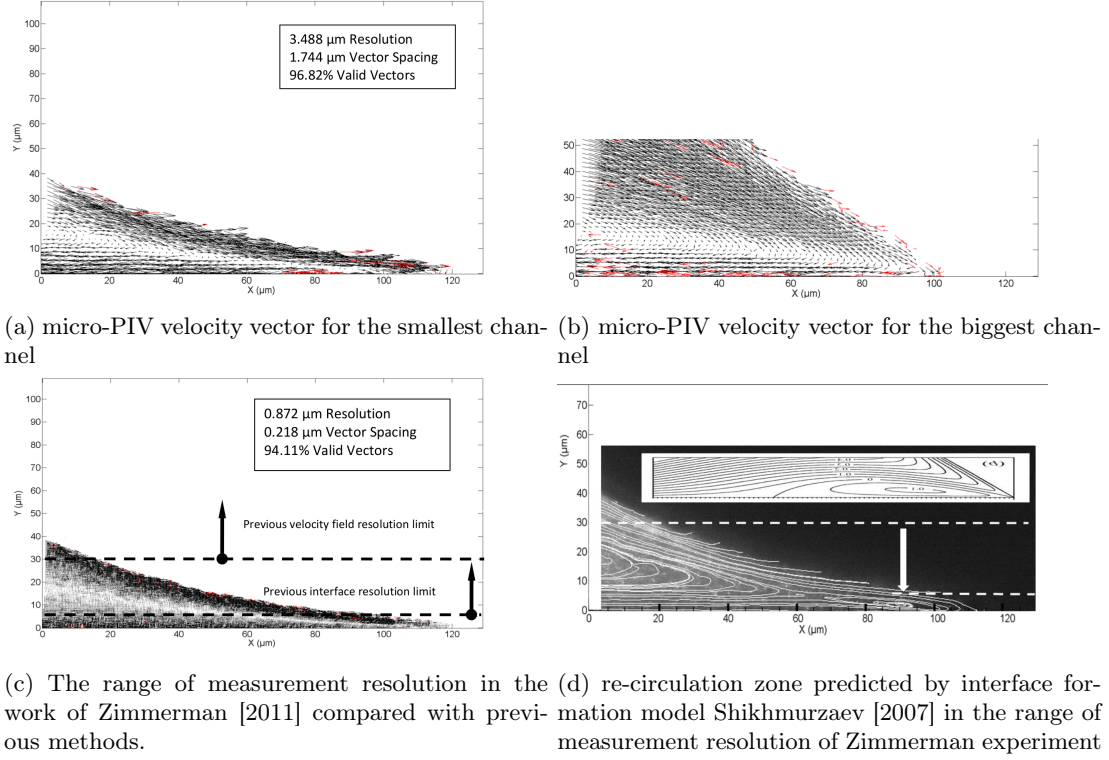


Figure A.13: Micro-PIV measurement of velocity near three-phase contact region Zimmerman [2011]

Simulation

We ran our simulation in accordance with Zimmerman's experiment. We used the same solver as the previous case, *InterFOAM*, in the *OpenFOAM* package, with our modification for calculating surface force with the SSF method. The geometry is a rectangle with the dimension of $0.1 \text{ mm} \times 0.01 \text{ mm}$. The fluid properties are set to produce the same dimensionless number as the experiment performed by Zimmerman. The meshing is performed by constructing a 2-D Cartesian mesh with the dimension of $0.1 \mu\text{m} \times 0.1 \mu\text{m}$. The Brakbill constraint limits time-stepping. The partial slip boundary condition value (α) in the *OpenFOAM* is expressed by a relationship between the slip length (λ) and the grid size (d) next to the wall [Le et al., 2012]:

$$\alpha = \frac{d}{d + 2\lambda}, \quad (\text{A.13})$$

where we used $\lambda = 1.6 \mu\text{m}$ for $\alpha = 0.6$ since the cell size is $d = 5 \mu\text{m}$.

Results and discussion

Initially, we allowed the wetting phase to move through the channel with its capillary pressure without imposing any value for the velocity. We consider the case where there is a thin film ahead of the wetting phase (fig.A.15). In this case, we see an area of re-circulation near the phase contact region. However, this is not the case for the flow without any film (fig.A.14). Then, we simulate the flow with the capillary number and interface velocity in the same range as Zimmerman's work. The same re-circulation can be seen for the case of the thick film ahead of the three-phase contact line (fig.A.16). Finally, we used partial slip for the fluid velocity on the solid wall (fig.A.17). Although the capillary number is small, the spurious current is not noticeable.

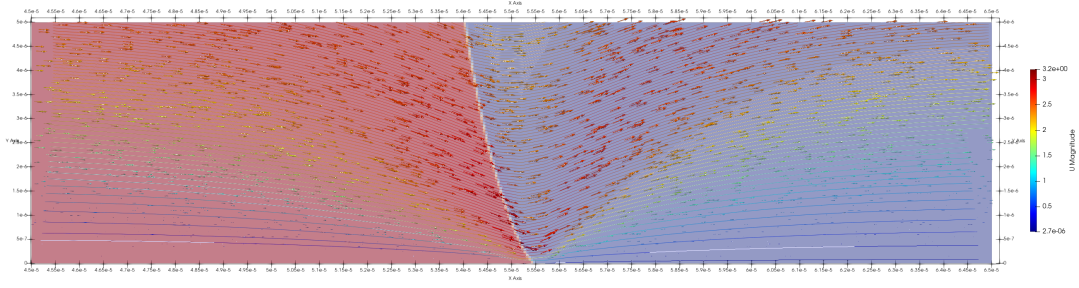


Figure A.14: VOF simulation of movement of wetting phase in the capillary channel.

