



Understanding and controlling the friction of human hair

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ABSTRACT

Pleasant sensory perception when touching, brushing, and combing hair is largely determined by hair friction. As hair ages and weathers, its friction increases, mainly due to the progressive loss of the protective 18-methyleicosanoic acid (18-MEA) monolayer on its surface. Hair also displays anisotropic friction due to the protruding edges of the cuticles, which can interlock when sliding towards the root of hair. Moreover, certain chemical (e.g. bleaching and colouring), thermal (e.g. straightening and curling), and mechanical (e.g. brushing and combing) processes can dramatically accelerate 18-MEA loss, leading to much higher friction and unsatisfactory sensory perception. Hair care products, and in particular conditioners, have been developed to temporarily repair this damage through the deposition of various chemicals on the surface of the hair. These formulations can reduce friction to levels similar to that measured for virgin hair. Other external factors can also affect hair friction, such as humidity and cleanliness, as well as biological characteristics, such as ethnicity and age. Here, we provide a perspective on the advances made in the field of hair tribology, meaning the friction, lubrication and wear of hair. Historic and state-of-the-art experimental, theoretic and computational techniques for measuring hair friction are reviewed. We discuss different hair friction mechanisms across the scales and review the roles of surface chemistry and surface roughness on hair tribology. The influence of hair care products on hair friction is further discussed. Finally, we highlight open challenges and opportunities for future hair tribology experiments and models.

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1. Introduction

Biortribology, the study of friction, wear and lubrication in biological systems, [1] plays a central role in our everyday lives [2]. For example, the feeling when we touch, brush or comb our hair is affected by the friction between the hairs, as well as between hair and the polymers that are commonly used for the brush and comb prongs [3]. The surface of hair is covered by a scaly layer of overlapping cuticle cells, which are approximately 0.5 μm high and 5 μm long [3]. The microscale roughness due to the cuticle edges leads to characteristic stick-slip friction behaviour [4,5]. When healthy hair is brushed or combed conventionally (from root to tip), friction is relatively low [2]. However, when hair is backcombed (teased) in the opposite direction (from tip to root), a ratcheting mechanism from the cuticle edges can lead to much higher friction [6]. This is known as the differential friction effect (DFE), which has also been reported for other keratinous fibres, such as wool [7]. The DFE is more pronounced at high relative humidity, [8] or when the hair is chemically damaged by bleaching, [9] which is due to lifting of the cuticle edges. Bleaching also leads to increased hair friction through other non-topological nanoscale effects [10]. In particular, bleaching damages the protective 18-methyleicosanoic acid (18-MEA) monolayer on the outer surface of the cuticle, which can lead to dramatic increases in friction [11].

Hair is composed of dead cells that mostly contain α -keratin protein, which cannot be repaired through biological means. Therefore, the only way to restore the low-friction properties of damaged hair is to physically repair it by depositing beneficial compounds onto the hair surface from hair conditioners or other hair care products [12]. In many instances, the reduction of hair friction and adhesion is desirable for styling and combing hair [13]. Low hair friction is particularly beneficial for avoiding hair entanglement [13] and for providing a pleasant sensory perception [14] and high combability [15]. The development of hair care products that maintain low hair friction after rinsing requires insights from the nanoscale to the macroscale of both the hair fibre and the hair care formulations. A wide range of experimental techniques have been developed to measure the friction of hair sliding against various materials. Several experimental techniques have been applied to provide structural insights into the hair surface and its interactions with

hair care ingredients. Although hair has been found to deform even metallic materials such as steel, [16] it is still a relatively soft material, which can make surface characterization experiments difficult [17]. Computational methods, such as molecular dynamics simulations, have also become an integral tool for studying the nanoscale structure and friction of human hair [10,18].

The estimated value of the global hair care market is expected to exceed 100 billion US dollars by the end of 2024.[19] The development of the next generation of hair care products is driven by customer demands for an improved product performance and regulatory and societal requirements for more sustainable, environmentally-friendly formulations [20]. It is becoming increasingly important to improve biocompatibility and biodegradability by replacing common hair care ingredients derived from crude oil, sulphate-based surfactants (e.g., SDS or SLES), and silicones with surrogates produced from natural sources [20]. At the same time, consumers expect the product performance, e.g., the cleansing efficiency, look and feel of hair not to degrade, or to even improve [20]. Achieving such a compromise requires an understanding of all relevant scales of soft surfaces — from the nanoscale (chemistry, structure) to the macroscale (look, feel).

This review provides a historical perspective of available tools and learnings in the realm of hair tribology. First, the physio-chemical details, structure of human hair and damage modes are introduced, as they are important to the understanding of hair tribology. Then, an overview of both macroscopic and nanoscale experimental techniques for measuring hair friction and adhesion will be given. Theoretical and numerical models such as molecular dynamics (MD) simulations and continuum approaches will be discussed subsequently, as they have become a cornerstone in hair care development in recent years. This first part of this work will follow a linear, mostly chronological fashion to adequately capture and honour the developments in hair tribology over the years. In the second part, we will put the contributions from experimental and numerical studies into context to review and discuss the relevant mechanisms that affect hair tribology and the appropriate handles for tuning it. Finally, an outlook of further challenges and potentials in the field of hair tribology will be provided.

This review will focus on the tribology of hair and how hair care formulations such as shampoos and conditioners can affect it. Additional key factors in the design of hair care products such as cleansing,

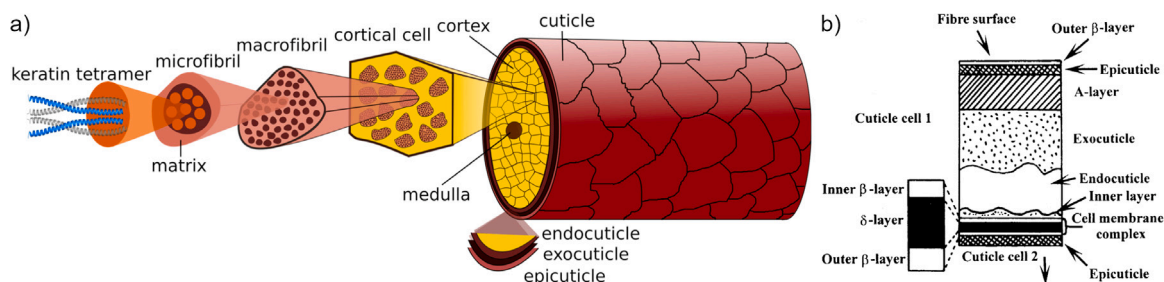


Fig. 1. Schematic representations of (a) the hierarchical structure of human hair and (b) the cuticle substructures.
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perfuming performance and formulation sustainability are discussed in detail elsewhere [19–23]. It is worth highlighting previous reviews on hair tribology-related topics: Luengo et al. [24] reviewed aqueous lubrication concepts in cosmetics. Bhushan [13] and Luengo et al. [25] previously highlighted nanoscale experimental techniques, particularly atomic force microscopy (AFM), to assess hair surface properties and the role of conditioners at this scale. Tokunaga et al. [26] reviewed degradation mechanisms of the hair surface, with focus on the epicuticle and the 18-MEA monolayer. Cunningham et al. [27] discussed the role of lamellar gel networks for hair conditioning formulations in a recent review. While many of these works are relevant for hair tribology and will therefore be covered here as well, this work also further extends to macroscopic hair tribology experiments, computational models and new advances in nanoscale hair tribology.

1.1. Structure of human hair

The human hair is a complex biological and hierarchical structure formed by several characteristic building blocks. The diameter of scalp hair is typically reported in the range of 50 – 100 μm [22,28–30]. A schematic representation of the hierarchical structure of hair due to Cruz et al. [31] is given in Fig. 1(a). The majority of the mass in hair is contained in keratin fibrils in the cortex giving rise to its elastomechanical properties [30,32,33]. In this work, we will focus on the surface of human hair which gives rise to its tribological properties. The reader is referred to further literature [34–36] for details on the cortex structure.

Popescu and Höcker [32] highlighted that the surface of healthy hair is hydrophobic, despite hair being hygroscopic, i.e., sensitive to absorbing water in humid environment. This is due to additional protective layers surrounding the cortex: The cortex is covered by overlapping cuticle cells, [37] which serve as a protective layer. The anisotropic, scale-like orientation of the cuticles in the root-tip direction is depicted in Fig. 2 which results in a directional dependence of hair friction [38]. The cuticle cells themselves consist of several characteristic layers. The original cuticle model due to Swift and Smith [39] is depicted in Fig. 1(b). A cell membrane complex (CMC) provides separation and adhesion between overlapping cuticle cells [30]. The outer layers of the cuticle are of particular interest in hair tribology as their chemical composition and structure are responsible for the surface characteristics of hair. The epicuticle and outer β -layer are largely constituent of cysteine residues [40]. The existence of the epicuticle layer has been reported in many studies, e.g., Refs. [39,41,42] but is not universally accepted. Recent evidence from AFM measurements due to Breakspear et al. [43] suggests that the outmost layer of the cuticle is directly connected to the A-layer and an epicuticle is not required. Some open questions remain on the formation processes of some of the cuticle layers which have been discussed elsewhere [44] but are not expected to be highly relevant to hair tribology.

In contrast, it is well-accepted that a fatty acid monolayer, consisting of the covalently bound 18-MEA, covers the cuticle cells of healthy

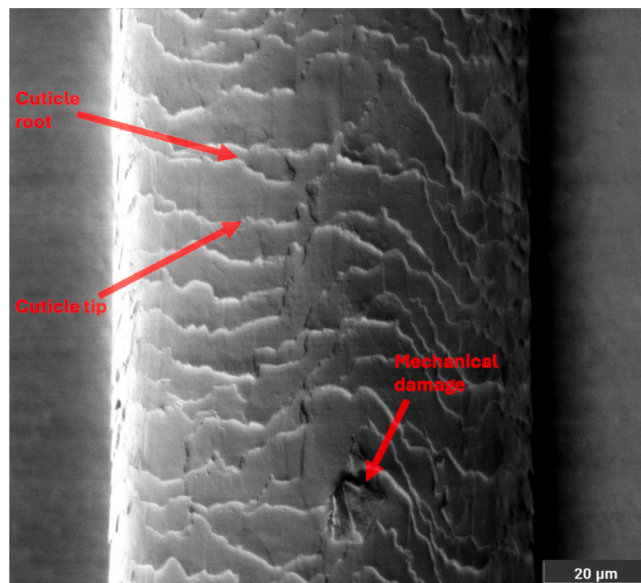


Fig. 2. Structure of weakly damaged hair from scanning electron microscopy (SEM) imaging obtained at a beam energy of 0.5keV (TESCAM). Courtesy of Marie-Louise Schlichting.

hair [11,40,45]. This *F-layer*, [46,47] is grafted to the cysteine-rich proteins in the epicuticle via thioester bonds [48]. The existence of 18-MEA on the hair surface has been highlighted in many studies [22,26,45,49–51]. The first systematic evidence of the F-layer on the surface of mammalian fibres was provided by Evans et al. [49] in 1985 by chemical extraction of the lipids from wool fibres. Jones and Rivett [45] predicted a disordered structure of the fatty acids due to the additional methyl branch of the 18-MEA which differentiates it from the linear eicosanoic acid ($\text{C}_{20}\text{H}_{40}\text{O}_2$). This results in additional resistance from environmental influences [45]. The intact 18-MEA monolayer also gives rise to the strong hydrophobicity of healthy hair [30,45].

Various models for the organization of the F-layer lipids have been proposed, including a closely packed monolayer [11,52] and more disordered structures [53–56]. Based on nanoscale adhesion experiments, [55] a heterogeneously ordered structure of the 18-MEA with patches of the exposed proteins is currently favoured [22]. Recent experimental investigations using AFM and X-ray photoelectron spectroscopy (XPS) [26] indicate a decrease in 18-MEA content on the hair surface from root to tip. These findings are consistent with earlier hypotheses [57] predicting weathering to lead to a non-uniform chemical composition of the hair from root to tip. McMullen and Kelty [58] highlighted the existence of micropores on hair which would only become visible in AFM imagery when bleaching or solvent-extracting hair. It was assumed that these pores were not a result of the chemical

bleaching routine but rather a natural feature of human hair. Furthermore, specific hair manipulations and damage modes can also have an effect on wear and hair chemistry:

1.2. Wear and damage modes on hair

Several hair damage modes have been identified in the literature. Damage to the internal hair structure, i.e., to the cortex, can occur from waving [59,60] and UV radiation from the sun [61,62]. The degradation of the F-layer can occur through dyeing, bleaching, rubbing, combing or UV exposure [62]. Certain health conditions may also affect hair fibre health [63] but are rare in comparison to damage from hair manipulations and weathering [64,65]. The structural damage due to weathering of untreated hair was found to be highly heterogeneous due to the non-uniformity of the external manipulations acting on the cuticles as they move away from the root of the hair in time [66]. Additionally, the overlapping nature of the cuticles leads to a higher exposure to wear near the tip of the cuticles. Increases in polarity in the tip region from surface potential measurements suggest that fatty acid coverage is reduced in this area compared to the cuticle root [67]. For long hair, prolonged weathering can also lead to cuticle fracture, lifting or complete cuticle cell delamination [65].

Hair without artificial treatment is commonly referred to as *virgin* hair in the literature. LaTorre and Bhushan define virgin hair as 'having an intact cuticle and absence of chemical damage' [5]. However, virgin hair may also show some degree of wear or mechanical [5] or chemical damage from normal weathering [56]. Heavy combing was found to strongly impact the cuticle structure, including microscopic damage such as holes in the cuticle and exposing parts of the endocuticle [68]. Both the interactions between hairs and the comb and hair-hair interactions were found to be relevant mechanisms for hair breakage due to combing [69]. The process of combing hair results in mechanical stress on the hair fibres, causing damaged cuticles to flake and strip away [68]. This is known as delamination [6] and can even lead to exposure of fresh cuticles with intact 18-MEA monolayers [70]. Severe bending and sun exposure can also induce fracture, splitting and cuticle delamination on the hair fibre [71]. UV irradiation can even result in the formation of small bumps (up to 5 nm height) on the cuticle surfaces [72]. Air pollution and cigarette smoke further induce measurable chemical damage of hair cuticles affecting both the fibre wetting and combing resistance [73]. Variations in hair breakage and mechanical damage can also be a result of different hair styles and morphological fibre differences among various ethnic groups. McMullen et al. [74] reported differences in mechanical properties, lipid content and fracture between hairs of African and Caucasian origin. Under strain, lifting of cuticles was found to be more pronounced in Caucasian than Asian hair, while undamaged African hair was more prone to fracture than Caucasian hair [75]. It is common to classify hair characteristics by the above three ethnic groups: African, Asian and Caucasian [5,74,75]. However, more refined classifications have also been proposed recently to account for more regional diversity [76–79].

One form of treatment is particularly damaging to the fibre and cuticles: Hair bleaching induces notable changes in hair morphology by chemically damaging the outer layers of the epicuticle [11,80,81]. Mechanical and chemical damage or a combination of both can lead to partial and even complete removal of the 18-MEA monolayer [50, 51,80]. Masukawa et al. [80] reported a strong sensitivity of the 18-MEA content on hair with the number of bleaching treatments. This is expected as hair does not have any natural repair mechanism.

