Capillary instabilities in thin polymer films
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Chapter 2

Principles of Liquid Polymer Films

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2.1 Polymers in History

The compounds known as polymers are comprised of tens, hundreds, thousands, up to millions of separate smaller molecules, known as monomers. The term polymer stems from the Greek language where *poly* means multiple and *mer* means parts. The chemical reaction binding monomer molecules together covalently is called polymerization. Since the discovery of natural rubber and the synthetic route to polyethylene, polymers have become an important type of material with properties that are easily manipulated, for instance by altering the chemical nature of the monomer, the number of monomers per chain and processing conditions. Although some very well known polymers are mass produced, such as polystyrene, polyvinyl chloride, poly(methyl methacrylate) and polyethylene, some polymers are tailor made and show remarkable properties.

An alternative term that is used for polymers is macromolecule. Synthetic polymers are actually only part of the larger group of macromolecules that also include biomacromolecules, such as DNA and proteins, but also semi-synthetic and inorganic polymer (natural silicates). Semi-synthetic macromolecules, such as vulcanized natural rubber, follow from a chemical reaction with a natural macromolecule. The versatility of polymers is clearly indicated by the many applications polymers are used for, such as rubber tires, bulletproof vests, plastic cutlery, Tupperware, soda bottles, household plastic, computer parts, organic technology (solar cells and light emitting diodes), and so on.

Polymers are commonly regarded as modern and purely synthetic materials. However, polymers actually have a rich history and are found widely in nature. Nature has formed her own brands of polymer, such as the blueprint of life DNA, proteins, tar, shellac, wood and timber and many more. Natural rubber was discovered and extracted from the trees by the Aztecs in 1600 BC. It is believed that the Aztecs used balls of natural rubber in ritual games and figurines in worship. Modern man rediscovered natural rubber in the 18th century. In the mid-19th century, uncured rubber was used as a water repelling additive to coatings applied to textiles. But it wasn’t until the chemical treatment of natural rubber, that the great potential of natural rubber was realized. By vulcanization of natural rubber, a discovery by Goodyear and Hancock, a durable material was obtained that could be molded in any desired shape and dimension prior to vulcanization. Vulcanized rubber deforms under a heavy load, but recovers entirely and returns to its original shape when the load is removed. Comparing rubbers to modern materials, such as steel, it is obvious that rubbers can be extended to several times their initial length and recover completely, whereas steel only allows reversible deformation of a few percent.

Celluloid and Bakelite were the first successful plastics. John Wesley Hyatt introduced Celluloid in 1869 as a surrogate for ivory in billiard balls, that had become increasingly difficult to obtain. The chemical reaction involved within the formation of Celluloid had already been known since 1832. Henri Braconnot added nitric acid
to starch or wood fibers, thereby converting the cellulose in the fibers to the unstable and highly explosive salt cellulose nitrate.

Camphor stabilized Celluloid was used up to the 1950s as photographic material in stills, movies and X-ray films. Due to the hazardous circumstances of manufacturing and processing Celluloid, the production was eventually discontinued.

Bakelite was synthesized in 1907 by Leo Baekeland and was applied in many household and technical applications, such as insulation for electrical wiring and housing for electrical appliances. Bakelite is formed by the condensation polymerization of phenol and formaldehyde. Phenol-formaldehyde (phenolic) resins are still used today as adhesives for composite wood products.

With the increasing application of rubbers and plastics and the continuing innovation that followed the inventions of Celluloid, Bakelite and the serendipitous discovery of polyethylene in 1930, engineering plastics with on-demand physical and chemical properties became a reality.

The majority of polymers used today are thermoplastics. Thermoplastic behavior is a consequence of the absence of chemical cross-links. Thermoplastics are liquefied and easily molded upon heating and return to their glassy or semi-crystalline solid state when cooled. Thermoplastic polymers are easily processed and reprocessed or recycled. Among the many examples of the thermoplastics are Cellulose, polyethylene (PE), polystyrene (PS), polymethyl methacrylate (PMMA), polyamide (PA), polycarbonate (PC) and polyvinyl chloride (PVC).

Natural rubbers are a typical example of a group known as thermoset polymers. Upon irreversible chemical or thermal curing, individual polymer chains are physically interconnected, thereby forming a polymer chain network that assumes the shape of the mold. Thermoset polymers are not easily recycled or reprocessed. Examples of thermoset plastics are Bakelite, polyester and epoxy resins (used in fibre reinforced composites).

### 2.2 Polymers & Properties

On the molecular level, a polymer, or macromolecule, can be considered as chain-like, where the chain is not stretched completely, but folded like a coil. A polymer is made up of a repetition of subunits, also known as monomers. If a single type of monomers is used, homopolymers are obtained. A polymerization with two different monomer units yields copolymers and that of three different monomers gives terpolymers. The monomers are connected by covalent chemical bonds and thereby form a chain. The chemical and physical properties of any polymer depends on the choice of monomer(s), the composition of the polymer, the length of the chains, the distribution in the chain length (i.e. the variation in chain length), purity and the method of processing.

Unlike biomacromolecules, which are identical and have a uniform chain length, the length of a polymer chain shows a variation. Some chains are longer than the
average value and some are shorter. This polydispersity is intrinsic to all polymers and is a result of a randomness induced by commonly used synthetic routes, such as addition polymerization and polycondensation. New polymerization techniques result in a very narrow polydispersity, such as living radical polymerization. The polydispersity \( P_d \) is defined as the ratio of the weight-averaged molecular weight \( M_w \) and number-averaged molecular weight \( M_n \). Low polydispersity polymers have a value of \( P_d \) close to unity, but no polymer is truly monodisperse.