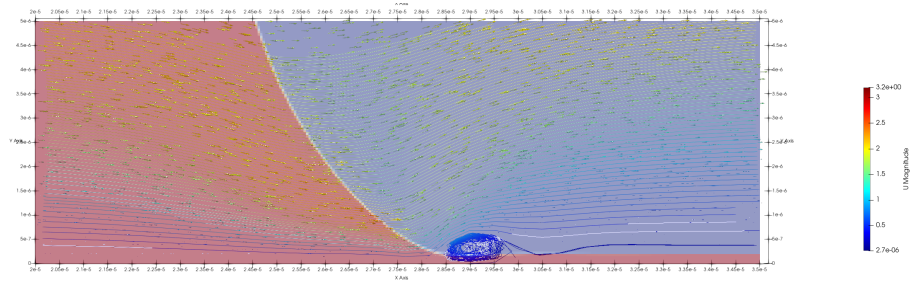


Figure A.15: VOF simulation of movement of wetting phase in the capillary channel with an initial film on the solid.

By comparing the simulation result in fig.A.15 and fig.A.16, we can infer that with increasing the film thickness, the size of the re-circulation zone is increased. Therefore, with this analogy, we can conclude that if the film thickness is in the order of the nanometer scale, then the re-circulation zone would be in the order of the Zimmerman experiment. However, this thin film can not be resolved practically with the VOF method since it would require a very fine mesh on the solid boundary.

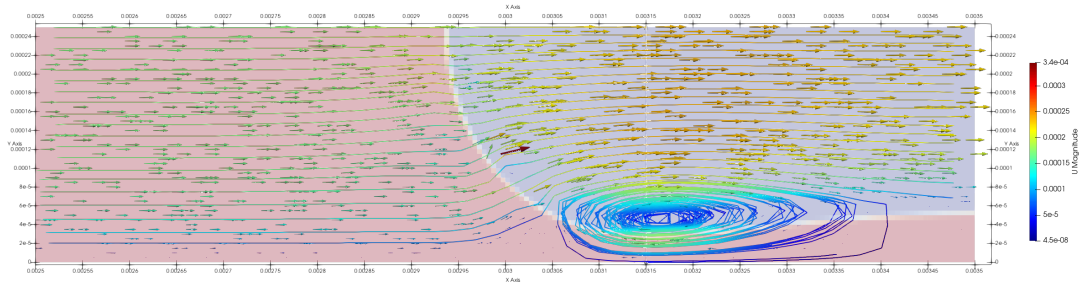


Figure A.16: VOF simulation of spreading of wetting phase with an initial film on the solid. The re-circulation can be seen in the three-phase contact region. Increasing the thickness of the film changes the size of this re-circulation zone.

The velocity field vector obtained by the partial slip boundary condition does not correspond to the Zimmerman experiment. The fluid velocity around the three-phase contact region is erratic (fig.A.17). Also, the profile does not seem physical.

Moffatt [1964] studied the Stokes flow with a focus on the streamline close to the walls. He proposed the existence of eddies close to the corner between the two plane boundaries. They considered the case where either one or two boundary planes in the corner is a rigid wall. Based on their calculations, they observed that when the angle of this corner is less than a critical value, the flow sufficiently close to the

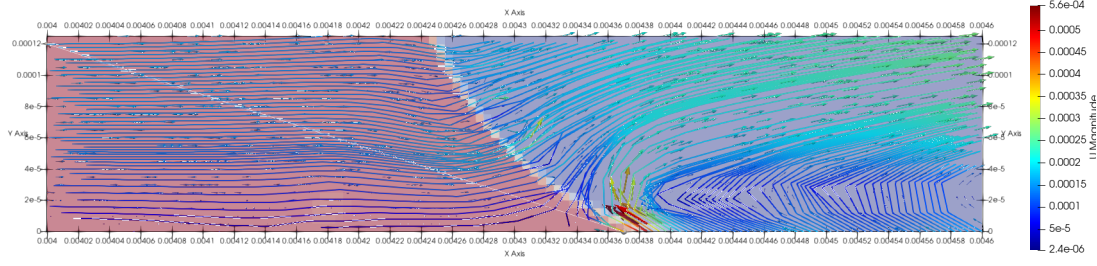


Figure A.17: VOF simulation of spreading of wetting phase with partial slip boundary condition.

corner experiences a sequence of eddies that disappear far away from the corner. Febres and Legendre [2017] demonstrated that if the condition of Navier-slip is imposed on the solid surface, Moffatt vortices do not appear in the three-phase region. It is plausible to assume that the solid boundary condition for velocity is of the no-slip form since some re-circulation appears in Zimmerman's micro-model experiment. However, one can try to compare those re-circulation with the Moffatt vortices.