The depletion of surface lipids results in a more hydrophilic behaviour due to the exposure of the polar proteins and oxidation to sulfonate groups [22,82]. A schematic of the F-layer damage due to bleaching is shown in Fig. 3 due to Korte et al. [82]. Tokunaga et al. [26] highlighted that upon removal of the 18-MEA from the cuticle, water spreads more easily between hairs in wet environment due to the reduced hydrophobicity. This was found to increase entanglement after

drying compared to virgin hair [26]. Ageing also affects the composition of the hair surface. Both the external and internal lipids content has been found to decrease in older individuals [83] and in grey hair as a result of ageing, which made hair more permeable [84]. Bloch et al. also noticed that curly hair was more prone to chemical damage from thermo-mechanical treatments due to higher mechanical resistance [85]. This was expected to affect hair of African origin more severely due to a higher occurrence of curliness. Higher combing forces in African hair were also attributed to mesoscale differences in the characteristic lengthscales of curls [85]. This illustrates the challenge that researchers and formulators are faced when asked to assess hair friction and optimize hair care products for low friction: Damage modes depend on both small-scale and mesoscale features which should be taken into account in their investigations.

The experimental techniques to quantify the degree of hair damage constitute chemical composition measurements of the hair surface, [26,84] surface energy or contact angle experiments, [86] surface charge, [82,87] or direct imaging and topography methods [80]. These approaches also present valuable references for setting up and validating new numerical models for hair tribology which we will discuss later in this work. Indirect indications of fibre damage can also be obtained from combing and friction force measurements on single hairs or bundles, which will be reviewed in a later section.

1.3. Hair care formulations

Hair care formulations play an integral role in the modification of hair tribology. Here, we discuss the relevant surface deposition mechanisms associated with such formulations before reviewing their tribological implications in later sections. More detailed reviews of the components found in shampoos and conditioners can be found elsewhere [21,23,88,89]. A typical shampoo is composed of 10 to 30 different ingredients [88]. Cleansing and conditioning are primary functions of most hair care products [88]. Additional functionality, such as anti-dandruff treatment by the addition of active ingredients, may further contribute to formulations [88]. Cleansing, i.e., the removal of dirt, excess lipids and sebum is typically achieved through an anionic surfactant base in shampoo formulations [23,89]. Anionic surfactants can also increase the product viscosity [23] through formation of aggregates such as wormlike micelles [90]. Conversely, conditioning is defined as restoring the surface and bulk properties of healthy hair, [88] as the fibres are exposed to prolonged external damage and wear. This is typically associated with an effective detangling performance, facilitated combing, [89] as well as a visually appealing look and pleasant feel [13]. Hair conditioning occurs either directly by applying standalone conditioners after the wash or by deposition of relevant conditioning molecules from a 'two-in-one' shampoo. Standalone hair conditioners typically contain functional molecules in the form of cationic surfactants, cationic polymers, fatty alcohols and silicones [13,91]. These conditioners usually exist in single-phase conformations, such as lamellar gel networks [27,92–94]. Conditioning products in liquid form act by adsorption of molecules from the aqueous formulation during application and rinsing. Cationic surfactants and polymers effectively deposit onto hair due to available negative surface charges. On chemically damaged hair, more cationic surfactants adsorb due to an increase in cysteic acid residues as more of the hydrophobic F-layer is oxidized [95]. Conditioners adsorption has been studied extensively and can span from single molecules lying flat on hair to the deposition of monolayer, bilayers and compact aggregates [96–98].

The addition of cationic polymers to a shampoo with an anionic cleansing base might not only be desirable for conditioning purposes, but also as viscosity modifiers [20]. A central mechanism in contemporary shampoos is the dilution-induced or 'precipitation-enhanced' [99] deposition of conditioning molecules such as cationic polymers [100–102] and silicones [103,104] to hair. This mechanism is based on a phase transition from a single-phase solution during application into

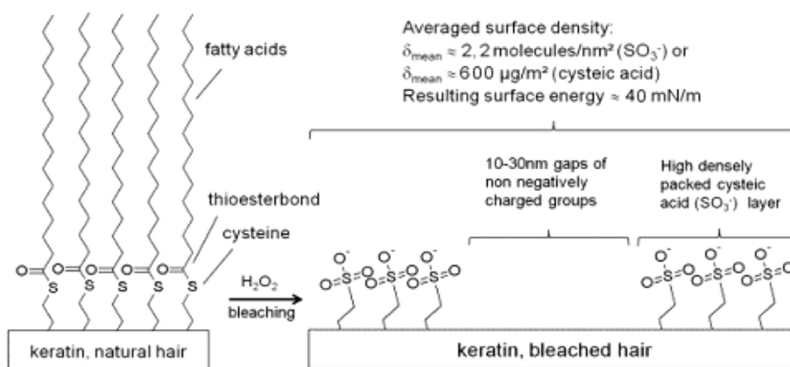


Fig. 3. F-layer damage mode due to hair bleaching.

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a two-phase region in the phase diagram during rinsing [99]. The baseline shampoo will typically contain polyelectrolytes and surfactants in concentrations where the polyelectrolytes are neutralized by micellar pinning, also referred to as ‘string of beads’ [105] or ‘pearl-necklace structures’ [106,107]. Additionally, free micelles are prevalent in solution. This is therefore referred to as the ‘resolubilized region’ [101] in the phase diagram. During rinsing, the surfactant concentration then decreases which leads to the formation of precipitates (dense viscous phase or ‘coacervate’) [106,108]. These precipitates contain high concentrations of polyelectrolyte-surfactant complexes and favourably deposits to the hair surface, thus providing a conditioning effect during the rinse.

On charged surfaces such as hair, the competition between anionic surface sites, polycation charges, anionic surfactants, counterions and excess salt complicates robust deposition predictions [109]. The ratio between the polyelectrolyte and surfactant concentration is one of the main control parameters determining the conformation of complexes and films adsorbed on surfaces. A wide range of precipitation regimes in solution have been observed in the literature [110]. This underlines the inherent complexity associated with the design of formulations containing more than one functional component with opposite charge and different concentrations. Recently, dilution deposition has seen an increase in research interest as more sophisticated but also more sustainable formulation designs are explored [102,109,111–113]. Thermodynamic models can predicting and explaining such processes in bulk [114,115] and on substrates [116,116–118]. Detailed reviews of polyelectrolyte-surfactant complexation and deposition are provided elsewhere for reference [101,106,107]. The known effects and challenges of oppositely charged polyelectrolyte-surfactant complexes on hair tribology will be discussed later.

2. Experimental techniques

The evolution of hair tribology experiments shows a clear trend from early macroscopic and mesoscale friction methods to incorporating more and more nanoscale friction microscopy and colloidal probe techniques. Early hair tribology methods stem from wool friction measurement for textile industry applications which will be briefly reviewed first. We then focus on macroscopic and nanoscale hair friction, adhesion and wetting experiments.

2.1. Macroscopic hair friction experiments

2.1.1. Early friction experiments of mammalian fibres

Historically, laboratory experiments have been the driving force in determining the tribological properties of hair. Early wool friction experiments [119–130] showed a close physiological resemblance to human hair fibres, [131] and paved way for systematic hair friction

studies. Speakman and co-workers [119,120] provided some of the earliest scientific reports on the resistance to extension of wool fibres under load in the context of industrial wool milling processes. Their work already suggested a ‘scaly’ fibre structure based on macroscopic water-submerged friction experiments. Gralén and Olofsson [124] measured the static and dynamic friction between two dry wool fibres using a crossed fibre friction metre and observed an anisotropic behaviour, i.e. DFE, [7] in the friction coefficient depending on the direction of motion. Mercer and Makinson [122,125] used a modified version of an experimental setup devised by Bowden and Leben [132] to record temporal friction signals on wool. Friction measurements were conducted between a straight hair and sheep horn and confirmed an anisotropic behaviour in dry and wet environment, although stick-slip events were more pronounced in the dry state. A molecular orientation mechanism was proposed as a potential explanation for the anisotropic friction behaviour [121]. However, the observations could be better explained by the overlapping, scale-like nature of wool cuticles, as observed from early electron microscopy imagery [133]. This ‘ratchet mechanism’ was also supported by directional friction measurements of metal-coated wool fibres [123] and systematic variations in the contact roughness of wool sliding against a flat secondary substrate [126].

Frishman et al. [127] observed a consistently higher friction coefficient of wet wool fibres compared to the dry state. Lindberg and Gralén [128] developed an alternative ‘fibre twist’ method where two fibres would be wrapped around each other in several turns to increase the area of contact and therefore the robustness of friction measurements. Their results confirmed the directional dependence of wool friction with reduced variability and clear adherence to the extended Amontons-Coulomb law as originally proposed by Derjaguin, [134,135] $F = F_0 + \mu \cdot F_L$. Wool friction was also found to increase after chemically treatment, e.g., with potassium hydroxide in ethanol (KOH) [129] and chlorine [130]. Treatment with soaps containing sodium oleate reduced the friction of chemically damaged wool fibres [130]. Grosberg [136] devised a new theory that DFE in wool was due to the anisotropic elastic properties of moist keratin. Later work by Flanagan [137] showed that no DFE was observed for wool if the counter-fibre had a radius greater than about 40 μm .

2.1.2. Friction between individual hair fibres

Many of the tribological characteristics of wool and fibre measurement devices are also transferable to hair tribology. A schematic overview of historically popular macroscopic measurement techniques for hair tribology is presented in Fig. 4. The experimental setups involving hair bundles will be discussed in the next section. Schwartz and Knowles [138] used a friction metre (*capstan* method) originally developed for textile fibres due to Röder [139] to study the static and dynamic friction of hair-hair contacts and single hair fibres in contact with a wide range of different comb materials. The *capstan* method

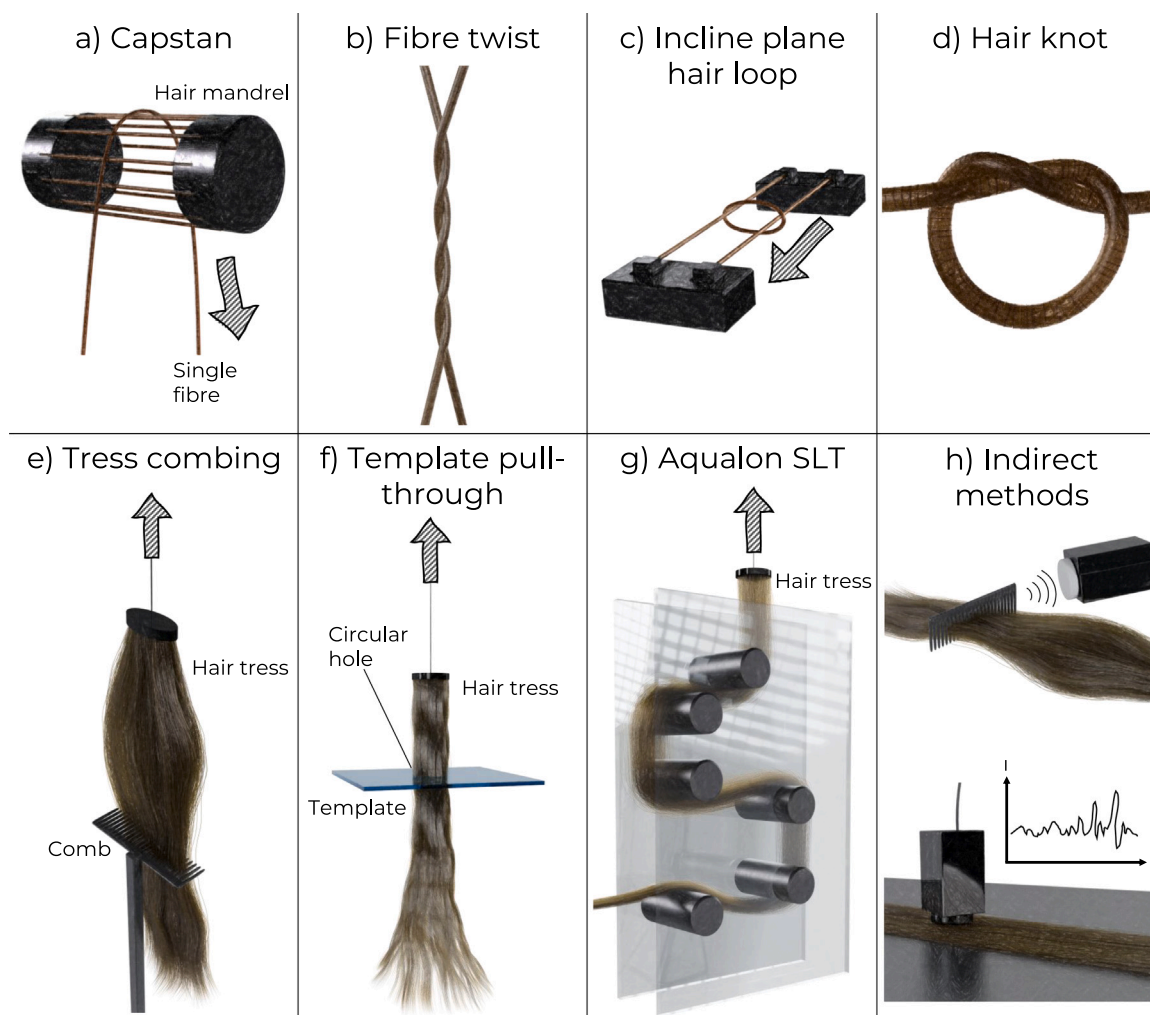


Fig. 4. Schematic overview of macroscopic experimental setups for hair friction (not to scale). Individual fibre tests (top row): (a) Capstan test, [138,139] (b) Fibre-twist method, [128] (c) Incline plane loop, [141] (d) Hair knot setup, [142] Tress test (bottom row): (e) Tress combing, [143] (f) Template pull-through setup, [144] (g) Aqualon SLT, [145] and (h) indirect methods using acoustic emissions [146] and Diffuse Reflectance Near-Infrared Spectroscopy (NIR-DR) [147]. Inspired by Refs. [128,138,139,141–143,145–147].

involves a single hair fibre wrapped around a cylindrical mandrel of different materials, including an array of hair fibres, as depicted in Fig. 4(a). The dynamic hair-on-hair and comb-on-hair friction coefficients obtained from this method were found to be consistently higher in wet than in dry hair. The authors further reported a strong increase in hair-on-hair friction due to bleaching and waving, while the application of conditioner formulations led to a restoration low friction on bleached and waved hair [138]. Scott and Robbins [140] applied a modified version of the *capstan* method to perform a comprehensive study of the effect of different ionic surfactants and background electrolytes on hair-on-comb friction at various degrees of bleaching with hydrogen peroxide and ammonia.

Adams et al. [148] used a crossed fibre setup between two hairs to compare hair treated with CTAB to hair contacts fully wet by water. Miyamoto et al. [149,150] recently compared how ionic polymer-surfactant hair care formulations could be effective at reducing both the average friction coefficient on hair and stick-slip behaviour of bleached hair. Remarkably, this mesoscale setup allowed for deriving a relatively detailed model of the expected nanoscale deposition of polymers and oppositely charged polyelectrolytes and surfactants.

Moreover, macroscopic single-fibre tests are capable of capturing mesoscale heterogeneities in hair. Typically, hair damage and 18-MEA content in the F-layer is increased at the fibre tip which has been exposed longest to external manipulations and wear [26]. Single-hair

high-load *capstan* test friction measurements of hair at various positions along the fibre showed an average 23% increase in friction force from root to tip when measured against the direction of the cuticles. When measured in the direction of cuticular growth, no clear trend was observed [151].