Polymers, as compared to low molecular weight molecules, such as water, have a much higher viscosity in the liquid state. Low molecular liquids are said to be Newtonian liquids as their viscosity remains constant with increasing flow rate. The viscosity of polymer melts and concentrated solutions is said to be non-Newtonian as it does not show the same linear behavior. \(^{30}\) In the experiments described in this thesis, the melt viscosity \( \eta \) is taken in the limit of zero-shear, or no flow velocity: \( \eta = \eta_0 \). The zero-shear melt viscosity \( \eta \) scales linearly with the molecular weight below an entanglement molecular weight (\( M_w^{1} \)). At this molecular weight, \( M_e \), the polymer forms a temporary network of entangled chains. These entanglements are not chemical in nature, as is the case with vulcanized rubber. They are only effective for a limited amount of time, wherein the constraints in the motion of individual chains suppress the flow and cause an additional increase in viscosity. The zero-shear melt viscosity was found to scale with \( M_w \) as \( \eta \propto M_w^{3.4} \).\(^{31}\)

Like other high molecular weight and glass forming liquids, polymers show a transition from the liquid melt to a glassy solid state. Often, this transition is explained by considering the specific volume, which is the inverse of the density. A so-called equilibrium liquid shows a continuous linear decrease of the specific volume during cooling, even up to 0 K. This liquid is assumed not to form a glass nor does it crystallize. The specific volume of a crystallizing liquid is linear in both the liquid and crystalline state, but with a different thermal expansion coefficient (the slope) that is lower in the solid state. Most crystallizing liquids contract during crystallization and show a discontinuity in the specific volume (a jump). Glass forming liquids also show a change in the thermal expansion coefficient during cooling. At the transition temperature from melt to glass, the specific volume is non-linear with temperature, but, unlike crystallization, it is continuous. A single glass transition temperature \( T_g \) is defined for the reversible transition from the melt (liquid) to the glassy (solid) state, although the \( T_g \) is not a singular point but a temperature range. The glass transition is found for amorphous polymers and for the amorphous fraction in (semi-)crystalline polymers. A melting temperature is found only in the crystalline fraction of (semi-)crystalline polymers. Usually, \( T_g \) is arbitrarily defined as the temperature at which the viscosity reaches \( 10^{12} \) Pa·s in simple liquids, or as the temperature at which microscopic relaxation times become larger than approximately \( 10^2 \) s.

The drop in thermal expansion coefficient from the melt to glassy state is often described using a free volume concept. The free volume is defined as the difference
between the specific volume and the occupied volume. The occupied volume is the minimum volume of the molecules at 0 K. The glass transition appears during cooling when the polymer chain mobility decreases rapidly and the rate of shrinkage of the specific volume falls behind that of the equilibrium liquid, thus trapping a certain amount of free volume. Below the glass transition temperature of the polymer, the specific volume (with the trapped free volume) is higher than that of an equilibrium liquid. Above the glass transition temperature, the polymer chain mobility increases and the volumetric behavior is that of an equilibrium liquid. This free volume concept was first applied by Eyring, Batchinksii and Doolittle to describe the influence of temperature on the properties of simple organic and polymeric liquids, such as diffusivity and viscosity. In some models, the free volume is divided into an interstitial free volume between molecules that is not readily rearranged and a hole free volume that provides molecular transport without costing energy. This part of the free volume is presented as holes in the order of molecular or monomeric dimensions. One of the free volume models is elaborated in Chapter 9, as an introduction to vapor sorption experiments. In these experiments, the absorption of solvent molecules by a polymer, is used to obtain a highly concentrated polymer solution.

2.3 Wetting & Capillarity

The principles behind the interactions of liquids and surfaces can be witnessed in everyday’s events. Favorable interactions allow water to be absorbed by soil and plants, a phenomenon known as capillarity. Unfavorable interactions between water and a fatty surface prevents the polar water from wetting the apolar fatty surface. Writing or drawing on a plastic surface with a water-based colored marker shows much of the same behavior. By forcing a dye film onto the plastic, the incompatibility between the dye and the plastic surface causes the retraction of the dye into droplets. This retraction of the water-based dye into droplets on the plastic surface is called dewetting.

For the manufacturing of coatings made of paints, dyes, lubricants, resins, anticorrosive layers and glues, it is vital that these coatings wet a given surface and cover it over an extended period of time. It is therefore important to understand the principles governing wetting and its connection to film stability.

Several phenomena connected to the wetting of a solid surface by a liquid are gathered in a theoretical approach called classical capillarity. In 1712, Taylor and Hauksbee observed the hyperbolic character of a meniscus by holding two flat glasses together and partially immersing these in water. In the 19th century, scientists such as Young, Plateau, Gibbs and Laplace described the phenomena of capillary rise, the shapes of pendant drop, menisci and postulated a relation between the forces and these phenomena. Since then, these topics have received considerable attention. In 1906, 1918 and 1921, Bell, Lucas and Washburn investigated capillary driven
flow and independently derived what is now known as the Lucas-Washburn relation. This relation describes the elevation of the liquid height \( h \) in a capillary tube. Recent studies, including those under reduced gravity conditions\(^7\), allowed an extension of the Lucas-Washburn relation \(( h \propto \sqrt{t}; \propto \) is "proportional to") to discriminate three flow regimes: \( h \propto t^2 \), \( h \propto t \) and \( h \propto \sqrt{t} \). Modern applications of capillarity focus on miniaturization of flow control devices, for instance for chemical analysis\(^2\) and drug delivery\(^5\)\,\(^6\)\,\(^8\)\,\(^9\). Often used are flow mechanics that are controlled by electro wetting\(^9\)\,\(^10\)\,\(^5\) or that depend on the existence of a wettability contrast on the substrate\(^2\)\,\(^3\). Electro wetting is an electrically induced change in the wettability that drives a flow of liquid through a capillary or slit pore. This technique, the principle of which is known since 1875\(^5\), has further led to the development of optical switches, electro wetting displays and other electro-optic devices\(^9\)\,\(^10\).

Figure 2.1: Schematic representation and photographic images of a capillary rise experiment. The right images show a capillary-driven flow of a silicone liquid into a Plexiglas tube with radius \( R \). The Plexiglass (PMMA) tube is partially immersed, leading to a capillary force that pulls the liquid column up into the tube\(^7\). Figures b) and c): courtesy of Michael Dreyer, ZARM - University of Bremen (http://www.zarm.uni-bremen.de/2forschung/grenzph/isoterm/cap_rise/cap_rise.htm).