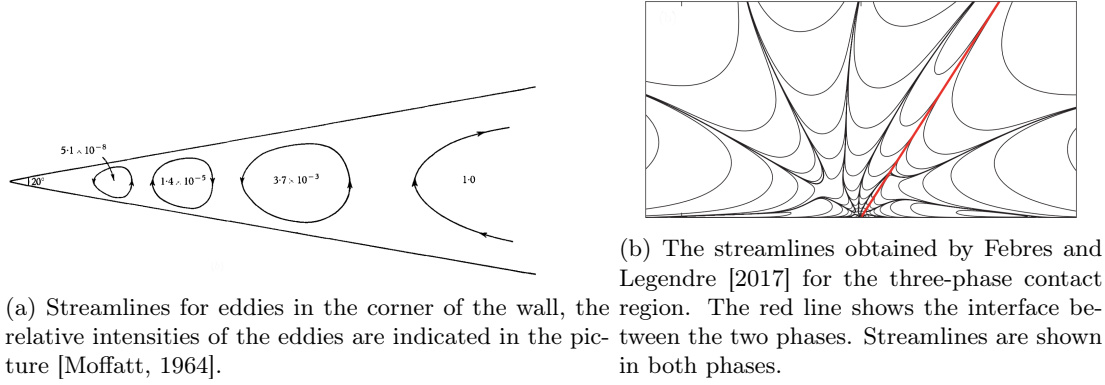


Figure A.18: The resemblance of the re-circulation in the three-phase region to the Moffatt vortices

A.2 Finite element method for P-B solver

We use the finite element discretization method to solve Eq. 4.3 for general electrolytes. To carry out the finite element method (FEM), we multiply both sides of the equation by the weight function and integrate it over the element:

$$\iiint_{\Omega^e} w \left(\nabla^2 \psi + \frac{e}{\epsilon_0 \epsilon_r} \sum_i z_i \rho_{i0} \exp \left(-\frac{e z_i}{k_B T} \psi \right) \right) dV \quad (\text{A.14})$$

by applying the product rule for divergence, $\nabla \cdot (w \nabla \psi) = w \nabla \cdot (\nabla \psi) + \nabla w \cdot \nabla \psi$, we have:

$$\iiint_{\Omega^e} \nabla \cdot (w \nabla \psi) dV = \iiint_{\Omega^e} w \nabla \cdot (\nabla \psi) dV + \iint_{\Gamma^e} \nabla w \cdot \nabla \psi dV. \quad (\text{A.15})$$

Next we use the divergence theorem, $\iiint_{\Omega^e} \nabla \cdot (w \nabla \psi) dV = \oint_{\Gamma^e} w \nabla \psi \mathbf{n} dA$, and substitute it:

$$-\iiint_{\Omega^e} \nabla w \cdot \nabla \psi dV = -\iiint_{\Omega^e} w \frac{e}{\epsilon_0 \epsilon_r} \sum_i z_i \rho_{i0} \exp \left(-\frac{e z_i}{k_B T} \psi \right) dV - \oint_{\Gamma^e} w \nabla \psi \mathbf{n} dl \quad (\text{A.16})$$

We simplify the problem for one and two dimensions in the following sections to evaluate the integral and obtain the coefficient of the stiffness matrix.

One- dimension

For one dimensional case the eq. A.16 becomes:

$$-\int_e \frac{\partial w}{\partial x} \frac{\partial \psi}{\partial x} dx = \oint \frac{\partial \psi}{\partial x} w dx - \int_e w \frac{e}{\epsilon_0 \epsilon_r} \sum_i z_i \rho_{i0} \exp\left(-\frac{e z_i}{k_B T} \psi\right) dx. \quad (\text{A.17})$$

We choose the following linear interpolation function for the weight function $w = [N_1, N_2]$, where

$$\begin{aligned} N_1(\zeta) &= \frac{1-\zeta}{2}, \\ N_2(\zeta) &= \frac{1+\zeta}{2}, \end{aligned} \quad (\text{A.18})$$

which is expressed for the master element. The coordination transformation from the domain to the master element is shown in Fig. A.19. We used the following transformation to convert the current

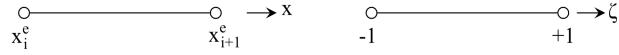


Figure A.19: One dimension linear elements, and the master element.

coordinate to the master element coordinate:

$$\begin{aligned} x &= x_1 N_1 + x_2 N_2, \\ \psi &= \psi_1 N_1 + \psi_2 N_2, \end{aligned} \quad (\text{A.19})$$

or we can simplify:

$$x = \frac{x_1 + x_2}{2} + \frac{x_2 - x_1}{2} \zeta. \quad (\text{A.20})$$

Therefore $\frac{\partial x}{\partial \zeta} = \frac{x_2 - x_1}{2}$ or $= \frac{l_e}{2}$ where l_e is the length of the element. Therefore we can write eq. A.17 for the master element coordinate as:

$$-\frac{2}{l_e} \int_{-1}^1 \frac{\partial w}{\partial \zeta} \frac{\partial \psi}{\partial \zeta} d\zeta = \frac{2}{l_e} \frac{\partial \psi}{\partial \zeta} w \Big|_{-1}^1 + \frac{l_e}{2} \int_{-1}^1 w - \frac{e}{\epsilon_0 \epsilon_r} \sum_i z_i \rho_{i0} \exp\left(-\frac{e z_i}{k_B T} \psi\right) d\zeta \quad (\text{A.21})$$

By substituting the weight function, we get a system of equations:

$$A_{i,j} \psi_j = F_i \quad (\text{A.22})$$

where:

$$A_{i,j} = -\frac{2}{l_e} \int_{-1}^1 \frac{\partial N_i}{\partial \zeta} \frac{\partial N_j}{\partial \zeta} d\zeta \quad (\text{A.23})$$

and

$$F_i = \frac{2}{l_e} \frac{\partial \psi}{\partial \zeta} N_i \Big|_{-1}^1 + \frac{l_e}{2} \int_{-1}^1 N_i \sinh \psi d\zeta \quad (\text{A.24})$$

The stiffness matrix is obtained by substituting N_i into the integral as:

$$A_{i,j} = -\frac{2}{l_e} \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix}. \quad (\text{A.25})$$

Finally, using the Newton-Raphson method to deal with the non-linearity [Chen and Singh, 2002]:

$$\psi^{it+1} = \psi^{it} - [A_T]^{-1} (A_{i,j} \psi^{it} - F(\psi^{it})), \quad (\text{A.26})$$

where $A_T = A_{i,j} - \frac{\partial F_i}{\partial Y_j}$ and 'it' is for the iteration.