The ‘fibre twist’ method due to Lindberg and Gralén [128] was later also applied to measure hair-hair friction and the corresponding effects of chlorine treatments [152]. Chlorine treatment of hair was accompanied by not only an increase in the mean static and kinetic friction coefficient, but moreover by an increase in the stick-slip amplitude in the friction signals. At an elevated number of chlorine treatment cycles or high chlorine concentrations, the cuticle structure was visibly damaged, as evident from scanning electron microscopy (SEM) measurements [152]. The authors attributed the increase in friction accompanied by a visibly smoother surface to a softening effect of the cuticle structure. Chevalier [142] recently proposed an easily repeatable measurement technique building on the previous ‘fibre twist’ works in Refs [128,152]. In this work, hair friction was evaluated by means of tying a knot in a single hair fibre as shown in Fig. 4(d). The technique accurately captured the previously observed trends in the mean and variation of friction coefficient in dry, wet and conditioner-treated hair. [142]

2.1.3. Hair tress friction & combing work

A wide range of macroscopic hair friction measurement techniques involve the use of hair bundles, or so-called *hair tresses* or *swatches*, as depicted in Fig. 4(e-h). Direct measurements of hair tress combing work were first conducted by Newman and colleagues [143]. They measured the resistance of detangled hair bundles dragged along a mounted comb. The method was able to pick up the quantitative combing force increase of wet compared to dry bundles and subsequent friction reductions due to conditioning of the wet bundles. High friction in wet hair was attributed to the swelling of the fibres due to water uptake and inter-fibre capillary forces [143]. In a similar tress combing rig designed to purposely eliminate the effect of hair entanglement using a double comb setup, Kamath and Weigmann [15] investigated the direct effects of treatments and different levels of humidity on friction between hair bundles and the comb. They found that moderate levels of humidity led to combing work reductions, possibly due to aqueous lubrication, while artificial wetting resulted in strong interfibre forces, consistent with Ref [143]. The existence of such strong capillary forces were later measured directly on model hair brush experiments [153].

Jachowicz [154] measured an increase in combing forces of few hundred percent for dry and wet hair treated with oxidative dye compositions. They hypothesized that the most damaging effect of the dye compositions on the properties of hair was the formation of dye deposits on the fibre surface, which they suggested could considerably increase the frictional coefficient and, consequently, combing force [154]. They showed that this problem could be circumvented by the post-dyeing application of suitable conditioners [154]. This observation implies that it was the oxidative properties of the hair dye (similar to bleaching [155]) that led to the increase in combing work, rather than deposition of dye compounds on the hair surface.

Garcia and Diaz [156] developed a similar tress combing measurement device to that of Newman et al. Their setup did not include any preliminary detangling step or pre-combing device to achieve a more realistic comparison with natural hair. Hair tresses were mounted on a tensile tester to measure the average and peak combing work under different treatment conditions. A range of commercial shampoo and conditioning products was ranked with regard to their effect on wet and dry hair tress (peak) combing work compared to either untreated or bleached baseline tresses. The authors highlighted the particular efficiency of quaternary ammonium surfactants in reducing the wet friction on bleached hair [156]. A setup lending from the rig due to Garcia and Diaz was used by Robbins and Crawford [144] to measure the work required to pull a hair tress through a circular holes of various diameters in plastic templates, see Fig. 4(f). The authors uncovered a linear relationship between the resisting work and the template diameter which was used to extrapolate to a 'zero work' diameter. This quantity was interpreted as a measure of *hair body*, which Robbins and Crawford defined as the 'apparent thickness or volume of an assembly of hair' [144]. While the method could not distinguish the effects of different selected shampoo formulations on hair body, an increase in the zero work diameter of tresses was found with increasing curliness (curvature) of hair tresses [144]. Robbins and Reich further used the method due to Garcia and Diaz to study the combing work of dry and wet hair tresses at different treatment conditions and related the combing work to different properties of the single hair fibre [157]. They reported a strong increase in macroscopic hair friction with increasing hair curvature and noticeable decreases in combing work with increasing fibre stiffness. Changes in fibre diameter were however not regarded to be particularly influential on tress combing work. The work further highlighted the mechanical properties that tend to influence hair friction and combing work at the mesoscale. Additionally, the effect of hair treatment with oily substances was found to contribute to a favourable detanglement of fibres and thus generally lower combing work [157]. An extension to the traditional tensile tester setup was presented by Vaynberg and Nall [145]. In the presented setup, named *Aqualon SLT* and shown in Fig. 4(g), a hair tress was pulled through an

arrangement of PTFE-coated pins using a tensile tester while recording the resisting work.

Hair tress combing experiments have also been used to systematically investigate the effect of specific components in hair care productions on combing force and hair friction. The effect of conditioning agents such as silicones, [141,158,159] free fatty acids, [160] cationic surfactants [161] and cationic polymers [100,162] on combing work and hair friction has been studied extensively using the tensile tester setup. Cationic compounds are of particular interest because they favourably adsorb on hair to form a protective layer, which is particularly desirable on chemically damaged hair. Tress combing experiments are also suitable for screening the tribological performance of more complex hair care formulations which aim to fulfil multiple functions such as cleansing and conditioning [100,162]. Hössel et al. [100] used wet combing experiments to benchmark different petroleum-based and bio-sourced cationic polyelectrolytes with anionic surfactants (sodium laureth sulphate, SLES) with regard to their combing force reduction on bleached hair tresses.

An advantage of macroscopic tress friction and combing experiment is that they are suitable to screen hair friction at a high throughput. This is highly beneficial for benchmarking different hair care products by their frictional response. This is also true for other noteworthy alternatives to direct single-fibre and tress combing friction measurements such as acoustic emissions from combing [146,163] and tress friction prediction using near-infrared diffuse reflectance [147] shown in Fig. 4(h). The biggest disadvantage of macroscopic setups is that details of the underlying tribological mechanisms are typically not directly accessible. Hair surface chemistry and small-scale structures can strongly influence hair friction without observing changes in larger-scale hair features in these macroscale experiments. It is possible to gain further mechanistic insights by coupling macroscopic experiments with other surface or bulk formulation characterization experiments. Gao et al. [86] for instance related combing work reductions on conditioner-treated hair to surface energy measurements from dynamic wetting experiments. Benhur et al. compared the rheology of oppositely charged polymer-surfactant conditioning shampoos to changes in combing force reductions [164]. For direct insights into the small-scale features and associated tribological mechanisms, tools from the realms of nanoscale experiments and simulations are more appropriate. Therefore, we also discuss these methods in depth later.

2.1.4. Skin-on-hair friction

While hair detanglement performance is closely associated with hair-on-hair and comb-on-hair friction, it is also important to consider the skin-on-hair contact in the context of hair tribology. This is because the sensory (or tactile) perception of hair softness is a direct outcome of the skin-on-hair interactions during rubbing and touching of hair with the human finger. Direct tactile evaluations by sensory panels [3,14,165–167] and friction experiments with either in-vivo skin [14,168] or an artificial skin probe [8,169–172] fall under the category of skin-on-hair friction.

Sensory panel tests allow for a direct evaluation of tactile perception by either untrained or trained panels. Panels can provide valuable insights to formulation designers on how a specific care product's performance will be perceived by customers in the absence of external product attributes such as marketing, pricing and packaging. The human finger is capable of distinguishing surfaces varying in roughness down to the nanoscale [173] and even changes in surface chemistry [174]. Pleasant sensory perception has been linked to low friction for a wide range of materials [174,175]. Tanamachi et al. related the sensory perception of moisture evaluated from panel tests to the temperature drop induced by evaporation cooling on hair [165]. They reported a clear effect of the temperature drop on the perception of moisture. This is a different interpretation to the previously discussed hypothesis of reduced (inter-fibre) friction due to lubricating effects as described by Kamath and Weigmann [15]. Tanamachi et al.

also reported a consistent effect of hair surface damage due to alkali treatment on the perceived dryness. This was attributed to a more pronounced macroscopic fibre entanglement caused by the 18-MEA removal [176]. In a trained panel test, Bloch et al. assessed various attributes of virgin and damaged hair tresses [166]. The score for the attribute 'smoothness' which is linked to the friction between skin and hair was found to be higher (smoother) for untreated hair compared to damaged tresses. However, the subjective assessment of combability was found to be little affected by artificial damage modes and only increased in UV-damaged (weathered) hair [166].

So far, few studies investigated the interactions between skin and hair with respect to tactile friction and sensory properties in-vivo. Zeng et al. [14] worked with participants who rubbed their finger against a hair bundle which was fixed on a force and torque transducer. Virgin, bleached and permed hair as well as virgin hair treated with various silicon-based and silicon-free conditioner products were considered. The in-vivo methodology and complementary sensory evaluations could clearly and consistently distinguish between the different hair treatments and hair care formulations applied. Interestingly, a decrease in the friction coefficient by means of the shear force was observed with increasing normal load. This suggests a departure from the (extended) linear Amontons-Coulomb law which is typically fulfilled in hair-on-hair contacts [5,177]. The authors attributed this behaviour by the strong viscoelasticity of skin resulting in a non-linear dependence of the friction force as a function of the normal load, as reported in previous skin friction work [178]. It was further reported that the wet macroscopic friction coefficient would decrease after hair bleaching, which is not in line with other macroscopic and nanoscale studies which considered various materials of the second substrate (skin, hair, AFM tip etc.) [8,171,177]. One reason for this discrepancy may be the lack of exact control over the applied normal loads and sliding velocities which were controlled by rubbing a human finger against the hair. Conversely, the measured friction coefficient in dry contacts moderately increased upon bleaching [14]. Kawasoe et al. [168] introduced an in-vivo setup in which participants rubbed their finger against a macroscopically flat polyimide surface mimicking the roughness features of hair cuticles at different feature heights and wavelengths. Friction tests with an artificial finger probe were also conducted for comparison. It was found that the irregular mesoscale roughness features associated with damaged hair rendered higher measured friction and perception of 'coarseness' [168]. While this is not directly transferable to real hair due to an effectively different surface chemistry, this study highlighted the potential importance of surface roughness features on hair friction. Similarly, Okuyama et al. [179] considered patterned hair mimic surfaces from polyimide resin to evaluate the tactile performance against skin under dry, wet conditions and after treatment with hair conditioning products.

Conversely, direct friction measurements on hair bundles with synthetic skin probes can provide more detail on macroscopic mechanisms influencing the skin-on-hair tribology. The use of an artificial skin probe also allows for mounting on a tribometer which greatly improves the repeatability and the control of normal load and sliding velocity. (Poly)-Urethane and PDMS substrates are commonly in use as skin mimics [3,8,168,170,172,180,181]. A polyurethane skin model probe on hair tribometer was used by Bhushan et al. [8] to measure friction on virgin, damaged and conditioner-treated parallel, aligned hair fibres. It was reported that both the applied normal load and the contact area did not influence the macroscopic skin-mimic-on-hair friction coefficients. Consistently with hair-on-hair contacts, hair damage led to higher friction, which could be mitigated by conditioner treatment. Bhushan et al. [8] also showed that the DFE for polyurethane-hair contacts was insensitive to temperature, but increased with relative humidity. The effect of hair ageing was assessed in a similar setup to that of Bhushan et al. [8], combined with sensory evaluations of hair properties ('finess, roughness and slipperiness') [169] associated with hair tribology.

The sensory evaluation scores of all considered hair properties monotonically decreased with the age of the hair sample donors (higher was better). The three properties were found to be closely correlated to the chosen respective measurement properties 'spectral centroid' (SC), surface roughness and friction coefficient [169,182]. Thieulin et al. applied finger-mimic tribometer measurements on a single hair fibre, considering either virgin, coloured or bleached hair [171]. Consistently with the previous studies, bleaching or colouring increased the mean interfacial friction and vibration levels. As opposed to previous studies opting for a chemical treatment with conditioners, a thermo-mechanical treatment routine was applied on damaged hair. This was found to have a smoothing effect on the damaged fibres, thus reducing the friction coefficient to levels associated with virgin hair. However, the treatment was also found to modify the mesoscale hair structure and brightness levels.

Sensory panel tests of similar perceived hair properties were compared to friction experiments conducted between various types of hair swatches with finger mimic urethane probe [3]. The study showed that both cleansing and conditioning shampoo formulations can effectively reduce friction compared to untreated hair. As expected, higher friction reductions were obtained with the conditioner-based formulation containing silicones and cationic polymers. The sensory panel results further indicated that friction alone does not necessarily correlate with the perception of softness. The authors argued that thinner hair was perceived as rougher due to a change in vibrational modes when in contact with the (inherently rough) skin surface.

Aita et al. performed human finger mimic friction experiments on wet hair bundles treated with either silicone oil, oil-water emulsions or water only [170]. A lubricating effect of silicone oil with water was observed which was maintained after drying. It was further reported that reductions in the surface temperature due to water evaporation on hair with either water or oil-water emulsions led to improvements in the perceived moisture of hair during drying, consistent with Ref [165]. Sano et al. used the finger probe on hair bundles setup to study how cationic surfactants influence skin-on-hair friction [172]. They reported stick-slip-like oscillations between the finger probe and hair in the case of pure water which was attributed to surface roughness features in both hair (cuticle edges) and the probe (artificial finger grooves).

Insights into friction mechanisms between hairs and skin could also be derived from computational approaches. To date, no openly accessible studies using computational models to assess the tribology of skin in contact with scalp hair exist to the best of the authors' knowledge. The feasibility and use of such heterogeneous contact models will be discussed later.

2.2. Nanoscale hair tribology experiments

2.2.1. Atomic, lateral & friction force microscopy

Small-scale contributions to friction on human hair are best resolved using mechanical force microscopy techniques. An overview of common nanoscale friction measurement setups is shown in Fig. 5. Atomic force microscopy (AFM) [183] has proven particularly successful for investigating the hair surface structure and tribology. One of the first AFM studies on the morphology of hair was performed by O'Connor et al. [184] who visualized the overlapping structure of cuticle cells on the hair surface. The authors chose a traditional scanning tip AFM setup, where a sharp tip mounted on a cantilever is used to 'scan' the substrate surface. This approach has since then been used extensively to scan the surface topography of virgin, [33,37,67,75,185–193] mechanically damaged [33,193] and chemically damaged hair [33,37,67,75,189,192,193]. While one could argue that the contact between an AFM probe and the hair is a tribological system by itself, we will focus on those AFM studies that specifically focus on hair friction or link changes in the surface topography to changes in the frictional behaviour.