Capillarity is a phenomenon that allows a liquid to rise into a thin tube (capillary) as a result of unbalanced adhesive and cohesive forces experienced by the liquid. Within a liquid, the molecules experience both attraction and repulsion in an equal manner. However, at the edge of the volume, a net, inward directed, attractive force is experienced by the molecules. This cohesive force gives rise to a surface tension that acts to minimize the surface area of the liquid. Attractive interactions of the liquid with a foreign body, such as the capillary, allows the liquid to wet this body. A balance between the adhesive and cohesive forces is established at the solid-liquid interface. To do so, the liquid rises in the capillary, as shown in Fig.[2.1].

At the periphery of the silicone liquid in the Plexiglass tube in Fig.[2.1], the liquid
is bent slightly upwards. This meniscus is a spherical cap that is concave (curved inwards) for a liquid that wets the capillary. It is convex (curved outwards) for a liquid that does not wet the capillary surface. The angle of the meniscus and the height of the liquid in the capillary are related to the forces that act on them. At equilibrium, the Young-Laplace capillary pressure $2\gamma/R$ is balanced by the fluid static pressure $\rho g R$. The height of the column $h$ is measured directly and is related to the angle of the meniscus $\theta$.\(^{35}\)

$$h_{eq} = \frac{2\gamma \cos \theta}{\rho g R} \quad (2.1)$$

![Figure 2.2: Schematic representation of a droplet on a solid surface. The three-phase contact angle $\theta$ is determined by a force balance of the surface tensions $\gamma_{SL}$, $\gamma_{SV}$ and $\gamma_{LV}$. From left to right: complete wetting, for $\theta = 0^\circ$, partial wetting, for $0^\circ < \theta < 180^\circ$ and non-wetting for $\theta = 180^\circ$.](image)

The surface tension $\gamma$ (in dyne cm\(^{-2}\) or N m\(^{-2}\)) is defined as the excess free energy at the liquid-air interface that stems from the imbalance in the attractive forces experienced by molecules at the surface of the liquid. To minimize the interfacial energy, a geometric shape with the highest possible volume to surface ratio, namely a sphere, is formed. On a solid surface, as shown in Fig.[2.2]b), a droplet with a finite liquid-solid interface is shown. In this figure, the interfacial energies are given by $\gamma_{SL}$, $\gamma_{SV}$, and $\gamma_{LV}$, for the solid-liquid, solid-vapor and the liquid-vapor interfacial energies, respectively. A droplet is said to partially wet a surface when the liquid/solid interface remains finite and the drop exhibits an equilibrium contact angle $\theta$. At the three-phase boundary of a droplet in equilibrium with the surface, the three horizontal components of the surface tensions (each with a tendency to retract their interface) are in balance.

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \quad (2.2)$$

Complete wetting (Fig.[2.2]a)) occurs when the droplet spreads over the solid ($\cos \theta = 1$), thereby maximizing the interactions of the liquid with the solid. Most liquids have a surface free energy $\gamma_{LV}$ less than 100 dyne cm\(^{-2}\) (water at 20\(^\circ\)C has $\gamma_{LV} = 72$ dyne cm\(^{-2}\)) and readily spread on a solid surfaces with surface energies larger
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than $\gamma_{LV}$. By completely wetting and covering surfaces with a higher surface energy, the overall surface energy is reduced ($\gamma_{LV} + \gamma_{SL} < \gamma_{SV}$).

The other extreme (Fig.[2.2c]) is the non-wetting regime ($\gamma_{SV} < \gamma_{LV} \cos \theta + \gamma_{SL}$), where the molecules of the liquid experience such high cohesive forces (metallic liquids) or such low adhesive forces (solids bounded by van der Waals forces or surfaces covered with an organic self-assembled monolayer), that the droplet remains spherical and has a contact angle $\theta$ that approaches $180^\circ$.

Both regimes are employed to form so-called self-cleaning surfaces. In recent years, titanium oxide thin films have been deposited on glass to form a photocatalytic and hydrophilic self-cleaning glass\textsuperscript{2}. The hydrophilic nature of titanium oxide allows the complete spreading of water on the glass. The absorption of UV-radiation ($\lambda < 390$ nm) by titanium oxide forms positively-charged holes that are highly reactive with water. Positively charged free hydroxyl radicals\textsuperscript{4} are formed that are strongly oxidizing. In a reaction with organic molecules, CO\textsubscript{2}, H\textsubscript{2}O and HCl (if halogen compounds are involved) are produced that evaporate or diffuse into the water film and are then carried away.

Also the non-wetting regime has been the focus of intensive scientific and industrial research\textsuperscript{5,27,41,83}. Applications on a macroscopic scale - such as textiles, ship hulls and self-cleaning traffic indicators - and on a microscopic scale - microelectromechanical systems (MEMS) and biological processes - employ water repellant properties\textsuperscript{28}. The application of a technique that mimics the surface texture of Lotus leaves greatly reduces the problems that plague MEMS, such as friction\textsuperscript{13}, condensation of water resulting in adhesion and meniscus forces\textsuperscript{75,76} and, of course, organic contamination of such surfaces. Following the discovery of the self-cleaning properties of the Lotus leaves by W. Barthlott\textsuperscript{6}, colloidal systems\textsuperscript{38,39} and surface modifications\textsuperscript{27} were employed to mimic the self-cleaning nature of butterfly wings and Lotus leaves. Other approaches to obtain surfaces with superhydrophobic properties include self-assembly\textsuperscript{88} and micro- or nanostructuring\textsuperscript{41}. It has for instance been shown that photocatalytic Zinc Oxide nanorods are able to switch from superhydrophilic to superhydrophobic, by exposure to UV radiation and darkness, respectively\textsuperscript{29}.