Two- dimension

For 2 dimensional case the Eq. A.16 becomes:

$$-\iint_{\Omega^e} \nabla w \cdot \nabla \psi dA = -\iint_{\Omega^e} w \frac{e}{\epsilon_0 \epsilon_r} \sum_i z_i \rho_{i0} \exp\left(-\frac{e z_i}{k_B T} \psi\right) dA - \oint_{\Gamma^e} w \nabla \psi \mathbf{n} dl \quad (\text{A.27})$$

The weight function for the triangular element is $w = [N_1, N_2, N_3]$, where each interpolation function is expressed with respect to the master element coordination as:

$$\begin{aligned} N_1 &= 1 - \zeta - \eta, \\ N_2 &= \zeta, \\ N_3 &= \eta. \end{aligned} \quad (\text{A.28})$$

The coordination transformation from the domain to the master element is shown in Fig. A.20. We used

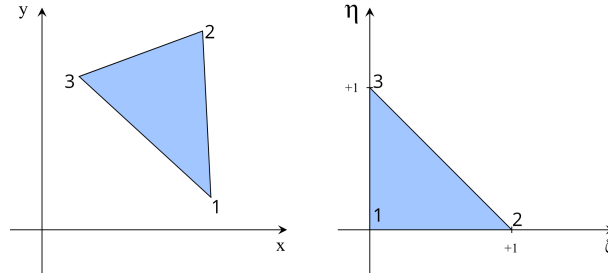


Figure A.20: Two dimension linear elements, and the master element

the following transformation to convert the current coordinate to the master element coordinate:

$$\begin{aligned} x &= x_1 + (x_2 - x_1) N_2 + (x_3 - x_1) N_3, \\ y &= y_1 + (y_2 - y_1) N_2 + (y_3 - y_1) N_3, \\ \psi &= \psi_1 N_1 + \psi_2 N_2 + \psi_3 N_3. \end{aligned} \quad (\text{A.29})$$

or we can simplify as:

$$x = \frac{x_1 + x_2}{2} + \frac{x_2 - x_1}{2} \zeta. \quad (\text{A.30})$$

In order to obtain the partial derivatives in the new coordinate, we write:

$$\begin{bmatrix} \frac{\partial N_i}{\partial \zeta} \\ \frac{\partial N_i}{\partial \eta} \end{bmatrix} = J \begin{bmatrix} \frac{\partial N_i}{\partial x} \\ \frac{\partial N_i}{\partial y} \end{bmatrix} \quad (\text{A.31})$$

where the Jacobian matrix is defined as:

$$J = \begin{bmatrix} \frac{\partial x}{\partial \zeta} & \frac{\partial y}{\partial \zeta} \\ \frac{\partial x}{\partial \eta} & \frac{\partial y}{\partial \eta} \end{bmatrix} \quad (\text{A.32})$$

therefore we can write:

$$\begin{bmatrix} \frac{\partial N_i}{\partial x} \\ \frac{\partial N_i}{\partial y} \end{bmatrix} = \frac{1}{|J|} \begin{bmatrix} \frac{\partial y}{\partial \eta} & -\frac{\partial y}{\partial \zeta} \\ -\frac{\partial x}{\partial \eta} & \frac{\partial x}{\partial \zeta} \end{bmatrix} \begin{bmatrix} \frac{\partial N_i}{\partial \zeta} \\ \frac{\partial N_i}{\partial \eta} \end{bmatrix} \quad (\text{A.33})$$

The determinant of J equals the two times the element area, $2A_e$. Therefore we can write the eq. A.27 for the master element coordinate as:

$$\begin{aligned} & -\frac{2}{A_e} \int_0^1 \int_0^{1-\eta} \left(\frac{\partial w}{\partial \zeta} \frac{\partial \psi}{\partial \zeta} + \frac{\partial w}{\partial \eta} \frac{\partial \psi}{\partial \eta} \right) d\zeta d\eta = \\ & \sum_i \frac{2}{l_e} \frac{\partial \psi}{\partial \zeta} w - \frac{A_e}{2} \int_0^1 \int_0^{1-\eta} w \frac{e}{\epsilon_0 \epsilon_r} \sum_i z_i \rho_{i0} \exp \left(-\frac{e z_i}{k_B T} \psi \right) d\zeta d\eta \end{aligned} \quad (\text{A.34})$$

The term $\sum$ on the right side is carried out on the edge of the element, and it is only necessary to calculate for the edges located at the boundaries. Therefore, the stiffness matrix and the constant matrix become:

$$A_{i,j} = -\frac{2}{A_e} \int_0^1 \int_0^{1-\eta} \left(\frac{\partial N_i}{\partial \zeta} \frac{\partial N_j}{\partial \zeta} + \frac{\partial N_i}{\partial \eta} \frac{\partial N_j}{\partial \eta} \right) d\zeta d\eta, \quad (\text{A.35})$$

and ,

$$F_i = \sum_i \frac{2}{l_e} \frac{\partial \psi}{\partial \zeta} N_i - \frac{A_e}{2} \int_0^1 \int_0^{1-\eta} N_i \frac{e}{\epsilon_0 \epsilon_r} \sum_i z_i \rho_{i0} \exp \left(-\frac{e z_i}{k_B T} \psi \right) d\zeta d\eta \quad (\text{A.36})$$