A predecessor to small-scale hair friction measurements was devised by Adams et al. [7] who use an intermediate-scale cantilever apparatus

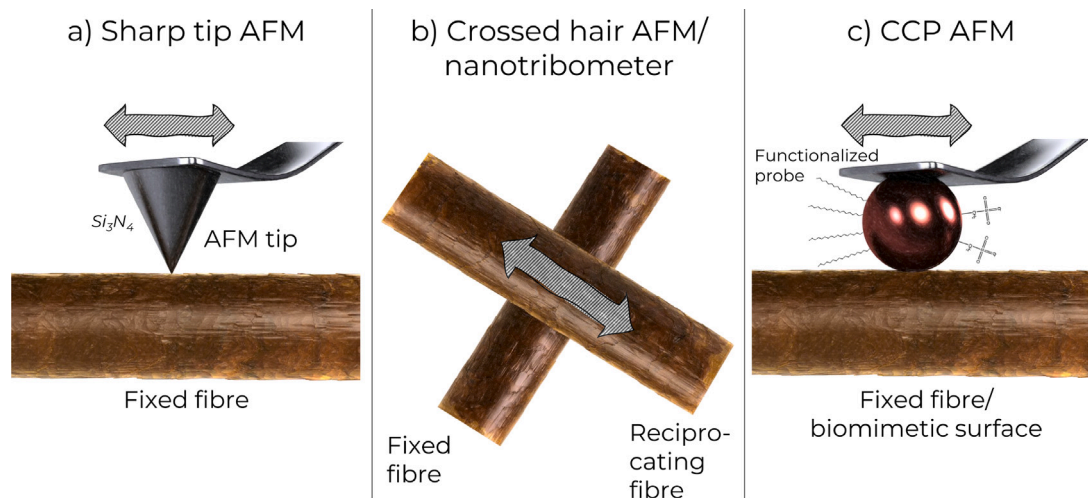


Fig. 5. Schematic overview of experimental setups to investigate micro/nanoscale hair friction. (a) Sharp tip AFM ($r \approx 10$ nm), (b) crossed hair AFM ($r \approx 10$ μ m), and (c) chemical colloidal probe (CCP) AFM ($r \approx 10$ μ m). The relative dimensions of the AFM probes and fibres are not to scale.

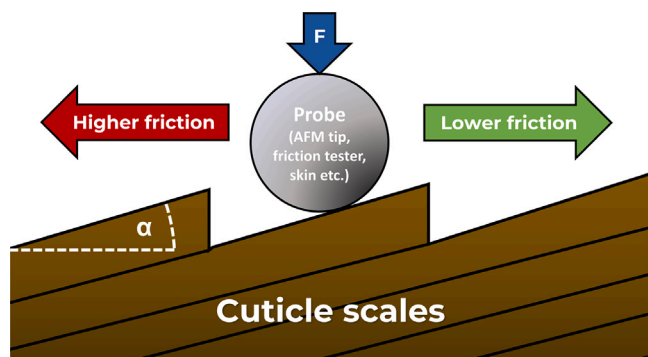


Fig. 6. Differential friction effect (DFE) on human hair arising from the anisotropic cuticle growth. Here, α indicates the cuticle offset angle, which can affect magnitude of the DFE.

to probe the DFE attributed to the cuticle structure of hair fibres. A schematic illustrating the DFE is shown in Fig. 6 Smith [185] used lateral force microscopy (LFM), [194] an extension to AFM which takes the torsional deformation of the AFM tip into account. Smith applied LFM to visually identify areas of higher friction between the LFM tip and the hair surface. The highest frictional forces were observed at the cuticle edges which mark the region of most pronounced variability in surface topography. McMullen and Keltly [58] applied AFM and LFM to specifically study hair friction and morphological changes of the fibre surface upon bleaching or solvent-extraction. Both hair manipulations led to a considerable increase in the slope of the reported friction signal as a function of the applied normal load at ambient conditions. Their results showed close adherence to the extended Amontons-Coulomb law with non-zero Derjaguin offset. The authors further considered virgin hair treated with a cationic polymer, which produced even higher dry friction forces compared to the chemically damaged cases.

Breakspear et al. [11] later applied AFM to measure friction and adhesion on natural hair surfaces with a fully intact 18-MEA lipid monolayer and an 18-MEA depleted fibre. The aim of this study was to identify the contribution of the 18-MEA to hair tribology as will be discussed later. They also compared the friction of untreated, bleached and hydroxylamine-treated hair fibres. Bleaching and hydroxylamine treatment led to a moderate increase in the relative friction coefficient. Grey hair was observed to render the highest friction coefficients across all investigated fibres. African hair overall rendered lower friction coefficients from the AFM than Caucasian hair.

At the same time LaTorre and Bhushan [5,28,92,180] published a series of AFM studies characterizing the friction and adhesion of various morphologically different hair surfaces. The authors measured hair friction using a sharp AFM tip setup (referred to as friction force microscopy, FFM, in their work) [195] coupled to experiments using macroscopic skin and hair probes on hair tresses [5]. They studied virgin, chemically-mechanically damaged and conditioner-treated hair of different ethnicity. The AFM results are shown in Fig. 7 A consistent increase in nanoscale friction with hair damage was reported, which could however be mitigated by treatment with a commercial hair conditioner. No strong differences among the hairs of different ethnicity (African, Asian, Caucasian) were observed. Treatment of damaged hair with conditioner over different number of cycles was found to monotonically reduce friction forces, while resulting in moderately increased frictional forces on virgin hair [28]. LaTorre and Bhushan further highlighted the anisotropy and scale-dependence of hair friction measurement techniques and provided fundamental hypotheses for why friction is different across the scales [180]. These will be reviewed separately when discussing hair friction mechanisms. The effect of different hair conditioner types including cationic surfactants and silicones was also probed by the authors using the same AFM and complementary macroscopic friction measurement setup as described above [92]. Wei and Bhushan extended LaTorre and Bhushan's previous AFM studies to include nanoscratch indentation tests on hair to consider [196]. They investigated the effect of different normal loads on indentation and cuticle wear at different hair treatments and ethnic origins. The nanoscratch technique was later applied to study the tribological properties of Brazilian hair [77]. Smith et al. [197] performed localized AFM friction and adhesion measurements on the cuticle surface of virgin. Notably, the exposure of new cuticles from partial delamination and wear potentially led to local reductions in friction coefficients. Using AFM experiments, Nazir et al. [198,199] showed that silicone oil droplets can significantly reduce the friction of virgin hair. Smaller silicone droplets led to more efficient deposition and lower friction [198]. Moreover, multilayered silicone oil droplets coated with high molecular weight polymers, i.e. quaternized chitosan and alginate, and low molecular weight compounds, i.e. diallyl dimethyl ammonium chloride and glycerol, further reduced the friction of virgin hair compared to silicone alone [199].

In perspective of the sensory perception of hair and real-life hair manipulations, gaining insights to hair friction in both ambient and wet conditions is desirable. Numerous studies have looked at measuring the nanoscale friction of wet hair [26,177,200] and hair at various levels of relative humidity [28] using the sharp AFM tip setup. Wet hair

AFM friction is typically measured using a *liquid cell* setup, in which both the substrate (hair fibre) and measurement device (AFM tip) are fully immersed in water. The liquid cell setup bears the advantage over measurements in humid conditions of removing any contributions from capillary adhesion to friction forces [177]. As with AFM under ambient conditions, the liquid cell setup can be used to study the effect of hair damage and chemical treatments such as conditioners [177,200].

It is also possible to combine hair AFM or FFM directly with macroscopic measurement techniques to draw a connection between nanoscopic and mesoscale friction mechanisms. Tanamachi et al. specifically focused on the effect of 18-MEA depletion on hair friction via FFM and linked frictional increases to changes in macroscopic wetting behaviour, surface energy and thus a degraded fibre detanglement performance on the mesoscale [176].

Atomic force microscopy has also been applied to study the hair-on-hair friction by mounting a small slice of a hair fibre to an AFM cantilever instead of using a sharp tip [9,201–203]. Max et al. [201] first applied this setup to study hair-on-hair friction in a *crossed* fibre configuration. This setup was originally developed to study friction between polyester fibres [204] and is shown in Fig. 5(b). Mizuno et al. also developed a similar setup for hair-on-hair nanoscale interfacial force measurements. [202]. As with the sharp AFM tip, this setup is suitable to study both friction and adhesive forces, but is capable of evaluating them directly between two fibres. Thus, the crossed hair AFM setup has been used to study hair friction and adhesion at various hair treatment conditions [201,202] and relative angles between the fibre primary axes [9]. The method is also capable of picking up the DFE induced by the anisotropic orientation of cuticle scales as shown by the spikes in the friction force signals in Fig. 8 due to Max et al. [201]. For evaluation of the surface chemistry, it is practical to only focus on the parts of the scans in which two surfaces of cuticles are in full contact, as roughness will be lowest in this area. Wood et al. compared measurements from the crossed hair AFM setup to macroscopic wet combing tests and a commercial friction measurement device to study hair treated with shampoos containing various conditioning polymers [203]. Bowen et al. used a nanotribo-meter to perform crossed-fibre friction tests on virgin and conditioned hair fibres [205]. Their setup also considered the evolution of the frictional response as a function of the operating cycles to include hair wear mechanisms. They showed that hair cleaned with hexane presented 25% higher friction coefficients than those retaining their sebum. When the cleaned hair was conditioned, the friction coefficient returned to a similar value as for the sebum-coated hair. The inherent anisotropic morphology of the hair cuticles also makes it difficult to separate surface roughness from surface chemistry effects on hair friction. In traditional AFM, only the sharp tip setup can somewhat eliminate these effects, as it can be locally restricted to only scan areas of the cuticle far away from the edges. As shown by Mizuno et al. [202], the crossed hair-on-hair AFM setup will typically include spikes in the friction signal when (purposely) scanning areas including cuticle edges.

2.2.2. Chemically-functionalized atomic force microscopy

Chemical colloidal probe (CCP) AFM [206] is an alternative approach to the hair-on-hair AFM setup where biomimetic surfaces are used to represent one or both hair surfaces. More generally, CCP-AFM can be used to study friction between two arbitrary substrates with a given surface functionalization and energy. In CCP-AFM, a (spherical) probe is chemically functionalized with a film which aims to represent a specific surface such as the healthy or damaged F-layer of hair. This setup is depicted schematically in Fig. 5(c). The setup is particularly useful for studying chemically and mechanically damaged hair, where surface roughness features might make it difficult to analyse the effect of the surface chemistry on hair friction. Sadaie et al. [207] gold-coated silicon-nitride AFM tip functionalized with octadecanethiols as a model probe for the 18-MEA on hair. Coefficients of friction were measured between the functionalized AFM probe and single virgin

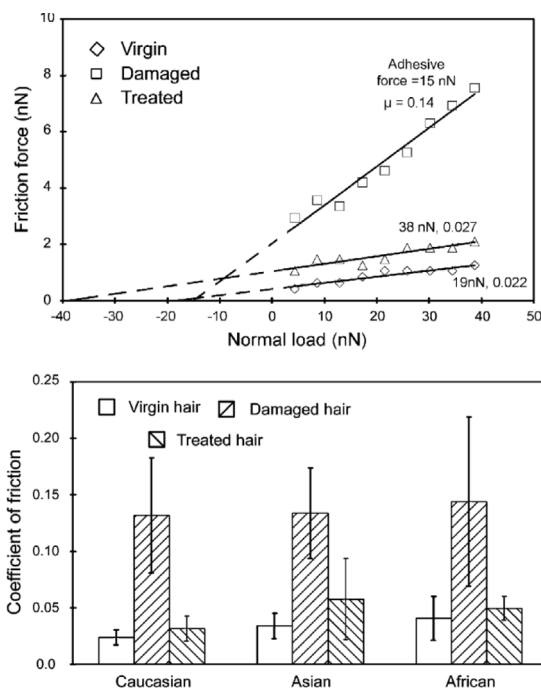


Fig. 7. Sharp-tip AFM friction measurements on virgin, damaged and conditioner-treated hair and for hair from different ethnic origins. Source: Reprinted from Ref. [5] with permission from Elsevier.

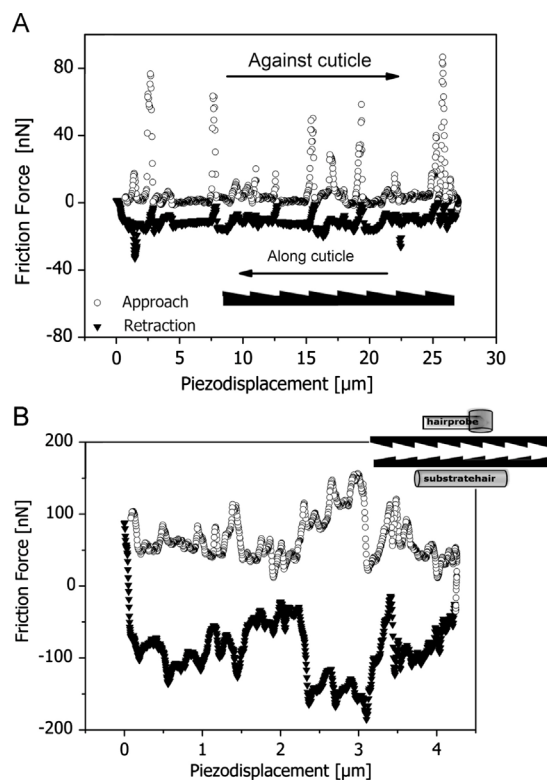


Fig. 8. Lateral force signals from crossed hair-on-hair AFM friction measured in and against the direction of cuticle growth (a) for the crossed hair-on-hair setup and (b) for parallel fibres.

Source: Reprinted from Ref. [201] with permission from Elsevier.

hair fibres. CCP-AFM using a functionalized spherical silicon probe on functionalized silicon wafers was applied to study the nanoscale friction of pristine and damaged hair biomimetic surfaces aqueous conditions (liquid cell) [10]. Pristine hair was represented by monolayers of octadecyl (C_{18}). Ultimately bleached hair, i.e. full removal of the F-layer lipids, was considered by sulfonate groups (SO_3^-). A strong increase in lateral friction forces was observed which was in good agreement with coarse-grained molecular simulations conducted in the same work.

Bhushan et al. [208,209] have also used AFM-based Kelvin probe to study the triboelectric effect in hair. The triboelectric effect or static electrification has been experienced by most of us; it causes our hair to stand up when it is rubbed with a balloon [210]. Triboelectric charging can also occur when combing the hair [211]. It is a major cause of ‘frizzy’ hair, [212] which generally leads to negative sensory perception [166]. Early macroscale studies found that the triboelectric charge density on hair depends on the materials used for rubbing, [213] relative humidity, [213] and the direction of rubbing [214]. They also suggested that chemical damage on hair such as bleaching and oxidative dyeing had no significant effect on the charge density [215]. Further studies showed that treating hair with antistatic agents (cationic surfactants or cationic polymers) could reduce triboelectric charging during combing [211,213]. Lodge and Bhushan [208] showed that rubbing hair with a macroscale latex finger caused triboelectric charging, with a larger change in surface potential for chemically damaged hair than virgin hair, which contrasts earlier studies [215]. Lodge and Bhushan [208] also found that triboelectric charging could be eliminated on both types of hair by treating it with a commercial silicone-containing conditioner. Seshadri and Bhushan [209] then validated these findings under more well-controlled conditions using a charged nanoscale AFM tip instead of a macroscale latex finger. They showed that uncharged silicone and cationic amino silicone conditioners both significantly reduce surface potential change by increasing the surface conductivity and lubricity [209].

Overall, nanoscale hair tribology experiments can clearly provide more or less direct insights into which mechanisms drive hair friction on the small scale. On the downside, these approaches are typically limited to investigating single hairs with probes that are not always resembling the true structure or even surface chemistry of real hair. CCP or small-scale crossed hair setups can mitigate this. Additionally, the above nanoscale experiments are usually restricted to manipulation speeds below realistic levels during hair manipulations such as rubbing or combing. This calls for integrating nanoscale experiments and models as one, but not the sole building block in the search for a complete picture of hair tribology.