\subsection{2.4 Capillary waves}

The surfaces of liquids are in motion; the interface between a liquid and its vapor is roughened by thermally excited surface waves. Based on X-Ray measurements on the surfaces of a cyclohexane-methanol mixture by Gilmer\textsuperscript{36}, Buff\textsuperscript{20} introduced a general theory of interfacial structure based on capillary waves. The capillary wave theory was supported X-Ray measurements of liquid surfaces of water, methanol, carbon tetra-chloromethane by Braslau\textsuperscript{15} and on alkanes by Ocko\textsuperscript{59}.

The largest and smallest capillary wave vectors that are sustained by the interface, $q_{disp}$ and $q_{grav}$, respectively, are determined by dispersion (or Van der Waals force,
Figure 2.3: a) Surface roughness induced non-wetting. The rough surface traps pockets of air between the drop and the surface, resulting in an unusually large contact angle.37,41 Reprinted by permission from Macmillan Publishers Ltd: S. Granick, Y. Zhu, and H. Lee, Nature Materials, 2003, 2, 221, Copyright 2003. b) Water droplets on a wood surface treated with BASF’s ”Lotus Spray”, which has made the surface extremely water-repellant (superhydrophobic).

Eq.[2.3]) and gravitational forces (Eq.[2.4]).

\[ q_{\text{disp}} = \frac{2\pi \gamma l^4}{A} \]  \hspace{1cm} (2.3)

\[ q_{\text{grav}} = \frac{\Delta \rho g}{\gamma} \]  \hspace{1cm} (2.4)

Wavelengths above this range are suppressed by gravitational forces, those below by dispersion forces. The average energy of each capillary wave is determined by the equipartition of energy. Equipartition of energy implies that molecules in thermal equilibrium have the same average energy associated with each independent degree of freedom of their motion. The energy per molecule is given by \( \frac{1}{2}k_B T \), where \( k_B \) corresponds to the Boltzmann constant and \( T \) to the temperature. Integrating over the spectrum of capillary waves, the average mean square displacement of the interface \( <\Delta \zeta^2> \) is found (Eq.[2.5]).

\[ <\Delta \zeta^2> = \frac{k_B T}{2\pi \gamma} \ln \frac{q_{\text{disp}}}{q_{\text{grav}}} \]  \hspace{1cm} (2.5)

In Eq.[2.3], the dispersive capillary wave vector \( q_{\text{max}} \) is a function of the surface tension \( \gamma \), the film thickness \( l \) and the Hamaker constant \( A \) for the interaction between the substrate and the air across the film. The Hamaker constant is estimated from
refractive index and dielectric constant data using an approximation based on the Lifshitz theory \(^{46,69,78,81}\). In the next section, a short introduction will be given about the van der Waals forces and the associated Hamaker constant, based on the book "Intermolecular & Surface Forces" \(^{46}\).

### 2.5 Van der Waals forces and Hamaker constant

Van der Waals discovered that real gasses do not obey the ideal gas law due to attractive intermolecular interactions, now known as the van der Waals forces. The van der Waals forces stem from polarization effects between permanent dipoles and/or induced-dipoles and consists of three contributions. The induction forces arises from the interplay of a permanent dipole with an apolar molecule, the orientation (or dipole) forces from the interaction of two permanent dipoles, and finally, the dispersive force from two apolar molecules.

Unlike gravitational and Coulomb forces, van der Waals forces are not pairwise additive. The force between molecules is affected by the presence of other nearby molecules. As a result, the field emanating from a molecule reflects off of other molecules, which are thereby also polarized. Hamaker showed that the van der Waals forces could be split into a purely geometrical part and a constant \(A\), called the Hamaker constant \(^{81}\). Initially, the van der Waals forces were crudely approximated, but to avoid the assumption of additivity, Lifshitz developed a theory for the interaction between condensed bodies that involved only the bulk optical properties over the entire electromagnetic spectrum. The Hamaker constant was determined with increasing accuracy since 1972, when the optical properties, including the absorption spectra in the far-UV region, became available for an increasing number of materials \(^{47}\).

The non-additive approach, useful for non-conductive media, was suggested by Lifshitz and Dzyaloshinskii, who related the van der Waals interaction energy to the reflective indices \(n_i\) and the dielectric constants \(\varepsilon_i\) of the materials (Eq.[2.7]). Here, the interactions between layers 1 and 3 are considered, acting across an intermediate layer 2. While Eq.[2.7] is an often used approximation for the non-retarded Hamaker constant, the full equation that follows from the Lifschitz' theory is more rigorous and involves the integration of the dielectric functions over the entire frequency spectrum (not shown here).

\[
A = A_{v=0} + A_{v>0} \tag{2.6}
\]

\[
A \approx \frac{3}{4} k_B T \frac{(\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}) \left(\frac{\varepsilon_2}{\varepsilon_2 + \varepsilon_3}\right) + \frac{3h_p \nu_e}{8\sqrt{2}} \frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{\sqrt{(n_1^2 + n_3^2)} \sqrt{(n_2^2 + n_3^2)} \left\{\sqrt{(n_1^2 + n_3^2)} + \sqrt{(n_2^2 + n_3^2)}\right\}} \tag{2.7}
\]

The first term is the zero-frequency energy of the van der Waals interaction \(A_{v=0}\)
and the second term gives the dispersion energy contribution ($A_{v>0}$). In Eq.[2.7], $n_1$, $n_2$, $n_3$ and $\varepsilon_1$, $\varepsilon_2$, $\varepsilon_3$ are the refractive indices and dielectric constants of the media 1, 2 and 3, respectively. Other parameters are the Boltzmann constant $k_B$, temperature $T$, Plank’s constant $h_p$ and the main electronic absorption frequency $\nu_e$; a value of $\nu_e$ of $3\cdot10^{15}$ s$^{-1}$ is commonly used. Eq.[2.7] is approximated by

$$A_{132} \approx (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}})$$

(2.8)

and allows the Hamaker constant $A_{132}$ to be described as a function of the Hamaker constants $A_{ii}$ (i = 1, 2, 3) of layers (1), (2) and (3). $A_{ii}$ is the Hamaker constant of two identical media $i$ (for example: air) acting across a third (for example: polystyrene). Entering $\varepsilon_1 = \varepsilon_3$, $n_1 = n_3$ in Eq.[2.7]:

$$A_{11} = A_{131} = \frac{3}{4}kT(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3})^2 + \frac{3h_p\nu_e}{16\sqrt{2}}\frac{(n_1^2 - n_3^2)^2}{(n_1^2 + n_3^2)^{3/2}}$$