The stiffness matrix becomes:

$$A_{i,j} = -\frac{1}{4A_e} \begin{bmatrix} y_{23}^2 + x_{32}^2 & y_{23}y_{31} + x_{32}x_{13} & y_{23}y_{12} + x_{32}x_{21} \\ A_{1,2} & y_{31}^2 + x_{13}^2 & y_{31}y_{12} + x_{13}x_{21} \\ A_{1,3} & A_{2,3} & y_{12}^2 + x_{21}^2 \end{bmatrix}. \quad (\text{A.37})$$

Gauss-quadrature

In the discretization step for the finite element method, we have to evaluate the integral for the constant matrix, F . The analytical integration can be cumbersome to obtain, especially in the case of two dimensions. Therefore, we need to use the numerical approach. Here, we choose the Gauss-Legendre quadrature approach since it provides a high accuracy and fast convergence compared with another method, such as Monte Carlo. To do so we have to change the domain of integration from the master triangle to a square ranging from -1 to 1 with the transformation as [de Souza and Aparecido, 2007] (see Fig. A.21):

$$\begin{aligned} \zeta &= \left(1 - \frac{v}{2}\right) u, & \eta &= \left(1 - \frac{u}{2}\right) v, \\ u &= \frac{1 + u'}{2}, & v &= \frac{1 + v'}{2}. \end{aligned} \quad (\text{A.38})$$

Therefore for the integral in the constant matrix (F), we have:

$$\int_0^1 \int_0^{1-\eta} f(\zeta, \eta) d\zeta d\eta = \int_{-1}^1 \int_{-1}^1 f(v', u') \left(1 - \frac{2 + u' + v'}{4}\right) \frac{1}{4} du' dv'. \quad (\text{A.39})$$

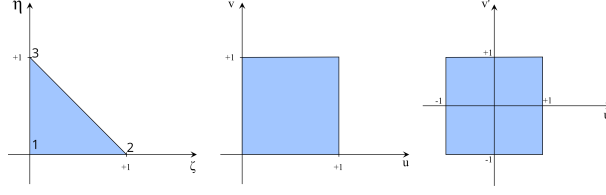


Figure A.21: Coordinate transformation of triangular element to a square

According to the Gauss-Legendre quadrature, we have:

$$\int_{-1}^1 \int_{-1}^1 f(v', u') \left(1 - \frac{2 + u' + v'}{4}\right) \frac{1}{4} du' dv' = \sum_{i=1}^n \sum_{j=1}^m w_i w_j \left(1 - \frac{2 + u' + v'}{4}\right) \frac{1}{4} f(u'_{(i,j)}, v'_{(i,j)}), \quad (\text{A.40})$$

where the points at (i, j) are the roots of n th order Legendre polynomial, and the weights are calculated according to:

$$P_n(x_i) = 0, \quad w_i = \frac{2(1 - x_i^2)}{(nP_{n-1}(x_i))^2}. \quad (\text{A.41})$$

For the one-dimensional case, we can readily use the Legendre polynomial roots and the weights calculated from the mentioned equation without the need to change the coordinate as the integration range is already $[-1, 1]$.

A.3 Analytical solution for one-dimensional Poisson-Boltzmann equation

The dimensionless form of Poisson-Boltzmann equation for symmetric electrolyte is:

$$\frac{\partial^2 \Psi(X)}{\partial X^2} = \sinh \Psi(X) \quad (\text{A.42})$$

with the boundary conditions:

$$\frac{\partial \Psi}{\partial X} = -s_0, \text{ at } X = 0; \frac{\partial \Psi}{\partial X} = -s_d, \text{ at } X = X_d \quad (\text{A.43})$$

or

$$\Psi = \Psi_0, \text{ at } X = 0; \Psi = \Psi_d, \text{ at } X = X_d \quad (\text{A.44})$$

after first integration we have:

$$\frac{\partial \Psi}{\partial X} = \pm \sqrt{2 \cosh \Psi + C}, \quad (\text{A.45})$$

where C is the integration constant. The analytical solution depends on the value of C : for $C \leq -2$

$$\Psi(X) = \bar{\Psi} - 2 \ln \left(\frac{\sin \phi_0 \operatorname{cn}(z, k) \operatorname{dn}(z, k) + \cos \phi_0 \sqrt{1 - k^2 \sin^2 \phi_0} \operatorname{sn}(z, k)}{1 - k^2 \sin^2 \phi_0 \operatorname{sn}^2(z, k)} \right) \quad (\text{A.46})$$

$$C = -2 \cosh \bar{\Psi}; k = \exp -\bar{\Psi}; \phi_0 = \arcsin \exp \frac{\bar{\Psi} - \Psi_0}{2}; z = \frac{X}{2\sqrt{k}}$$

for $-2 \leq C \leq 2$:

$$\Psi = \pm \operatorname{arcCosh} \frac{1 - k^2 \sin^2 \phi_0 \operatorname{sn}^2(z, k)}{\sin \phi_0 \operatorname{cn}(z, k) \operatorname{dn}(z, k) + \cos \phi_0 \sqrt{1 - k^2 \sin^2 \phi_0} \operatorname{sn}(z, k)} \quad (\text{A.47})$$

$$k = \sqrt{\frac{2 - C}{4}}; \phi_0 = \arcsin \frac{1}{\cosh \Psi_0/2}$$

for $C \geq 2$:

$$\Psi = 2 \ln \left(\frac{1}{b} \tan \left(\arcsin \left(\frac{\sin \phi_0 \operatorname{cn}(z, k) \operatorname{dn}(z, k) + \cos \phi_0 \sqrt{1 - k^2 \sin^2 \phi_0} \operatorname{sn}(z, k)}{1 - k^2 \sin^2 \phi_0 \operatorname{sn}^2(z, k)} \right) \right) \right) \quad (\text{A.48})$$

$$C = B^2 + b^{-2}; k = \sqrt{1 - b^{-4}}, b \geq 1; \phi_0 = \arctan(b \exp \Psi_0/2); z = \frac{bX}{2}$$