2.3. Adhesion measurements

Adhesive and cohesive forces can contribute as resistance to both lateral and surface-normal motion. While knowledge about these forces is important for the sensory perception of hair, appropriate adhesion measurement techniques can also provide valuable insights into the nanoscale structure of the hair surface. A common pathway to determine adhesion forces between two contacting substrates is to perform force-distance curve measurements. This involves bringing two surfaces of the same or different material in (approach) or out of contact (receding) in a controllable fashion. Atomic force microscopy (AFM), scanning probe microscopy (SPM) and the surface force apparatus (SFA) [216] are suitable devices for determining forces as a function of separation distance [53,202,217]. Bhushan et al. used a sharp AFM tip to probe the thickness of hair conditioners on virgin hair by means of force-distance curve modulation through the formation of a fluid meniscus [189,218]. Breakspear et al. [11] collected mean adhesion forces from force-distance curves on hair with and without 18-MEA lipids and found reduced adhesion forces in the 18-MEA-depleted hair. In combination with nanoscale friction tests in the same study, as discussed above, the authors postulated that the 18-MEA would cover

the epicuticle as a consistent, ordered monolayer, although some heterogeneity was to be expected. Recently, Labarre et al. [219] used sharp-tip AFM with methyl, carboxylic acid and amine functionalizations to probe hair adhesion forces in different environments (dry/wet) on virgin and platinum-bleached hair. This allowed to identify the magnitude of either hydrophobic or electrostatic force contributions to adhesion [219] and are therefore a suitable tool for investigating the surface chemistry of both untreated and conditioned hair.

SPM deflection was used by Maxwell et al. to record force-distance curves of on hair and other keratin fibres in low relative humidity and in highly humid and wet environments [53]. A consistent decrease in mean adhesion forces from low to high relative humidity (RH) and wet contacts was observed which was attributed to a water-induced change in the surface chemistry of keratin fibres. The authors suggested that lipids and proteins on the epicuticle surface would reorient, effectively turning the surface more hydrophilic. More generally, this study sparked considerations of an alternative epicuticle structure of keratin fibres such as hair of wool compared to that of an ordered lipid monolayer [11]. The proposed configuration suggests a more disordered intercalation of surface lipids with the underlying protein matrix [53,54,177]. Baghdadli and Luengo [55] performed adhesion force mapping on virgin and bleached hair using a thiol-coated hydrophobic AFM tip. The nanoscale resolution from the AFM suggested that virgin hair is predominantly dominated by hydrophobic regions with local hydrophilic patches which supported a heterogeneous distribution of an 18-MEA monolayer on top of a protein matrix. In the same experiments, the overall hydrophobicity was drastically decreased upon bleaching but could be restored with a polyelectrolyte treatment [55].

The effect of bleaching and combing on hair topography, elasticity and adhesion was probed using hybrid-mode AFM [68]. The hybrid setup extends the traditional approach and receding setup by inducing an oscillation in the distance between the tip and substrate while monitoring the forces exerted on the AFM tip. This would allow for recording both adhesion, stiffness, elasticity and topography at the same time [68,220]. Both bleaching and combing led to a reduction in the mean of adhesion forces and a narrower force distribution. Thorough combing was even more effective in reducing adhesion which was also reflected by severe mechanical damage observed in the cuticle topography leaving behind holes and even partial exposure of the endocuticle.

In the previous section, the application of the crossed hair fibre AFM setup for friction measurements was discussed. The setup is equally suitable to investigate adhesive contact properties by means of force-distance curves in both the approaching and receding direction [201,202]. In humid environments hair-on-hair adhesion is almost always influenced by capillary effects from residual water [201]. Previously, capillary adhesion between hair fibres was also identified as a contributing factor to high friction in wet, but not fully immersed hair [143,148,153]. In the liquid cell setup, capillary effects can be eliminated which allows for investigating the effect of hair surface chemistry and adsorption on adhesion and even out-of-contact forces (e.g., van der Waals and Coulombic forces) [202,219]. Mizuno et al. [202] reported a faster decay of long-range van der Waals forces between two hairs by treatment with a cationic model surfactant. The study also showed that theoretical models such as DLVO theory can appropriately describe the force-distance curves at various surfactant and salt concentrations. The surface force apparatus (SFA) is another device suitable to conduct adhesion measurements. Cristiani et al. [217] modified the SFA to conduct automated screening of adhesion forces between two virgin hairs in the crossed fibre configuration. The automated setup significantly extended the scanned area and obtainable force statistics compared to previous studies. Adhesion measurements were further compared to predictions from an adhesion model operating on hair topography scans from a laser confocal microscope. The agreement between the model and adhesion scans was

linked to the strong influence of surface morphology and roughness on adhesion.

A macroscopic approach to quantifying hair adhesion forces was chosen by Kamath et al. [221]. A crossed fibre configuration was adopted to measure adhesion between single hairs as well as between two synthetic fibres. While no adhesion was evident from the virgin hair samples, treatment with a cationic cellulose-derived polymer (2,3-epoxypropyl-trimethyl-ammonium chloride quaternized hydroxyethyl cellulose, referred to as JR-400) reversibly increased the adhesive interactions with a large variability across the hair surface. Several other wetting liquids such as glycerol and commercial hair tonics were found to increase adhesion compared to virgin hair which was attributed to rheological and capillary effects which would heavily depend on the size of the contact area [221]. Treatment with synthetic sebum also increased adhesion between single hair fibres [221]. This may explain the tendency for greasy hair to clump together [24]. In a second step, Kamath et al. [221] conducted dynamic pull-out experiments of hair tresses from an aluminum cylinder. The recorded force from withdrawing the hair tress was attributed to adhesive forces from multiple contacts within the hair tress and the contact with the external cylinder. While the authors reported that the withdrawal force is essentially constant above a certain level of hair tress packing, the chosen setup cannot fully separate adhesive inter-fibre forces from dynamic friction caused by a higher lateral load on the cylinder wall due to changes in packing.

The pull-out setup due to Kamath et al. [221] highlights an important aspect which connects dynamic sliding friction with adhesion: In a sliding contact, adhesive forces are commonly attributed to the so-called Derjaguin offset [134]. The Derjaguin offset appears in the extended Amontons-Coulomb law [135] as a non-zero contribution to friction at zero load. Through NEMD simulations, both the surface chemistry [222] and surface roughness [223] have been found to directly influence the Derjaguin offset in the boundary lubrication regime.

2.4. Wetting experiments

While not directly falling under the classical definition of tribology, the surface energy and wetting behaviour of a substrate provide valuable insights which are often transferable to the substrate's expected frictional and adhesive response. Wetting studies, either by means of dynamic [29,50,51,56,57,176,224–226] or static [56,97,226] contact angle measurements are a historically proven tool to determining the surface energy of pristine, damaged and treated hair. Water contact angles larger than 90 degrees are generally associated with a hydrophobic surface, while those lower than this threshold would be associated with a more hydrophilic surface.

2.4.1. Dynamic contact angle experiments

The macroscopic contact angle on hair can be measured using the Wilhelmy force balance method [227]. In a series of publications, Kamath et al. [50,57,224,225] were among the first to thoroughly explore the dynamic wetting of single human hair fibres using the Wilhelmy force balance. For undamaged hair, a water contact angle greater than 90 degrees was observed in the advancing stage, suggesting an overall hydrophobic surface [57]. The work of adhesion and contact angles however strongly varied across different hair fibres. Notably, the authors also found a large difference between the wetting force during advancing of the fibre into the liquid and the stationary wetting. They suggested that this might be due to a reorientation of polar groups on the hair surface during prolonged wetting. Contact angles and the work of adhesion in polar (water) and apolar liquids (diiodomethane) were further reported to be dependent on both the direction of the fibre and the dynamic wetting mode (hair advancing into or receding from the liquid bath). The difference in wetting was most pronounced between two different possible orientations of the hair fibre in relation

to the liquid during the receding stage. The authors explained this by the likelihood of uneven damage on the cuticle edge which might render different surface chemistries on the front and dorsal side of the cuticle. Potential meniscus effects during the receding stage were also highlighted [57].

Dynamic wetting experiments in the presence of adsorbed cationic polymers or surfactants suggest that cationic compounds can drastically alter the wetting forces and contact angles on virgin hair [224]. Cationic polymers such as JR-400 were found to heterogeneously adsorb on virgin hair which was reflected by drastic fluctuations in the recorded wetting forces. The investigated surfactants and polymers were found to partially desorb upon multiple fibre immersions. On chemically damaged hair by oxidation, wetting forces substantially increased effectively rendering the surface hydrophilic. It was inferred from the further increase in wetting forces that subsequent polymer adsorption was greatly increased on oxidized hair. The authors identified the hysteresis ratio of wetting forces between the advancing and receding stage as a qualitative measure of surface coverage of adsorbed molecules and surface heterogeneity [224]. Wettability with polymers or surfactants was also found to be highly sensitive to the temperature during the treatment stage [50].

Kamath et al. [225] later used similar wetting force experiments to study the effect of additional anionic surfactants in solution on the deposition of cationic polymers to hair. Wetting forces directly allowed for quantifying whether the complexes of polymers and surfactants would be hydrophobic, where polymer cationic sites would be neutralized by surfactants, or hydrophilic, suggesting that polymers were 'overcharged' due to excess surfactants adsorbing. Hydrophilic complexes were found to render a lower adsorption density due to the reduced affinity to the anionic sites on hair. Kamath et al. also highlighted the importance of dilution which could lead to a maximum in the adsorption density of the polymer-surfactant complexes due to an undergoing phase change [225]. The implications of this mechanism, later referred to as 'coacervation' will be discussed below.

Molina et al. [51] confirmed the hydrophobic nature of virgin hair by advancing contact angle measurements at various pH ($\approx 102^\circ$ for pH = 1 – 13). Treatment with alkaline and alkaline hydrogen peroxide reduced the contact angle to values as low as 53° , associated with hydrophilic surfaces. This reduction in surface hydrophobicity was attributed to the removal of fatty acids on the hair surface. Further evidence of the exposed sub-18-MEA structure was given by performing a variation study of the pH value of the wetting fluid. Higher pH values correlated an increase in the acid-base contribution to the total adhesion work. This was interpreted as proof for the exposed cysteic acid residues (SO_3^-) found in the epicuticle [51]. This is consistent with values of contact angles of untreated and chemically damaged hair due to Lodge and Bhushan [29] who performed additional dynamic contact angle experiments on chemically damaged hair which was subjected to treatment with a gel conditioner containing cationic surfactants. Both initially dry hairs and hairs pre-soaked in water were investigated. It was found that conditioner treatment could increase contact angles compared to the chemically damaged hair but could not restore the full hydrophobicity of untreated virgin hair. On the other hand, application of conditioner on the healthy hair would result in a decrease in contact angles compared to the untreated case. This was interpreted be a result of 'overconditioning' due to excess cationic surfactants hydrophobically adsorbing on hair and exposing their cationic headgroup to the liquid phase, thus reducing the overall surface hydrophobicity [29]. Moderate overconditioning on virgin hair was consistently made in later experimental dynamic and pseudo-static contact angle measurements after treatment proteolipids [226] and recent molecular dynamics simulations of cationic surfactants (CTAB) on biomimetic hair surface models [97]. However, excess surfactants do not notably change the lubrication performance of virgin hair which Lodge and Bhushan attributed to capillary forces remaining relatively unchanged during sliding. Weiland et al. [97] also hypothesized that excess surfactants

might be easily depleted from the sliding contact due to the external shear, which is consistent with reports of carboxylic acid surfactants on mica [228]. Another important finding due to Lodge and Bhushan was the distribution of conditioner formulations on the hair surface. Based on hysteresis of the contact angle in untreated and conditioner-treated hair, the authors concluded that conditioner is mainly deposited at the base of the overlapping cuticle scales, leaving their edges exposed to external influences [29,218]. Subsequent treatment of bleached hair with cationic surfactants and amino acids was found to partially restore the hydrophobicity of pristine hair. The treatment with alanine was particularly effective with regard to mitigating chemical damage from bleaching [229]. Similar improvements in hair wetting as well as improvements in tensile properties and water uptake were observed when treating bleached or permed hair with keratin peptides or keratin proteins [230].

Dynamic contact angle experiments on hair due to Tanamachi et al. [176] confirmed previous reports of changes in the wetting behaviour during the receding mode when probing single hair fibres with or against the direction of cuticle growth [51,57]. The depletion of the 18-MEA across hair was also directly linked to a reduction in both advancing and receding contact angle, where the reduction in contact angle in the latter was most pronounced.

Gao et al. evaluated the surface energy on virgin, damaged and treated hair by measuring dynamic advancing contact angles using a fully apolar wetting liquid (diiodomethane) and a polar liquid (benzyl alcohol) [86]. The application of Owens–Wendt theory [231] allowed for directly determining the polar and dispersive contribution of the surface energy from measuring the wetting with these two types of liquids. The dispersive component of the surface energy was found to increase between virgin and bleached hair while the polar component was reported to remain approximately constant. This is surprising since bleaching would be expected to remove the 18-MEA lipids from the surface, thus leaving behind a more polar and hydrophilic surface. This may be due to the choice of using benzyl alcohol as a second wetting liquid which produced similar contact angles between virgin and bleached hair. It is also possible that the bleaching routine could be different from other studies which reported much more pronounced decreases in advancing contact angles with another polar wetting liquid (water) [51,176]. The effect of the exposure time, temperature and chemistry of the bleaching solvent on wetting had indeed been shown to have a severe effect on the advancing contact angle of water on bleached hair [51].

The microscale distribution of hydrophobic group on untreated hair was further investigated by Wortmann et al. [66] who provided evidence of periodic patterns in the surface chemistry on the hair surface obtained from the Wilhelmy force balance. The observed patterns were attributed to weathering of the natural hair and shows that an idealized homogeneous fatty acid monolayer might be insufficient to describe the interactions of the hair surface with wetting fluids. The existence of damage patterns has been further studied by Korte et al. [82] who performed nanoscale adhesion force measurements on bleached hair. Korte and co-authors were able to visualize micro- and nanoscale damage patterns for simplex bleaching with hydrogen peroxide. This confirmed the observations observed in Ref. [66]

2.4.2. Pseudo-static wetting experiments

Static wetting experiments on the other hand allow for eliminating some anisotropic effects such as capillary formation on cuticle edges during dynamic wetting. A potential downside of static contact angles is that droplets are microscopic compared to a liquid bath which can lead to other dynamic perturbations such as, for instance in the case of pure water, rapid evaporation or absorption into the hair fibre [190,226]. We therefore refer to the following experiments more generally as pseudo-static [226] although some wetting liquids have been suggested to be more suitable in avoiding the above transient effects. Dupres et al. [67,190] linked the static wetting behaviour of various wetting

liquids on hair to AFM topography images and surface potential maps in both virgin and lipid-extracted fibres. Squalane was found to be a suitable alternative to water due to its much slower evaporation. The AFM results showed no particular hints of strong inhomogeneities on both virgin and delipidated hair surfaces. However, the authors still suspected the existence of such patterns on 18-MEA-extracted fibres due to the observed wetting behaviour of small droplets which adhered to the damaged surface even far from the cuticle edges. For virgin hair, squalane was only found near the cuticle edges which was attributed to the strong hydrophobicity of the centre of the cuticle surface. Liquid would thus quickly de-wet from this area and only wet the region around the cuticle edge which was found to be more polar [67].