(2.9)

The value of $A_{11}$ can be determined using several methods. 1) The Hamaker constants can be calculated using the Lifshitz’ theory. The accuracy relies on the quality of the experimental dielectric data and the accuracy of the spectral representation, not only in the ultraviolet spectral region, but also in the infrared. Some solids (not included in Table[2.1]) show a large contribution to the retarded van der Waals forces that stem from absorption in the infrared. Without detailed knowledge of the absorption in the IR spectrum of materials that show a dominant influence on the retarded Hamaker constant, large errors are introduced in the retarded Hamaker constant (>10%). 2) The Hamaker constants can also be obtained by measuring the enthalpy change when immersing a solid into a non-polar solvent. Medout et al. showed that the Hamaker constant relates to the immersion enthalpy as:

$$A_{11} = 24\pi D_0^2 \frac{\gamma_L}{\gamma_L} \frac{1}{2} \left(1 - \frac{\Delta_{imm}H}{k_B} + \gamma_L \right)^2$$

(2.10)

In Eq.[2.10], the immersion enthalpy is $\Delta_{imm}H$, the surface tension of the non-polar liquid is $\gamma_L$ (in J/m$^2$), the equilibrium distance between two identical materials in vacuum, when the Born repulsion is taken into account, is $D_0$, and finally, the Boltzmann constant is $k_B$.

When the dielectric constant of the middle layer (3) has a value that is intermediate to those of the two delimiting interaction layers (1 and 2), the Hamaker constant is negative ($A_{11} < A_{33} < A_{22}$). The repulsive van der Waals forces tend to increase the thickness of medium 3 (and thereby disjoin layers 1 and 2) in order to lower the free energy. A repulsive or negative pressure related to the van der Waals forces is called the disjoining pressure. The corresponding pressure for positive or attractive van der Waals forces is called the conjoining pressure. Due to the $1/h^2$ dependence of the interface potential ($\phi \propto A/12\pi h^2$, see also Eq.[2.23]), the van der Waals forces are long-range forces and act significantly over distances up to about 10–20 nm.
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Table 2.1: Hamaker constants
Sources: *Visser81, †Dunlap26, §Wasserman85, ‡Israelachvili46, ††Meli55, ‡‡Hough44, ¶Bergström11, ‡Seemann65,66.

Often, only the non-retarded Hamaker constant is considered. Especially when considering the interactions between macroscopic bodies, however, the effects of retardation can be important. At distances exceeding \( \approx 5 \) nm, the dispersion contribution to the van der Waals forces decays as a result of retardation. The dispersion forces act over both short and long distances and include the attraction and repulsion of neutral atoms and molecules due to induced-dipole induced-dipole interactions. As a result of the retardation, the Hamaker constant can change sign at some finite distance.

2.6 Thin film stability

The behavior of viscous liquid films on flat solid substrates has been under intense investigation since the middle of the 20th century. Non-volatile viscous silicone oils were used in experiments designed to investigate wetting of surfaces held at various angles and of different geometries7,17,45,52,77. The behavior of a thin liquid film on a substrate shares many similarities to the earlier described wetting cases (partial, complete and non-wetting). It is therefore not surprising that shortly after intense investigations of the principles behind wetting, dewetting phenomena gained in popularity.

A typical thin film is a liquid layer on a substrate with a (free) surface where the liquid is exposed to air (or a gas) or another fluid. Film deposition techniques, such as spin-coating, dip coating or vapor deposition, are used to prepare a thin film on a substrate. The thickness \( h \) is commonly much smaller than the lateral extent of the film \( L \), and as a result, the flow of liquid primarily takes place in the lateral direction (parallel to the substrate). A liquid film, obtained this way, will not necessarily remain intact. A film of a liquid that spontaneously wets a substrate is stable to distortions or perturbations. However, a film of a liquid that does not spontaneously wet (partial wetting or non-wetting scenario) a surface may not withstand the development of
either nucleated or spontaneously developing instabilities.

A widely used approach to analyze thin film stabilities is analogous to that of Cahn\textsuperscript{22} and Vrij\textsuperscript{82}. Vrij was the first to include van der Waals forces in the stability analysis of soap films. The now as classical regarded model of thin film breakup by Vrij regards the capillary instability mechanism of thin film breakup by thermal fluctuations as an analogue to spinodal decomposition in fluid mixtures. In this model, the height fluctuations correspond to composition fluctuations in a fluid mixture. The analogy ends with the driving forces that are associated with the processes. The surface energy, rather than the fluid interfacial energy, is the driving force for the film rupture process\textsuperscript{87}.

Cahn investigated the growth of composition fluctuations during the spinodal decomposition of immiscible (metallic) fluids. He remarked that initially there would be a spread of wavelengths present and that some would grow while others would decay. In a linear stability analysis, infinitesimal perturbations (capillary waves) bring the film out of its initial state. The perturbations are assumed to be sinusoidal in shape and are given by Eq.[2.11].

$$h(x, t) = h_0 + \zeta e^{iqx + \frac{t}{\tau}}$$  \hspace{1cm} (2.11)

The liquid flow is governed by the macroscopic momentum equations (Navier-Stokes equations) that apply Newton’s second law of motion to a volume element. Since we are dealing with a thin film, where the thickness $h$ is far smaller than the length scale of the developing instability, we obtain a thin film or long-wavelength approximation. Due to the similarities with the classical lubrication theory, this approach is also called the lubrication approximation\textsuperscript{16}.

$$\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} = -\nabla \frac{p}{\rho} + \eta \Delta \mathbf{v} + \mathbf{g}$$ \hspace{1cm} (2.12)

In the resulting flow of a non-volatile fluid, the fluid density $\rho$ is constant (incompressible) and the continuity equation ($\frac{\partial \rho}{\partial t} + \rho \nabla \cdot \mathbf{v} = 0$) therefore requires that the material flux in all directions $\nabla \cdot \mathbf{v} = 0$. For an incompressible Newtonian fluid, with a constant density $\rho$ and kinematic viscosity $\eta$, the Navier-Stokes equation is given by Eq.[2.12].