The value of C is obtained by substituting the boundary condition in the proper equation. In order to choose the proper equation first we need to determine the solution for $C = \pm 2$ by substituting X as the distance between the plate in the following:

$$\Psi = 2 \ln \frac{1 + \exp X \tanh \Psi_0/4}{1 - \exp X \tanh \Psi_0/4}, C = -2 \quad (\text{A.49})$$

$$\Psi = 2 \ln \frac{\exp \Psi_0/2 - \tan X/2}{1 + \exp \Psi_0/2 \tan X/2}, C = 2$$

For the case of Neumann boundary condition we can use $s^2 = 2 \cosh \Psi + C$.

A.4 A.Derivation of lubrication model

In this section we derive the lubrication model presented in section 5.2.2. The derivation relies on the integration of the Navier-Stokes equations over the film thickness including the fluid-fluid interfacial boundary conditions.

A.4.1 Governing equations

Mass and momentum balance equations

We consider a two-dimensional film as shown in Fig. 5.1. For an incompressible fluid, the equation of continuity in the film reads

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0, \quad (\text{A.50})$$

and the momentum equations are,

$$\begin{aligned}\rho \left(\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} \right) &= -\frac{\partial p}{\partial x} + \mu \left(\frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial x^2} \right), \\ \rho \left(\frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} \right) &= -\frac{\partial p}{\partial y} + \mu \left(\frac{\partial^2 v}{\partial y^2} + \frac{\partial^2 v}{\partial x^2} \right),\end{aligned}\tag{A.51}$$

where ρ and μ are the density and viscosity of the wetting film, respectively, $[u, v]$ is the velocity vector and p is the hydrostatic pressure field (in Pa). Assuming creeping flow regime and that within the wetting film the flowlines are parallel to solid surface, the momentum equations simplify to,

$$\begin{aligned}0 &= -\frac{\partial p}{\partial x} + \mu \frac{\partial^2 u}{\partial y^2}, \\ 0 &= -\frac{\partial p}{\partial y}.\end{aligned}\tag{A.52}$$

Fluid-solid boundary conditions

Because the fluid cannot penetrate into the solid surface, the normal component of the fluid velocity is always,

$$v|_{y=0} = 0.\tag{A.53}$$

Far from the triple line, the condition at the fluid-solid interface can be a no-slip condition, i.e. the normal and tangential components of the velocity is zero on the solid wall [Stokes, 1846, Stokes et al., 1851],

$$u|_{y=0} = 0,\tag{A.54}$$

or a partial slip (also called Navier slip), i.e. the tangential component of the fluid velocity on the wall is proportional to the shear rate [Navier, 1823]:

$$u|_{y=0} = \lambda \left. \frac{\partial u}{\partial y} \right|_{y=0}.\tag{A.55}$$

where λ is the slip length. Notes that the partial slip condition encompasses the no-slip condition if $\lambda = 0$.

Fluid-fluid boundary conditions

For a film of thickness, $h(x)$, the continuity of mass on the fluid-fluid interface ($y = h(x)$) states,

$$v|_{y=h(x)} = \frac{\partial h}{\partial t} + u \frac{\partial h}{\partial x},\tag{A.56}$$

and the continuity of the stress is

$$\left(\mathbb{T}^{(2)} - \mathbb{T}^{(1)} \right) \cdot \mathbf{n} = -\kappa \sigma \mathbf{n} + \frac{\partial \sigma}{\partial s} \mathbf{t},\tag{A.57}$$

where $\mathbf{n} = \frac{1}{\sqrt{1+h_x^2}}[-h_x, 1]$ and $\mathbf{t} = \frac{1}{\sqrt{1+h_x^2}}[1, h_x]$ are the normal and tangential vector, $\mathbb{T}^{(1)}$ and $\mathbb{T}^{(2)}$ are the stress tensor in the non-wetting and wetting fluid, respectively, $\kappa = \frac{h_{xx}}{\sqrt{(1+h_x^2)^3}}$ is the interface curvature, σ is the surface tension. The first and second space derivative of the height are noted, $h_x = \frac{\partial h}{\partial x}$ and $h_{xx} = \frac{\partial^2 h}{\partial x^2}$, respectively. In the right-hand side of Eq. A.57, the first term is the surface tension

force due to the curvature of the interface, and the second term is attributed to the change in interfacial tension across the arc length of the interface defined as $ds = \sqrt{1 + h_x^2} dx$.