Dynamic and pseudo-static wetting experiments were conducted on virgin hairs, artificially weathered hair and hairs subjected to various degrees of bleaching before and after treatment with cationic proteolipids [226]. Reductions in the dynamic advancing contact angle were more pronounced for strongly bleached than for weathered hair. Pseudo-static contact angles of water droplets on medium bleached hair confirmed that treatment with proteolipids could restore the hydrophobicity of virgin hair.

Weiland et al. [56] coupled dynamic contact angle wetting experiments with coarse-grained molecular dynamics of static nanodroplet contact angle measurements of water and hexadecane on pristine, damaged hair surfaces. The nanoscopic wetting of hair surfaces treated with cationic surfactants were also considered recently using the same molecular hair surface model [97]. The dynamic contact angle experiments were in good agreement with previous wetting experiments [29, 51,226] and the molecular dynamics results. This allowed for determining a refined estimate of the expected F-layer damage virgin and bleached hair. More details on molecular hair surface models will be discussed in the next section. Estimates of the total surface energy from static wetting of the coarse-grained molecular dynamics model of the F-layer due to Weiland et al. [56,97] are also in good agreement with the results from dynamic contact angle measurements due to Gao et al. [86]

3. Computational techniques

3.1. Models of the human hair surface

3.1.1. Mechanical hair models

Numerical models of human hair have been developed with the incentive to serve as a complimentary tool to experiments. Before focusing on hair surface models, we will briefly summarize other available modelling techniques for investigating mechanical and computer graphics properties of human hair. At the largest relevant scales, efficient hair entanglement simulations could be a welcome extension to combing experiments with the key advantage of being able to resolve individual fibre dynamics. However, these macroscopic hair models are still relatively rare in the literature. Lee et al. presented a continuum model to study fibre entanglement in carding machines [232]. Plumb-Reyes et al. [233] recently presented a numerical thin filament model based on Kirchhoff–Cosserat theory to model human hair detanglement. However, no friction forces were included in the model so investigations of different surface chemistries are not yet accessible. The model due to Plumb-Reyes et al. was further used by Hughes et al. [234] to compare to automated combing experiments. Further multi-fibre hair models are available in the field of computer graphics [235–237]. These models are mostly aimed at producing a realistic or stylized appearance of hair styles. However, some of these models may also be leveraged for conducting physics-based simulations. One such example is the work due to Daviet et al. [237] where Coulomb friction was incorporated into a simulation framework for hair dynamics [237].

On smaller scales, molecular models of hair have become more common in recent years. These models allow for capturing nanoscale interactions and surface chemistry effects which can be difficult to impossible to capture by experiments. Atomistic structures can provide

further insights into the surface properties of hair and its interactions with hair care products under various damage modes. With the increase of computational power and robust biomolecular force fields for atomistic [238] and coarse-grained [239] molecular dynamics simulations, this pathway has recently become more popular and has opened up new opportunities for the virtual screening [240,241] of formulated hair care products [242]. Some focus has been placed on modelling the hair cortex to investigate mechanical properties of the hair fibre and the affinity of the core towards external molecules [243–246]. While mechanical properties of the fibre are certainly directly relevant for tribological investigations, we will in the following focus on modelling the hair surface which gives rise to the hair's frictional and surface chemistry properties.

3.1.2. Mean-field hair surface modelling

For tribological purposes, models of the surface of human hair are of particular interest, as friction, lubrication and wear mechanism are localized in this part of the hair. Two approaches have been commonly chosen to study nanoscale hair surface interactions, namely mean-field theory approaches and the molecular dynamics route. Mean-field approaches allow for insights into the thermodynamics and structure of formulations near interfaces and in bulk, while neglecting short-distance density fluctuations [247]. Banerjee et al. used self-consistent field theory (SCFT) to study the interaction of oppositely charged polyelectrolytes and surfactants in bulk [248] and subsequently near biomimetic surfaces representative of healthy and bleached hair [116]. Guzmán et al. [118] extended this to studying different polyelectrolyte-surfactant architectures and formulations in their adsorption behaviour. Leermakers et al. [117] further applied SCFT to tune the wettability of hydrophilic surfaces, comparable to virgin hair, to allow for the deposition and spreading of hair care formulations.

SCFT is certainly suitable to study adsorption and aggregation of complex solutions to hair, which can provide qualitative ideas on which tribological response can be expected, such as the relevant lubrication mechanisms and wetting as a result of the surface chemistry of deposited compounds. However, these equilibrium models are not directly applicable to predicting friction and other non-equilibrium phenomena quantitatively. SCFT also typically considers the solvent as implicit, which is usually not suitable for resolving friction as the role of water or other solvents under load has been found to be critical for hair friction mechanisms [10]. It was also observed in experiments that non-equilibrium processes might already exist during adsorption of polyelectrolyte-surfactant complexes in reality, [118,249] which can also not be captured by equilibrium theories such as SCFT. To conclude, we argue that SCFT is highly valuable for the initial stage of the tribological modelling process, when predictions of equilibrium structures and deposition is relevant. However, for exact tribological investigations, they should be complemented by explicit particle models as outlined in the next section. A coupling between mean-field approaches and molecular dynamics could also be advisable and will be discussed towards the end of this work.

3.1.3. All-atom hair surface models

Molecular dynamics and dissipative particle dynamics (DPD) on the other hand consider explicit atoms (all-atom MD) or groups of atoms (united-atom, coarse-grained MD, DPD) as discrete beads and can accurately capture three-dimensional structures and dynamics on the nanoscale. MD simulations typically consider van-der-Waals (vdW), electrostatic and intramolecular interactions such as bonds, angles and dihedrals to obtain a force balance on each bead which is then integrated in time to obtain a physical trajectory of the simulated system. The first known MD representation of the human hair surface was developed in the early 2000s by Beard and Hare [250], who modelled the cuticle as a sheet of polypeptide chains to study the adsorption of quaternary amine surfactants. Practical applications for molecular hair models go beyond the use for the hair care industry.

Efremenko et al. [251] studied the adsorption of explosive molecules by the hair surface. They conducted density functional theory (DFT) and MD simulations to study how explosives adsorb on 18-MEA molecules and on hair proteins. McMullen and Kelty [252] presented an united atoms model in the GROMOS96 force field [253] of both eicosanoic acid (EA) and the 18-methyleicosanoic acid (18-MEA) fatty acid monolayers, the latter of which is the predominant constituent on the F-layer on hair. An extended all-atom MD model of the 18-MEA monolayer on ultra-high sulphur protein beta-sheets of the virgin hair endocuticle was developed by Natarajan and Robbins [254]. They considered the experimentally-observed [255] thioester linkage between the 18-MEA and the cuticular protein matrix below. They used the antifreeze protein from snow fleas as a simplified protein model [254]. This model was later validated through a combination of Raman, infrared, and vibrational circular dichroism experiments [256]. The grafting density chosen by Natarajan and Robbins. [254] resulted in a disordered 18-MEA monolayer, which was in agreement with previous X-ray photoelectron spectroscopy (XPS) thickness measurements of the F-layer [257]. An extension to the comparison between EA and 18-MEA was presented by Cheong et al. [52] using the OPLS-AA forcefield for carbohydrates [258,259]. The authors considered various lipid grafting densities for both EA and 18-MEA to obtain structural insights of the thioester-grafted monolayers in vacuum and in the presence of water. They were able to predict an optimum lipid separation distance (0.49–0.65 nm) for the 18-MEA from a thermodynamic free energy minimum with respect to the packing distance and by quantitatively comparing the thickness of the observed monolayers with transmission electron microscopy (TEM) measurements on hair [260]. Cheong et al. also commented on the observation of a higher monolayer thickness in their MD study (2.0–2.6 nm) compared to previous XPS measurements on hair (0.9 nm) [261,262]. They propose multiple solutions to this discrepancy: the potential removal of free and covalently bound fatty acids in the experiments, the variability of hair across different people and the possibility of perturbations due to vacuum conditions in the XPS experiments [52]. Another noteworthy characteristic of their model is the simplification of the protein matrix below the F-layer. They used a stack of graphene sheets as surrogate, which was also useful for systematically varying the grafting density of the 18-MEA and has since been used in recent coarse-grained models of the F-layer [18,56]. This approach is deemed suitable for the investigation of processes in which deposition onto the F-layer, rather than penetration of compounds into the cuticle is relevant and in absence of large degrees of mechanical or chemical damage.

Sanders et al. [263] used the all-atom OPLS4 forcefield [264] to model the 18-MEA with explicit covalent bonds to ultra-high sulphur proteins to study the wetting and adsorption of free lipids on virgin hair. Their model differed from the previous model by Natarajan and Robbins not only by the different choice of force field but also in a more accurate protein representation and packing density of the 18-MEA in the F-layer (1.26–1.41 molecules/nm²). This could be particularly useful when accuracy is required — not only for studying adsorption, but also for investigating the penetration of compounds into the cuticle, i.e., *absorption*. An extension to this model was recently developed by Wang et al. [265] in form of an all-atom model considering both healthy and damaged hair. Their model consisted of both the F-layer and a keratinous protein matrix were considered in dry and wet conditions. Besides grafted 18-MEA lipids, the authors also incorporated free 18-MEA lipids. The number of bound lipids was assigned based on the number of available sulphur atoms on the underlying protein matrix as a degree of damage, while the number of free lipids was chosen as a parameter. This model was able to accurately capture properties observed in experiments and previous models. It also highlights that free 18-MEA lipids are likely required in the models and that the simplification of treating the protein matrix by a graphene sheet can limit the heterogeneity of cysteine acid residues and absorption properties.

3.1.4. Coarse-grained hair surface models

Larger length and timescales compared to all-atom MD can be captured by using so-called coarse-grained molecular models. These models typically compromise resolution for performance by grouping several atoms into larger beads. Šindelka et al. [98] used DPD to model the pristine F-layer of hair in the presence of lamellar-phase hair care products containing cationic surfactants and fatty alcohols. Adsorption and desorption mechanisms of various product compositions were studied in equilibrium conditions and under an external shear flow. A coarse-grained molecular model of the F-layer on hair [56] was developed based on the all-atom model by Cheong et al. [52]. The coarse-grained MARTINI 2 forcefield [266,267] was used to represent each 18-MEA lipid individually. The model was able to capture a wide range of chemically-induced degrees of damage. The grafting density of lipids and negatively charged sulfonate groups representing chemically damaged regions on a simplified graphene sheet representation of the endocuticular proteins was derived from existing charge density measurements on hair [82]. Coscia et al. [18] presented a modified-MARTINI coarse-grained model of the F-layer with larger cylindrical damage patches to study the tribological interactions with thick films containing polyelectrolytes and ionic surfactants. Further details of this model will be discussed in the next section on hair friction modelling.

3.2. Hair friction modelling

Models for investigating the tribology of hair have become more accessible in recent years. Special interest has been expressed in studying the behaviour of hair under the influence of shear. A multiscale finite element hair follicle model has been proposed by Zamil et al. [268] to study stresses and the coefficient of friction during hair growth at the root. Most friction-related hair models have been focusing on the nanoscale, as this directly allows insights into the chemistry and molecular kinematics at length and time scales which cannot be resolved accurately in experiments.

Non-equilibrium molecular dynamics [269] allow for measuring shear stresses for two contacting surfaces under normal load and for single surfaces with an applied external shear. This is particularly useful for applying the aforementioned molecular models to obtain a direct estimate of friction while also including the tribological effect of different existing and novel formulation chemistries. Morozova et al. [270] conducted adsorption and shear simulations of polymers on biomimetic hair surfaces. A two-dimensional coarse-grained model of the human hair surface was established by a Fourier transform approach which captures randomly patchy hydrophobic-hydrophilic surfaces representing the 18-MEA and oxidized regions on hair. They considered in an extension to this work, polymer architectures found in biodegradable polysaccharides were benchmarked against a more traditional rigid polyelectrolyte architecture from petrol with respect to the adsorption and desorption behaviour under equilibrium conditions and in the presence of a linear shear flow [271].

Weiland et al. [10] studied the friction of biomimetic flat surfaces representative of the F-layer in human hair using a coarse-grained molecular dynamics model of the hair surface, [56] as discussed above. The authors tested dry and wet contacts at a wide range of random replacement of 18-MEA chains by cysteic acid groups, mimicking the oxidation of hair due to chemical treatments such as bleaching. The study also established realistic degrees of contact hydration by applying so-called squeeze-out simulations, as initially introduced by Ewen et al. for organic friction modifiers [272]. This dedicated squeeze-out step is an essential step to capture the contact composition for a given normal load in the MD simulations. A monotonic increase of the friction coefficient was reported with increasing surface damage at physiologically relevant sliding velocities. This was further supported by biomimetic surface chemical colloidal probe AFM experiments of pristine and fully oxidized surfaces. For wet surfaces in particular, the authors further highlighted the potential importance of counterions in the contact

which could contribute to friction increases. Those counterions are added to the system as a consequence of the molecular dynamics algorithms which require a net charge of zero. Therefore, an increasing degree of oxidation to the negatively charged cysteic acid groups also goes along with an increase in sodium counterions [10].

A subsequent study [97] using the same coarse-grained model of the F-layer investigated the adsorption of cationic and anionic model surfactants on hair as well as the effect of different adsorption densities of cationic surfactants on hair-hair friction and hair wettability. This work provided detailed molecular structures and kinetics of adsorbed cationic surfactants, specifically cetrimonium bromide (CTAB), in NEMD simulations for virgin and bleached F-layer models. It was found that the cationic surfactants preferably adsorb as a monolayer on both virgin and bleached hair. At high bulk concentrations bilayer contributions were also found. Regardless of the adsorption structure, it was found that CTAB can restore the hydrophobic, low friction behaviour for damaged hair surfaces close to values of virgin hair. Fig. 9 shows the effect of total surface coverage on the friction coefficient, reprinted from Ref [97]. This shows that the surfactant coverage is a driving factor for friction reductions with surfactants adsorbing in a layered manner.

Coscia et al. [18] modelled contacts between two hair surfaces containing cationic polyelectrolytes and ionic surfactants in the hydrodynamic lubrication regime. Their fully-deformable F-layer model discussed in Section 3.1 was used as a representation of the hair surface. Fig. 10 shows the coefficients of friction evolution in time and snapshot of their NEMD simulation trajectories containing either petrol-based polymers (M100, M2003) or a cationic amphiphilic polysaccharide (PS), namely quaternized 3-deoxy-6-deoxy cellulose copolymers. M100 or Merquat 100TM is a linear cationic homopolymer, while M2003 or Merquat 2003TM is a zwitterionic copolymer [18]. The simulations further contained ionic surfactants typically used in hair care formulations, such as the anionic surfactant sodium laureth sulfate (SLES) and the zwitterionic surfactant cocamidopropyl betaine (CAPB). Additionally, excess salt was added to their formulation, which can be beneficial for tuning the formulation viscosity in the presence of the chosen surfactant types [164,273]. Their model successfully demonstrated the capability to simulate the tribological response of nanoscale hair-on-hair contacts containing large aggregates of polyelectrolytes close to realistic molecular weights and oppositely-charged surfactants.