The flow of a polymer melt usually occurs under creeping flow conditions and is represented by Reynolds number $\mathcal{R} \ll 1$. The creeping flow assumption implies that the fluid inertia is negligible. The inertia term in the Navier Stokes equation is smaller than the viscous term and therefore can be ignored ($\mathbf{v} \cdot \nabla \mathbf{v} \approx 0$). For films of thickness $h \ll L$ ($L$ is the lateral extent of the film), and below the capillary length $h < l_{\text{cap}}$, we obtain the Navier-Stokes equation for a laminar flow in $x$-direction in quasy-static-state ($\partial v_t \approx 0$).
Figure 2.4: Schematic drawing of a thin polymer film of thickness $h$. Thermally excited surface waves induce periodic thickness fluctuations with wavelength $\lambda = \frac{2\pi}{q}$, where $q$ is the wave vector. The Poiseuille-type flow is indicated by a parabolic flow profile with velocity $v$.

\[ 0 = -\frac{\nabla p}{\rho} + \eta \Delta v \]  

(2.13)

The vertical component of the velocity (normal to the surface plane) is neglected. The velocity therefore only depends on the $x$-coordinate ($v_z = 0, v = v_x$). In addition, the variation of the pressure in the film is assumed to depend only on the lateral coordinate ($\partial_z P = 0$), leading to

\[ 0 = -\partial_x P + \eta \partial_{xz} v \]  

(2.14)

\[ \partial_{zz} v = \frac{\partial_x P}{\eta} \]  

(2.15)

\[ v = \frac{1}{2\eta} (\partial_x P) z^2 + az + b \]  

(2.16)

The variables $a$ and $b$ are obtained by inserting the boundary conditions at the two interfaces (Eq.[2.17]). At the liquid-solid interface ($z = 0$), a no-slip boundary condition is assumed ($b = 0$), and the liquid-vapor interface, $z = h$, is assumed to be stress-free.

\[ z = \begin{cases} 
0 & : \quad v = 0 \\
h & : \quad \sigma = \eta v_z = 0 
\end{cases} \]  

(2.17)
\[ v = \frac{1}{2\eta} (\partial_x P)(z - 2h)h \] (2.18)

The average velocity, given by Eq.[2.19], is of the Darcy form: the advancing velocity is proportional to the pressure gradient\(^50\). The resulting 1-dimensional flux \( J \) through a surface \( A = h \) is then given by Eq.[2.20].

\[ \bar{v} = \frac{1}{h} \int_0^h v dz = \frac{h^2}{3\eta} (-\partial_x P) \] (2.19)

\[ J = A\bar{v} \]

\[ J = \frac{h^3}{3\eta} (-\partial_x P) \] (2.20)

The quadratic velocity profile (Poiseuille type flow), given by Eq.[2.20], describes the velocity in the liquid film. The velocity profile also introduces another requirement, namely volume conservation. In a one dimensional case this means that a change in volume has to be accompanied by a change in the film thickness.

\[ \partial_t h + \partial_x J = 0 \] (2.21)

Combining Eq.[2.21] with Eq.[2.20], we have the equation of motion for a system that corresponds to Fig.[2.4].

\[ \partial_t h = \partial_x \left[ \frac{h^3}{3\eta} (\partial_x P) \right] \] (2.22)

In the lubrication model, the polymer film in its melt state is treated as a Newtonian liquid. The assumption of Newtonian behavior is justified for polymers having short chains, well below the entanglement length of polystyrene\(^57\), or at time scales far larger than the time constant \( \tau_t \) that follows from the disengagement time that is defined in the framework of the reptation model\(^34,60,80,86\). For higher molecular weights, polymer chains are restricted in their motion by entanglements and \( \tau_t \) is the time the polymer chain needs to explore the extent of its confinement.

It should also be noted that the no-slip boundary condition is an assumption that is under investigation and may not always be justified\(^18,19,43,48,62,79\). It does not necessarily hold for polymer melts, however, it is used for the sake of simplicity. It was proposed in 1979 by de Gennes that entangled polymers show highly anomalous slip, represented by the slip length \( b \), when flowing near a smooth passive surface. The slip length for a simple shear flow is the distance beyond the interface at which the liquid velocity extrapolates to zero\(^18\).
2.7 Dewetting

Initially, macroscopic films of silicone oils and alkanes, with thicknesses between 20–50 µm, were used to investigate the dynamics of dewetting\textsuperscript{61}. The holes in the films were created by capillary suction with a glass capillary or by a jet of dry air. Not soon after, in 1992 by G. Reiter, thin polystyrene films with film thicknesses below 1 µm were investigated\textsuperscript{64}. It had been predicted that a hole in a liquid film would continue to grow if its lateral size exceeds a critical value\textsuperscript{73}. With the knowledge that macroscopic films of silicon oils and alkanes destabilized through the nucleation of holes, it was expected that the rupture mechanism for thin polymer films is spontaneous. However, evidence for the breakup of films by spinodal dewetting remained limited. Some observations of dewetting of polymer thin films were consistent with the model describing spinodal dewetting, but without kinetic studies of thin film breakup, the relation to the theoretical model, was not proven. The morphology obtained from the spinodal dewetting of liquid metal films\textsuperscript{14} was a break-through and led to the conclusion that most observations of dewetting of polymer films corresponded to the heterogenous nucleation mechanism. In 1998, Xie \textit{et al.} reported

Figure 2.5: SEM image of PS drops on a silicon substrate covered with a self-assembled monolayer of octadecyltrichlorosilane. The measured contact angle is 50°\textsuperscript{58}. Courtesy of Mihaela Nedelcu.