The projection of Eq. A.57 onto the x and y axis yields in the following two equations,

$$\begin{cases} -h_x T_{11}^{(2)} + T_{12}^{(2)} = \kappa \sigma h_x + \frac{1}{\sqrt{1+h_x^2}} \frac{\partial \sigma}{\partial x} - h_x T_{11}^{(1)} + T_{12}^{(1)}, \\ -h_x T_{21}^{(2)} + T_{22}^{(2)} = -\kappa \sigma + \frac{1}{\sqrt{1+h_x^2}} \frac{\partial \sigma}{\partial x} h_x - h_x T_{21}^{(1)} + T_{22}^{(1)}. \end{cases} \quad (\text{A.58})$$

The shear stress reads, $\mathbf{T} = -p\mathbf{I} + \tau_{i,j}$, where the viscous stress is $\tau_{i,j} = \mu \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)$. Because of the lubrication approximation, the velocity in the film is $[u(y), 0]$, and we have $\tau_{11}^{(2)} = \tau_{22}^{(2)} = 0$ and $\tau_{12}^{(2)} = \tau_{21}^{(2)} = \mu \frac{\partial u}{\partial y}$. Along the same line, it is reasonable to assume that only the tangential component of the viscous stress in the non-wetting fluid is non-zero, i.e. $\tau_{11}^{(1)} = \tau_{22}^{(1)} = 0$ and $\tau_{12}^{(1)} = \tau_{21}^{(1)} = \tau$. For a free surface, $\tau \ll \tau_{12}^{(2)}$ and this term is negligible. For thin film, the normal component of excess pressure (Π) known by disjoining pressure and we have, $T_{11}^{(1)} = T_{22}^{(1)} = -p + \Pi$. Equation A.58 becomes,

$$\begin{cases} h_x p + \tau_{12} = \kappa \sigma h_x + \frac{1}{\sqrt{1+h_x^2}} \frac{\partial \sigma}{\partial x} - \Pi h_x + \tau, \\ -h_x \tau_{12} - p = -\kappa \sigma + \frac{1}{\sqrt{1+h_x^2}} \frac{\partial \sigma}{\partial x} h_x + \Pi + h_x \tau. \end{cases} \quad (\text{A.59})$$

If we multiply the second line by h_x and add it to the first line, and multiply the first line by h_x and subtract it from the second line, we obtain

$$\begin{cases} \tau_{12}(1 - h_x^2) = \frac{\partial \sigma}{\partial x} \sqrt{1 + h_x^2} + \tau(1 + h_x^2), \\ p(1 + h_x^2) + 2h_x \tau_{12} = -(1 + h_x^2) \kappa \sigma - \Pi(1 + h_x^2). \end{cases} \quad (\text{A.60})$$

Finally, using the long-wave approximation, $h_x \ll 1$, these conditions become,

$$\begin{cases} \mu \frac{\partial u}{\partial y} = \frac{\partial \sigma}{\partial x} + \tau, \\ p = -\sigma \frac{\partial^2 h}{\partial x^2} - \Pi. \end{cases} \quad (\text{A.61})$$

We can rewrite the hydrodynamic pressure in eq. A.61 with a hydrostatic pressure due to gravity as: $p = -\sigma \frac{\partial^2 h}{\partial x^2} - \Pi + \rho g h$.

A.4.2 Integration

The lubrication model governing the evolution of the film thickness, $h(x)$, is obtained by integrating the governing equations, Eqs. A.50-A.52, over the film thickness along with the conditions at the fluid-fluid and fluid-solid boundaries.

Integration of the mass balance equation

The integration of the continuity equation across the film gives,

$$\int_0^{h(x,t)} \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right) dy = 0. \quad (\text{A.62})$$

It follows that,

$$\int_0^{h(x,t)} \frac{\partial u}{\partial x} dy + v|_{y=h(x)} - v|_{y=0} = 0. \quad (\text{A.63})$$

The derivative and integral operators are interverted using Leibniz integral rule:

$$\frac{\partial \int_0^{h(x,t)} u dy}{\partial x} - u|_{y=h(x)} \frac{\partial h}{\partial x} + v|_{y=h(x)} - v|_{y=0} = 0. \quad (\text{A.64})$$

Finally, using the definition of the depth-averaged velocity, $\bar{u} = \frac{1}{h} \int_0^{h(x)} u dy$, the fluid-fluid interface condition, Eq. A.56, to simplify $v|_{y=h(x)}$, and the condition $v|_{y=0} = 0$ at the solid surface, we obtain,

$$\frac{\partial h}{\partial t} + \frac{\partial h \bar{u}}{\partial x} = 0. \quad (\text{A.65})$$

Integration of the momentum balance equation

The depth-averaged velocity, $\bar{u}$, is obtained by integrating the momentum equation, Eq. A.52, along the film thickness. The velocity in the film, v , has a parabolic profile, $u(y) = Ay^2 + By + C$, where the coefficients A, B, C are obtained from the momentum equation (Eq. A.52) the boundary conditions at the fluid-solid interface (Eq. A.55) and at the fluid-fluid interface (Eq. A.61). We have,

$$\begin{aligned} A &= \frac{1}{2\mu} \frac{\partial p}{\partial x}, \\ B &= 2Ah + \frac{1}{\mu} \left(\frac{\partial \sigma}{\partial x} + \tau \right), \\ C &= \lambda B, \end{aligned} \quad (\text{A.66})$$

which leads to the velocity profile,

$$u(y) = \frac{\partial p}{\partial x} \left(\frac{1}{2\mu} y^2 - \frac{h}{\mu} (y + \lambda) \right) + \frac{1}{\mu} \left(\frac{\partial \sigma}{\partial x} + \tau \right) (y + \lambda). \quad (\text{A.67})$$