The low viscosity-pressure coefficient of bulk water [274] makes a fully developed film rare in aqueous contacts, unless viscosity modifiers are present. Hair friction in the boundary and mixed lubrication regime was studied for cationic polyelectrolytes and anionic surfactants adsorbed on virgin and bleached hair [275] using the F-layer model by Weiland et al. [56]. This work considered a sequential adsorption routine in which short chains of the plant-based polysaccharide guar gum were first introduced to hair before saturating the surfaces with adsorbed polyelectrolytes with anionic SDS. Preliminary squeeze-out simulations were conducted to remove any excess water and anionic surfactants from the contacts for a given normal load. After squeeze-out, NEMD simulations were conducted to study the friction at various sliding velocities and normal loads. An overview of the shear stress as a function of the sliding velocity from CG-MD simulations is shown in Fig. 11. Synergistic effects between guar and SDS led to significant friction reductions at low normal loads compared to pure wet contacts and contacts lubricated by either CGG or SDS with water. This was attributed to a confined layer of SDS and water between pre-adsorbed guar chains. These observations further suggest that viscous, thick films might not be a necessity to provide a favourable lubrication performance on hair.

4. Hair friction mechanisms

The previous sections provided an overview of historic and state-of-the-art experimental and numerical techniques to study hair tribology.

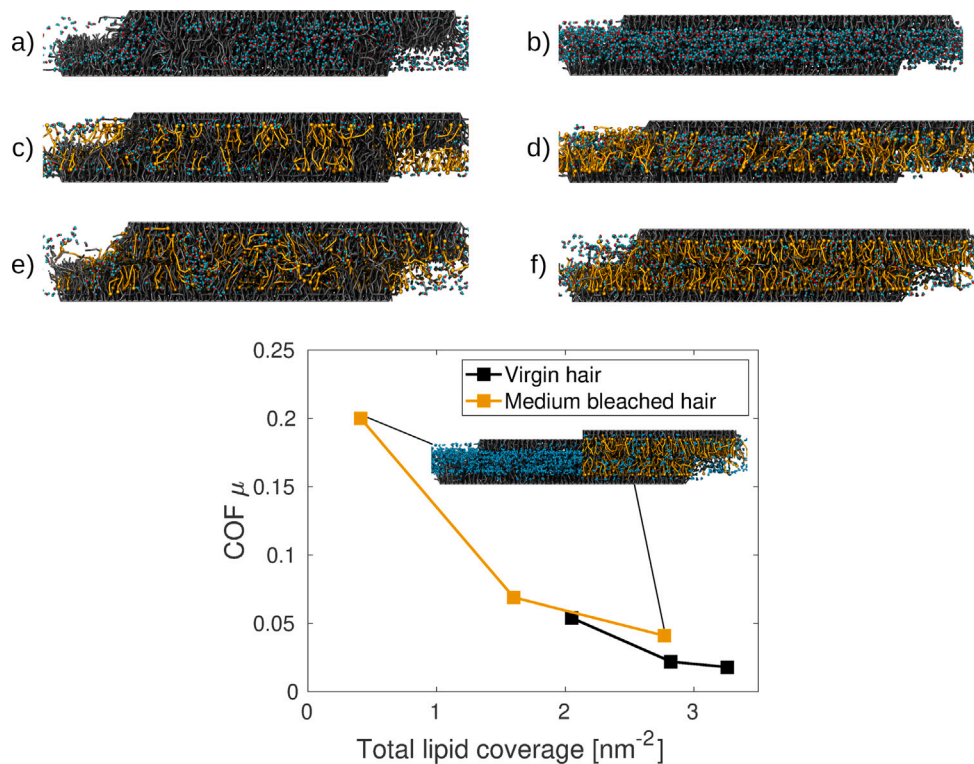


Fig. 9. Top: Snapshots of NEMD systems considered in this work at $\sigma = 10$ MPa: (a) virgin hair, (no CTAB), (b) medium bleached hair, (no CTAB), (c) virgin hair, (low CTAB coverage), (d) medium bleached hair, (low CTAB coverage), (e) virgin hair, (high CTAB coverage) and (f) medium bleached hair, (high CTAB coverage). 18-MEA (grey), CTAB (orange) and water (cyan/red) molecules are shown. Bottom: Effect of the total lipid coverage (CTAB and 18-MEA) on virgin and bleached model hair surfaces on the mean friction coefficient.

Source: Adapted from Ref. [97] licensed under a CC-BY 3.0 license.

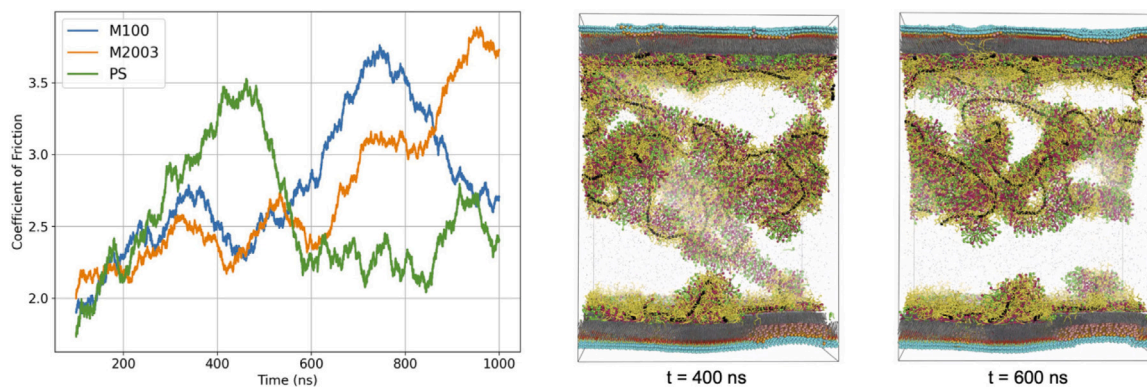


Fig. 10. Coarse-grained non-equilibrium molecular dynamics simulations of F-layer contacts containing aqueous solutions with either petrol-based polymers (M100, M2003) or quaternized 3-deoxy-6-deoxy cellulose copolymers (PS) plus CAPB, SLES and excess sodium chloride.

Source: Reprinted from Ref. [18] by Coscia et al. licensed under a CC-BY-NC 4.0 license.

Now, we will provide a review of the relevant mechanisms for that affect hair friction in particular. We will further discuss the appropriate handles for tuning hair friction and sensory perception which is particularly important in the context of formulating hair care products. It is worth noting that many of the highlighted mechanisms are expected to be closely coupled, which is why, as will be shown,

small-scale experiments tend to be more successful at isolating specific mechanisms.

4.1. Humidity & wetting effects

The wetting state of hair strongly affects its frictional response. In humid environments, residual water is present on the hair surface and

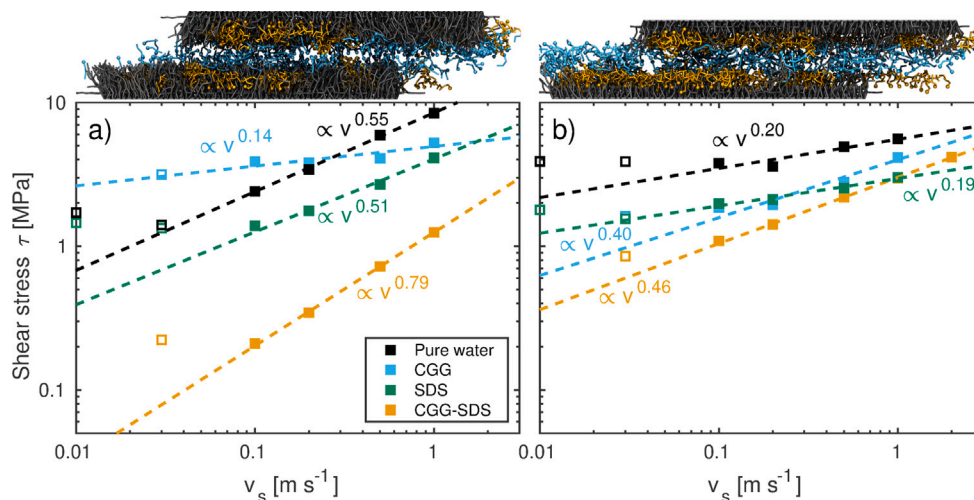


Fig. 11. Shear stress as a function of the sliding velocity v_s in boundary lubrication contacts of (a) virgin and (b) bleached biomimetic hair surfaces with sequentially adsorbed cationic guar gum and anionic surfactants (SDS). The contact pressure was 10 MPa for all shown data.

Source: Reproduced from Ref. [275] under a CC-BY-NC 4.0 license.

also within the cell membrane complex between cuticle cells [230,276]. Fully dry hair is therefore expected to be encountered rather rarely in most ambient environments but will also be discussed to some extent below. Conversely, fully wet conditions are encountered during and after washing and rinsing. Wet hair has also been studied extensively in laboratory conditions using the liquid cell setup as discussed earlier in perspective of nanoscale friction and adhesion measurements [177, 201,202].

Differences in nanoscale hair friction between fully dry and water-immersed setups for virgin and bleached hair were reported by Nikogeorgos et al. [177]. For both virgin and chemically damaged hair, the friction coefficient increases in the wet case [138,177]. Over the years, two mechanisms have been brought forward that aim at explaining this observation:

1. Water is absorbed by hair leading to a swelling which in turn increases the softness and contact area during sliding [92,177, 184]. On damaged hair the swelling is further amplified due to a higher internal water uptake as the hydrophobic protection from the F-layer is removed. [230]
2. 'Proteolipid reorientation' as a surface chemistry-induced mechanism for increased friction in (fully) wet hair was first proposed by Maxwell et al. [53] and later considered in AFM friction experiments on hair [177,197]. It was proposed that the F-layer lipids on hair or wool would reorient away from the solution, with the hydrophilic protein matrix of the epicuticle being exposed.

There is clear evidence of swelling of the hair surface and cuticle softening in aqueous environment [184,196,277,278]. This discovery was soon followed by a search for an accurate description of the organization of the covalently bound 18-MEA lipids on the epicuticle. Some studies proposed a densely packed monolayer structure of lipids [11]. A heterogeneous distribution of covalently bound lipids is generally more accepted now due to evidence of hydrophilic patches on virgin hair from nanoscale adhesion measurements [43,55]. Nikogeorgos et al. [177] proposed that the reorientation of 18-MEA lipids might only be possible if sufficient lipids had already been removed in the first place due to chemical treatment. This was explained by the observation that the friction increases between dry and fully wet states was more pronounced in KOH-treated hair than on virgin hair. On virgin hair, reorientation would be substantially limited as a result of the dense 18-MEA packing [177].

The key morphological difference of hair in humid environments compared to either fully dry or immersed conditions lies in the existence of capillary effects due to a triple phase boundary between the substrate, the wetting liquids and the ambient vapour phase. Capillary forces further increase wet hair friction and therefore combing forces [148,225]. However, it is difficult to separate these forces directly from the friction increases due to the hair swelling and softening mechanism, which will naturally also occur to some extent in humid environments. In contrast to the observations due to Nikogeorgos et al. [177] a moderate decrease in friction on virgin hair was observed by LaTorre and Bhushan [92] for soaked hair. The authors attributed this to the lower degree of water uptake in virgin hair due to its hydrophobic protection. However, it is also worth noting that the soaked hair friction was measured at relative humidity of 50%, so capillary effects might still play a role. Avoiding capillary effects is also beneficial for reducing the scatter of nanoscale friction experiments under laboratory conditions. Lee et al. [200] reported that friction measurements in a liquid cell drastically reduced the statistical scatter observed in ambient conditions when studying the effect of polyelectrolytes on the surface.

The sensory perception of wet hair is not only influenced by friction forces but can also be tuned by means of a surface temperature drop from evaporation cooling [170]. This underlines that hydrating hair conditioning products are indeed beneficial for providing a feeling of 'moisture' for some time after application (1-2 h) according to Ref. [170].

4.2. Hair damage

Clear evidence has been provided that artificial mechanical [5, 68] and chemical treatments [5,177] as well as weathering and ageing [169,279,280] induce an increase in hair friction. Chemical treatments such as bleaching, colouring and perming strongly alter the surface properties of hair and therefore represent a particular area of research. Hair care formulations may also be tailored to particularly focus on repairing chemically damaged hair. Fig. 12 shows an overview of the relative increase in the friction coefficient induced by chemically damaging hair from macroscopic, [28,171,180] microscopic [180] and nanoscale experiments [5,58,177] and molecular simulations [10]. The relative friction coefficients are defined as the ratio between the friction coefficients of chemically treated and virgin hair.

A relatively strong scatter in the magnitude of the relative friction increases is evident. Relative friction coefficients from nanoscale

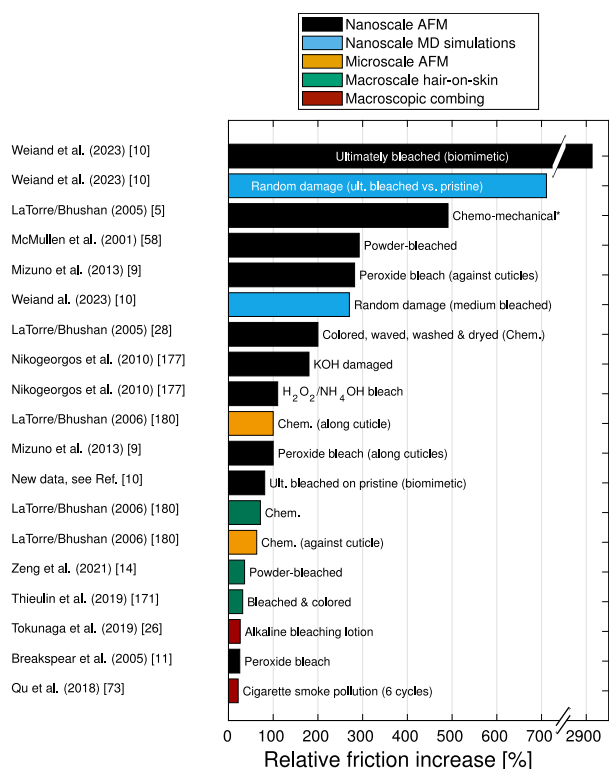


Fig. 12. Relative kinetic coefficients of friction from experiments and simulations between untreated (virgin) and chemically damaged hair in ambient/dry conditions. The values from Ref. [14] measuring friction in and against the direction of cuticle growth were averaged. *Chemo-mechanical treatment in Ref. [5] constitutes colouring, waving, washing, drying and combing.

experiments and simulations are significantly increased compared to either microscale AFM or macroscopic experiments (combing and model skin-on-hair). The probe material might be one factor leading to the difference in relative friction increase. However, the microscale AFM results with a silicon oxide spherical probe [180] also show similarly low friction increases, which might suggest that lengthscale effects might also play a major role. This hypothesis will be discussed further in the next section. Surprisingly, the largest difference in friction increases is observed between the two nanoscale AFM studies due to Breakspear et al. [11] and LaTorre and Bhushan [5]. Breakspear et al. also considered hydroxylamine-treated hair which was expected to have all 18-MEA removed, but reported comparable friction increases (+30%) as observed with bleaching. While both studies used a similar AFM setup, Breakspear et al. considered lower normal loads during friction measurements between 0.5–4 nN while LaTorre and Bhushan considered normal forces in the range of 5–45 nN. However, for adherence to the extended Amontons-Coulomb law a difference in normal load would be expected to render such differences in the friction coefficient increase as long as both results are extracted from the slope of the linear fit to the friction force data versus normal load. LaTorre and Bhushan also considered mechanical damage due to combing on top of the chemical treatment, which might also explain why their nanoscale AFM results showed the highest friction increases across all considered studies. Here, we also show new experimental CoF data measured between heterogeneous biomimetic contacts representative of ultimately bleached and pristine hair. These experiments are similar to those described in Ref. [10]. Here, the flat silicon wafer surface was functionalized as ultimately bleached hair, while the chemical colloidal probe AFM was functionalized with C₁₈ to resemble pristine hair. Consequently, the relative friction increases between C₁₈-C₁₈ contacts and the new data from heterogeneous contacts is much lower than for purely ultimately bleached contacts due to Ref. [10].