Figure 2.6: Effective interface potential \(\phi\) as a function of the thickness of a PS film. The dotted curve corresponds to a stable system, the dashed curve to a metastable system, and the solid curve to an unstable system\textsuperscript{67}. Reused with permission from R. Seemann, S. Herminghaus, C. Neto, S. Schlagowski, D. Podzimek, R. Konrad, H. Mantz, and K. Jacobs, Journal of Physics: Condensed Matter, 17, S267-S290 (2005). Copyright 2005, Institute of Physics.
that thin polystyrene films on silicon wafers dewet spontaneously for film thicknesses below approximately 10 nm\textsuperscript{87}.

An important finding by Seemann et al. was the influence of the native oxide layer on silicon substrates on the Hamaker constant of the experimental system\textsuperscript{65,66}. By modifying the thickness of the silicon oxide layer, the stability of a thin polystyrene film on a silicon-silicon oxide substrate could be changed from stable to metastable, or to unstable (Fig.[2.7]).

The dynamics of a spontaneous dewetting process are modelled using the conjoining/disjoining pressure concept and the lubrication theory, a concept first described by Derjaguin in 1965. Considering only the non-retarded van der Waals forces acting on a polymer thin film, in the absence of other external forces, the free energy per unit area varies with the film thickness $h$ as

$$\phi_{vdW}(h) = c_{Si}h^8 + \frac{A_{Si}}{12\pi h^2}$$

(2.23)

where $A_{Si}$ is the non-retarded Hamaker constant (Eq.[2.7]) and $c_{Si}$ is the strength of the short-range interaction on the silicon wafer\textsuperscript{65}. It should be noted that at this stage, the stabilizing Laplace pressure due to the surface tension is excluded. Including the native oxide layer on the silicon, Eq.[2.23] has to be adjusted to represent a stacking of silicon/silicon oxide/polystyrene/air\textsuperscript{65}.

$$\phi_{vdW}(h) = c_{SiO}h^8 - \frac{A_{SiO}}{12\pi h^2} + \frac{A_{SiO} - A_{Si}}{12\pi (h + d_{SiO})^2}$$

(2.24)

In Eq.[2.24], the interactions of the polymer with the silicon oxide of strength $c_{SiO}$ ($\propto 10^{-77}$ J m\textsuperscript{-6}) are included in the first term. The second term is the interaction potential of polymer with the silicon oxide layer with thickness $d_{SiO}$ and the third is the difference between the interactions of the polymer with the silicon and the oxide layer. $A_{SiO} = 2.2\times10^{-20}$ J and $A_{Si} = -1.3\times10^{-19}$ J are the experimental Hamaker constants of PS on Si and on SiO that were used by Seemann et al.\textsuperscript{65} and $h$ is the polymer film thickness.

Fig.[2.7] shows three plots, corresponding to a stable film (dotted line), a metastable film (dashed line) and an unstable film (solid line). The morphologies, corresponding to the different film destabilization mechanisms, are shown in Fig.[2.7]. A stable system, such as PS on bare Si, has a positive value of the effective interfacial potential $\phi_{vdW}(h)$ that decreases with increasing film thickness. Capillary waves increases the surface area and thereby the free energy. A state of minimal free energy can not be reached by destabilizing the interface.

A metastable system, described by Eq.[2.24] and shown in Fig.[2.7](c), shows a global minimum at $h = h^*$ and a maximum at $h = h_{max} > h^*$, where $h^*$ is the equilibrium film thickness. An example is PS on Si with a native SiO layer of $\approx 2$ nm. Film destabilization and film rupture occurs by heterogenous nucleation for $h > h_{max}$.
Figure 2.7: Mechanisms of a) spontaneous dewetting, b) thermal nucleation and c) heterogeneous nucleation. Thermal nucleation occurs at $\phi''_{vdW} \approx 0$, in between the criteria for spontaneous dewetting and heterogeneous nucleation. The thermal nucleation of holes is random and proceeds continuously throughout time. Reprinted figure with permission from R. Seemann, S. Herminghaus, and K. Jacobs, Physical Review Letters, 86, 5534 (2001). Copyright (2001) by the American Physical Society.

where $\phi''_{vdW}(h) > 0$ (double derivative of $\phi_{vdW}(h)$), and by spontaneous dewetting for $h^* < h < h_{max}$, where $\phi''_{vdW}(h) < 0$. Chemical heterogeneities and dirt particles on the surface create a "dry" spot in between the film and the substrate from where the instability develops. Withdrawal of the film from this nucleus proceeds by the formation of a hole. The dependency on heterogeneities on the surface leads to a random distribution of holes in the initial phase of dewetting. In the final stages of dewetting, the retracting polymer material is gathered in droplets on the surface that have a contact angle that is given by Young’s law (Eq.[2.2]).

Another example is shown in Fig.[2.7] where a PS film had retracted from a self-assembled monolayer that was grafted onto a silicon substrate with a native oxide layer. This Si/SiO/OTS/PS system is metastable (solid line in Fig.[2.7]) and the interfacial potential is given by Eq.[2.25].

$$\phi_{vdW}(h) = \frac{c_{OTS}}{h^8} - \frac{A_{OTS}}{12\pi h^2} + \frac{A_{OTS} - A_{SiO}}{12\pi(h + d_{OTS})^2} + \frac{A_{SiO} - A_{Si}}{12\pi(h + d_{OTS} + d_{SiO})^2}$$  \hspace{1cm} (2.25)

Eq.[2.25] includes additional interaction terms for the octadecyltrichlorosilane monolayer. The effective Hamaker constants are given by $A_{OTS}$ (OTS/PS/air), $A_{SiO}$ (SiO/PS/air) and $A_{Si}$ (Si/PS/air), the polymer film thickness by $h$ and the thicknesses of OTS and SiO by $d_{OTS}$ and $d_{SiO}$, respectively.