Therefore, the mass flow rate, $q_s = h\bar{u}$, is

$$q_s = \int_0^h u dy = -\frac{1}{\mu} \frac{\partial p}{\partial x} \left(\frac{h^3}{3} + \lambda h^2 \right) + \frac{1}{\mu} \left(\frac{\partial \sigma}{\partial x} + \tau \right) \left(\frac{h^2}{2} + \lambda h \right), \quad (\text{A.68})$$

that is recast into

$$q_s = -M(h) \frac{\partial p}{\partial x} + T(h), \quad (\text{A.69})$$

where,

$$M(h) = \frac{1}{\mu} \frac{\partial p}{\partial x} \left(\frac{h^3}{3} + \lambda h^2 \right), \quad (\text{A.70})$$

is the fluid mobility, and,

$$T(h) = \frac{1}{\mu} \left(\frac{\partial \sigma}{\partial x} + \tau \right) \left(\frac{h^2}{2} + \lambda h \right), \quad (\text{A.71})$$

accounts for shear stress with the non-wetting fluid and the Marangoni effect. The driving force is:

$$\mathbb{P} = -\sigma \frac{\partial^2 h}{\partial x^2} - \Pi + \rho gh \quad (\text{A.72})$$

Finally, the evolution equation for the film thickness is obtained by combining the mass flow rate with the depth-integrated continuity equation (Eq. A.65). We have,

$$\frac{\partial h}{\partial t} = \frac{\partial}{\partial x} \left(M(h) \frac{\partial \mathbb{P}}{\partial x} \right) - \frac{\partial T(h)}{\partial x}, \quad (\text{A.73})$$

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Modélisation des effets de mouillabilité pour les écoulements diphasiques en milieux poreux géologiques

Résumé :

Piéger un fluide dans des milieux poreux par des forces capillaires est crucial dans de nombreux processus souterrains, tels que la capture et le stockage de carbone dans les aquifères salins profonds, la dépollution des eaux souterraines et la récupération assistée du pétrole dans les réservoirs pétroliers. Dans ces processus, les propriétés de mouillabilité près de la région de contact à trois phases sont essentielles pour comprendre les mécanismes de piégeage et la stabilité à long terme des gouttelettes piégées. Cependant, la mouillabilité de la roche et, par conséquent, l'écoulement multiphasique peuvent être modifiés par un changement des propriétés physico-chimiques de l'eau interstitielle (pH, salinité) et des propriétés physiques et physico-chimiques interfaciales. La mouillabilité des surfaces minérales est traditionnellement décrite par des angles de contact, mesurés visuellement dans des expériences de laboratoire. Cette approche ne reflète pas bien l'altération effective de la mouillabilité en raison des changements dans les propriétés du système, comme le pH et la salinité. Alternativement, la mouillabilité du système peut être estimée via les interactions intermoléculaires.

L'interaction intermoléculaire dans la région de contact à trois phases est étudiée à travers les différentes composantes de la pression de disjonction. La pression de disjonction comprend les interactions de Van der Waals (VDW), de la double couche électrique (EDL) et les interactions structurales. Dans cette étude, nous avons examiné et montré le rôle de la géométrie en forme de coin de la région de contact pour les interactions VDW et électrostatiques, généralement ignorées dans la littérature. Ensuite, nous avons développé un modèle de lubrification basé sur des principes physiques pour les films minces afin de modéliser l'altération de la mouillabilité. Nous avons utilisé une pression de disjonction dépendante de la pente, dérivée de l'hypothèse de géométrie en forme de coin. La pression de disjonction dépendante de la pente et l'épaisseur du film précurseur modifient la stabilité de l'étalement. Les travaux futurs se concentreront sur l'intégration du modèle de lubrification dans un simulateur d'écoulement diphasique et l'étude de l'effet de la mouillabilité dans un milieu poreux géologique.

Mots clés : Modèle de lubrification, Ecoulements multiphasiques, Mouillabilité, Double couche électrique, milieux poreux, Physico-chimie des interfaces

Modelling contact line dynamics in multiphase porous media

Abstract :

Trapping fluid in porous media by capillary forces is critical in many subsurface processes, such as carbon capture and storage in deep saline aquifers, groundwater remediation, and enhanced oil recovery in petroleum reservoirs. In such processes, wettability properties near the three-phase contact region are crucial in deciphering trapping mechanisms and the long-term stability of trapped droplets. However, the rock wettability and, consequently, the multiphase flow can be altered by a change in pore water physico-chemical properties (pH, salinity) and interfacial physical and physico-chemical properties. Mineral surface wettability is traditionally described via contact angles, measured visually in lab experiments. This approach does not reflect the effective wettability alteration well due to the changes in the system properties, such as pH and salinity. Alternatively, the wettability of the system can be estimated via the intermolecular interactions.

The inter-molecular interaction for the three-phase contact region is studied through the different components of the disjoining pressure. The disjoining pressure comprises Van der Waals (VDW), electric double layer (EDL), and structural interaction. In this study, we investigated and showed the role of wedge-shaped geometry of the contact region for the VDW and the electrostatic interaction, which is usually ignored in the literature. Then, we developed a physically-rooted lubrication model for thin films to model wettability alteration. We utilized a slope-dependent disjoining pressure that originates from the assumption of wedge-shaped geometry. The slope-dependent disjoining pressure and the precursor film thickness alter the stability of the spreading. Future work will focus on integrating the lubrication model in a two-phase flow simulator and studying the effect of wettability in a geological porous medium.

Keywords : Lubrication model, Multiphase flows, Wettability, Electrical double layer, porous media, Interfaces physical chemical