In this view of the van der Waals pressure on a thin polystyrene film, the Laplace pressure contribution due to the curvature of the interface was disregarded. A curved liquid surface will generate a Laplace pressure inversely proportional to the radius of curvature. The Laplace pressure $P_L$ stabilizes the film by damping out all perturbations and can be related to the surface tension $\gamma$ and the film thickness $h$ as.
\[ P_\mathcal{L} = -\gamma \partial_{xx} h \] (2.26)

### 2.8 Linear Stability Analysis

Adding the Laplace pressure contribution to the equation of motion Eq.[2.22], the following equation is obtained, where the disjoining pressure, in terms of the interface potential, is then defined as \[ \Pi = -\mathcal{P} = -\partial_h \phi. \] \( \mathcal{P} \) is a sum of the pressure contributions that act on the film.

\[ \partial_t h = \partial_s \left[ \frac{h^3}{3\eta} (\partial_x \mathcal{P} - \gamma \partial_{xxx} h) \right] \] (2.27)

\[ \mathcal{P} = P_0 + P_{vdW} + P_{el} + P_{\Delta T} + \ldots \] (2.28)

\( P_{vdW}, P_{el} \) and \( P_{\Delta T} \) stem from the van der Waals forces, an applied electric field and an temperature gradient, respectively. The contributions are additive and act on polymer/air interface that shows periodic fluctuations that are induced by capillary waves. Other pressure effects, such as gravity, magnetic fields, acoustic pressure, double layer interactions, and so on, are not included in the analysis presented in this thesis.

The temporal evolution of the liquid-air interface is governed by Eq.[2.27]. By taking the derivative of Eq.[2.27] and using the definition for the film thickness as presented in Eq.[2.11], a linear stability analysis of a free liquid film, subjected to a pressure \( \mathcal{P} \) is performed.

\[
\begin{align*}
\partial_t &= \frac{h^2}{\eta} (\partial_x h) [\partial_x \mathcal{P}] + \frac{h^3}{3\eta} [\partial_{xx} \mathcal{P}] \\
&= \frac{h^2}{\eta} (\partial_x h) [-\gamma (\partial_{xxx} h) + (\partial_h \mathcal{P})(\partial_x h)] \\
&\quad + \frac{h^3}{3\eta} [\gamma (\partial_{xxxx} h) + (\partial_{hh} \mathcal{P})(\partial_x h)^2 + (\partial_h \mathcal{P})(\partial_{xx} h)] \quad (2.31)
\end{align*}
\]

In the long-wavelength limit, where the amplitude of the surface waves are much smaller than the film thickness \((\zeta \ll h_0)\), terms of order \( \mathcal{O}(\zeta^2) \ll \mathcal{O}(\zeta) \), where \( \partial_x h \propto \zeta \). Therefore, terms non-linear in \( \zeta \) (\( \mathcal{O}(\zeta^2) \)) are disregarded. Eq.[2.31] simplifies to

\[
\partial_h = \frac{h^3}{3\eta} [-\gamma (\partial_{xxxx} h) + (\partial_h \mathcal{P})(\partial_{xx} h)] \quad (2.32)
\]
This coupling of a force balance to the capillary wave spectrum yields a dispersion relation (Eq.[2.33], Fig.[2.8]) that describes the temporal evolution of the sinusoidal perturbations in \( h \). Perturbations with wave vector \( 0 < q < q_c \) and a growth rate \( \tau^{-1} > 1 \) are exponentially amplified, whereas they are damped for \( \tau^{-1} < 1 \ (q > q_c) \).

\[
\frac{1}{\tau} = -\frac{k^3}{3\eta}\left[\gamma q^4 + q^2 \partial_h \mathcal{P}\right]
\]  

(2.33)

\( \mathcal{P} \) is \( \partial_h \phi \), and in case of the earlier described non-retarded van der Waals forces, \( \mathcal{P} = \partial_h \phi_{vdW} \). For \( \phi'' \) (or \( \partial_h \mathcal{P} \) > 0, capillary waves at the liquid-air interface are exponentially amplified. The fastest growing mode \( q_m \) dominates the morphology of the destabilized film.

\[
q_m = \sqrt{-\frac{\partial_h \mathcal{P}}{2\gamma}}
\]  

(2.34)

Figure 2.8: Graphical representation of the dispersion relation (Eq.[2.33]). Capillary waves at the liquid-air interface are either damped (dashed lines) or exponentially amplified (solid line). The force balance at the interface, with contributions from the viscous forces, surface tension, van der Waals forces, and externally applied forces, yields a dominant mode \( q_m \) with corresponding growth rate time \( \tau_m^{-1} \).
2.9 Concluding Remarks

In this chapter, the principles of polymers and thin liquid films were introduced. A polymer is a glass forming macromolecular compound with a high viscosity in the melt state. The physical properties of polymers depend on the monomer, the polymer chain length, the polydispersity, the processing condition, temperature and so on. Some polymers, such as polystyrene and poly(methyl methacrylate), are glassy at room temperature, but liquid at an elevated temperature. Because polymers are not volatile and any change in a polymer film is frozen-in when reducing the temperature below the glass transition temperature, polymers are ideal to investigate thin film instabilities.

A thoroughly investigated instability is related to destabilizing molecular forces. Destabilizing molecular interactions lead to film rupture if these are sufficiently strong to overpower the stabilizing surface tension. The latter opposes film thickness fluctuations in very thin liquid film. A spontaneous instability develops and causes the retraction of the liquid into droplets. While these molecular forces act over a limited distance, applying a much stronger force allows film destabilization to be investigated in thicker films. The characteristics of the induced instability and the morphology that is observed in the films are similar. Examples of these forces stem from an applied electric field and temperature gradient. In the next chapter, the experimental techniques are introduced, after which, the instabilities are discussed.
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