Two tribological mechanisms for the friction increases due to chemical damage have been proposed:

1. Increasing surface roughness increases the number of asperities in contact and therefore friction by means of a ‘nanoscale ratchet mechanism’. [5,13]
2. Surface chemistry changes modify the interaction forces between the contacting substrates.

Increases in the surface roughness were observed on multiple accounts across the relevant lengthscales for both chemical damaging [5,169] and mechanical damage due to combing [68]. However, it was also reported that both bleaching and treatment with methanolic potassium hydroxide (KOH) did not notably increase the surface roughness, as determined by AFM scans [177]. NEMD simulations of hair surfaces subjected to random heterogeneous nanoscale damage of the F-layer [10] yielded similar increases in the friction coefficient as the AFM experiments due to LaTorre and Bhushan [5]. The surface roughness in the numerical experiments also did not increase due to the nature of the model which considered an atomically smooth slider to graft the F-layer onto. In the same study, further colloidal probe AFM experiments on smooth pristine and oxidized biomimetic hair surfaces consistently showed that surface roughness is not necessary to observe friction increases on chemically damaged hair. In summary, it seems that while changes in the (mesoscopic) surface roughness will most probably also affect the friction coefficient on hair, [168] hair treatments of chemical nature do not always necessarily induce this morphological change. Homogeneous or nanoscopically heterogeneous modifications to the surface chemistry due to treatment could be sufficient to explain certain increases in hair friction. In reality, both modes might contribute to changes in hair tribology, especially when hair subjected to a combination of chemical damage, mechanical stress and weathering. This has directly been observed in hair subjected to air pollution which resulted in observable cuticle degradation and loss of the 18-MEA [73]. Theoretical and computational models coupling both the nanoscale insights and surface roughness features across the lengthscales might be helpful in predicting the frictional response and expected sensory perception.

Hair ageing represents a much more long-term degradation mode. It has been found that hair ageing increases in both the perception of slipperiness and the measured hair friction [169] which is probably due to the depletion of hair lipids with ageing [281]. Meanwhile, the hair surface roughness also increased with age [169]. Weathering of hair also induces a reduction of F-layer lipids from the root to the tip of hair [26]. This is reflected in higher friction coefficients at the tip as observed in single fibre friction tests. [151]

4.3. Scale-dependence of hair friction measurements

In the previous section, it was shown that the relative increase in the friction coefficient from macroscopic friction experiments was lower compared to nanoscale AFM measurements on chemically damaged hair. There is a variety of morphological influences which could contribute to such a lengthscale-dependent frictional response of hair. Naturally occurring roughness features such as the overlapping cuticle scale arrangement, [7] the existence of striations on the sub-cuticle scale of virgin hair [6,66,68,207,282] and weathering effects [26,151] have all been found to render anisotropic and non-uniform friction force profiles. The screening of roughness features with an AFM tip contributes to the high variability in friction forces when measured at different positions on the hair surface [197,200]. LaTorre and Bhushan consistently suggested that the tribological mechanisms observed at the nanoscale and at the macroscale might be fundamentally different [180]. They highlighted potential contributions at the macroscale such as capillary effects, surface roughness and (morphological) cuticle edge effects [5,28,92,180] which are expected to be less pronounced or non-existent at smaller scales.

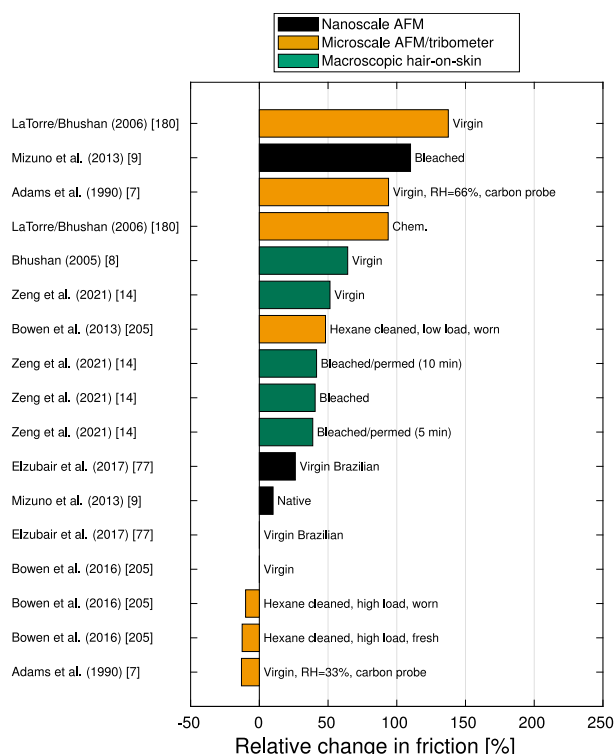


Fig. 13. Relative change in friction forces when scanning ‘against’ the direction of cuticle growth compared to scanning ‘along’ cuticles from experiments. For the experiments by Bowen et al. [283], ‘low’ and ‘high’ loads indicate $F_N = 10$ mN and $F_N = 100$ mN respectively, while ‘fresh’ and ‘worn’ indicate data after 30–100 and 100–10⁴ scratch cycles.

At the cuticle scales, we previously highlighted the influence of the DFE. The relative change in friction force when measuring friction against or along the direction of hair growth from several experiments across the scales is summarized in Fig. 13. Scale-dependent effects are less evident here than with damage-induced changes in the frictional response discussed in the previous section. Moreover, we observe no clear trend with respect to the treatment type. However, the majority of experiments confirm the trend of higher friction forces when measuring against the cuticle growth direction as opposed to measuring along the growth direction.

When taking into account hair bundles, additional complexity arises due to multiple points of fibre-fibre interaction and interactions with the external manipulator such as a comb or finger. Here, hair entanglement also plays a major role. Macroscopic hair features can change the frictional response of hair bundles: Konno et al. [181] recently compared the friction coefficients of straight, curly and wavy hair bundles using a macroscopic finger probe and highlighted that the contact area between the probe and hair bundles directly depends on the hair morphology.

Tokunaga, Tanamachi et al. [26,176] proposed that changes in the nanoscale chemistry of hair directly influence the interplay of hair wetting and entanglement and therefore macroscopic hair friction. The authors suggested that the increase in hair hydrophobicity due to the depletion of the F-layer lipids would facilitate water distribution and therefore entanglement during drying. Their hypothesis was corroborated by wetting experiments as well as nanoscale, macroscale friction tests and macroscopic evaluation of hair bundle structure between different levels of hair damage and conditioner treatments. A schematic overview of the effects of removing the 18-MEA from hair due to Tokunaga et al. [26] is shown in Fig. 14. This further supports the idea that the nanoscale surface chemistry influences the macroscopic hair structure and the frictional response.

Macroscopic features and nanoscale surface chemistry effects are not necessarily contradictory. There are clear arguments that justify further continuing the macroscopic tribological research on hair: High-throughput screening of formulation effects on the sensory perception is one advantage of macroscopic setups, which is only starting to become practical in nanoscale simulations but is still limited to few examples in nanoscale experiments, e.g. Ref. [217]. Furthermore, previous sensory perception studies have found that the feel of hair might also be influenced by inherent macroscopic properties of the hair such as the diameter [3]. This underlines the need for integrating knowledge from all accessible lengthscales into the development of hair care products if both the direct effect and underlying mechanisms of a specific hair treatment are of interest. This is in fact not unique to hair but a challenge common to many other soft tribological contacts [284]. Multiscale hair friction studies are rare in experiments to date (e.g., Ref. [28]) but could become more accessible due to computational models, especially when an *educated* high-throughput screening approach is desired. Reproducing and thus understanding trends from sensory perception in repeatable laboratory experiments is also essential to enabling fine-tuning of hair care formulations to consumer needs. Some work has already been performed in this area, including wetting, combing and friction experiments [3,14,285]. Nonetheless, these macroscopic approaches should be complemented by mechanistic insights from smaller scales which will be explored as part of this work.

4.4. Influence of contact load & sliding velocity

It is essential to consider the difference in the normal load that is subjected to hair contacts in different laboratory setups and real environments. Most experimental studies reported the friction coefficient as a linear fit to lateral forces versus normal load according to the extended Amontons-Coulomb law [5,58]. The linear increase of friction forces opposing the direction of sliding as a function of the normal load is usually attributed to an increase in contact area [5]. However, irreversible processes at the nanoscale are equally relevant, [135] as has been confirmed in numerous NEMD studies where the macroscopic contact area was kept constant for varying normal loads [10,97,135,222,272]. The nanoscale heterogeneity, surface potential and local amount and distribution of lubricants within the contact all contribute to friction, although might be masked by surface roughness effects in macroscopic measurements. The contact composition as a function of the normal load has been identified to strongly influence the shear stress when varying the contact pressure in NEMD simulations, which is why preliminary squeeze-out simulations were introduced for different normal loads [10,272]. An exception to an ideally linear behaviour has been observed on damaged and subsequently conditioned hair in AFM friction measurements, where a step-wise linear behaviour was reported [177]. This was attributed to the depletion of cationic surfactants at higher loads under shear.

AFM experiments allow for accessing the nanoscale tribology of hair but are inherently limited to sliding velocities in or below the range of $\mu\text{m s}^{-1}$ to avoid hydrodynamic perturbations [202]. This is much lower than what would be considered physiologically relevant (on the order of tens of centimetres per second) assuming manipulation scenarios such as combing and rubbing against skin [143,286]. NEMD simulations on the other hand are still limited to higher sliding velocities than the AFM but can well reach physiologically relevant sliding speeds of a couple of centimetres per second [10]. Recent NEMD simulations of dry and wet model hair surfaces indicated a shear stress cross-over between different degrees of chemical hair damage at realistic sliding velocities [10,275]. This once more shows that not all trends from nanoscale experiments and simulations cannot always be extrapolated to physiologically relevant operation conditions. In some instances, sufficient amounts of data might allow for fitting to either the extended Amontons-Coulomb law, or even more general frameworks such as stress-augmented thermal activation models [228,287,288]. The latter was done in Ref. [10] for dry and wet hair which allowed extrapolating the observed high-velocity sliding friction to lower speeds.

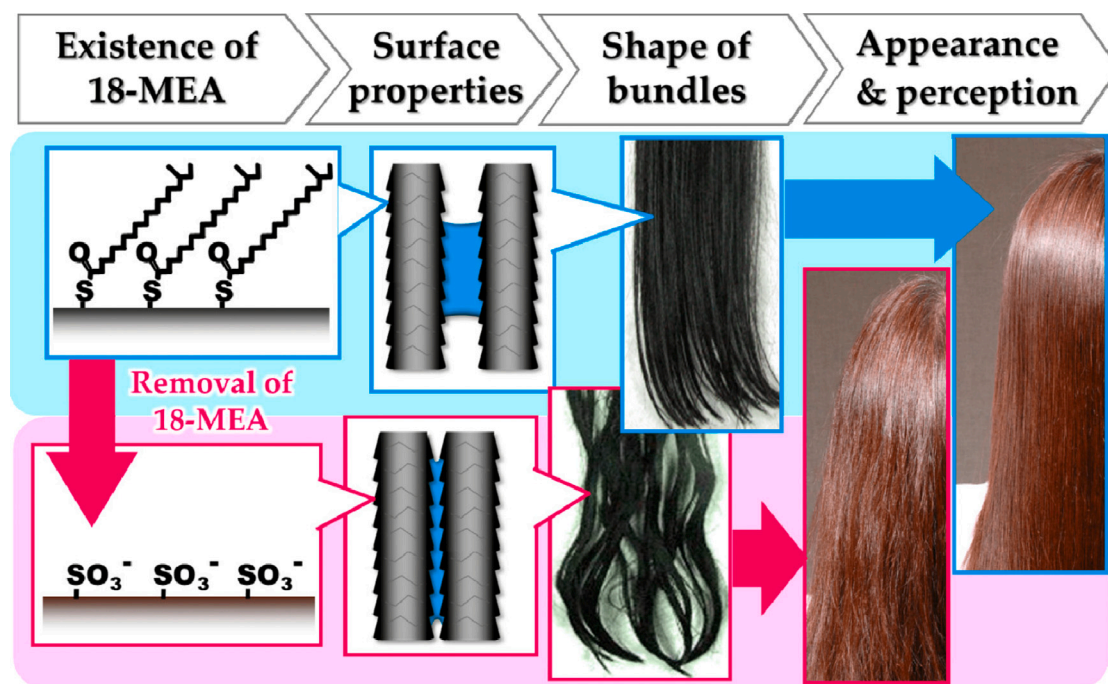


Fig. 14. Effect of 18-MEA removal on hair entanglement, appearance and perception.
Source: Reprinted from Ref. [176] licensed under a CC-BY 4.0 license.

4.5. Hair care formulations

By definition, conditioning formulations are intended to repair damaged hair and provide a smooth appearance, a pleasant, soft sensory perception and good hair detanglement performance [13]. Shampoos should typically also serve a cleansing role, [21] removing excess oils and detritus. Secondary roles such as perfuming, hair root and scalp treatments are not discussed here, as the involved compounds in the formulations are not expected to be highly relevant to hair tribology at typical concentrations. Rather than discussing shampoos and conditioners separately, we will differentiate by the capability of a formulation to undergo a macroscopic phase transition upon dilution. Finally, we will also review in this section how, and if at all, the bulk properties of a hair care formulation can be linked to the friction response of treated hair.

4.5.1. Single-phase conditioning formulations

It has been long-known that cationic surfactant conditioners reduce hair friction [138,140]. Scott and Robbins measured the friction coefficient as a function of the cationic surfactant concentration and observed a minimum friction value on several comb materials at relatively low surfactant concentrations (0.005% for CTAB in a pH-buffered solution) [140]. A contribution from the formation of micellar aggregates on elevated friction was ruled out by additional experiments with different surfactants or salt addition to control the onset of the critical micelle formation (cmc) concentration, which produced similar coefficients of friction. The frictional response as a function of the surfactant concentration in Ref. [140] showed a clear resemblance with a typical Stribeck curve. However, the authors argued that hydrodynamic lubrication due to an increase of surfactants in the contact was likely not responsible for the non-monotonic nature of friction with CTAB. They rather suggested that this behaviour might be due to a change in the electrostatic nature of the contact, where negatively charged sites on bleached hair are neutralized at intermediate surfactant concentrations but excess surfactants lead to a net-positive surface charge. Scott and Robbins also observed that such excess cationic surfactants could be easily rinsed off the hair surface [140]. Crossed fibre tribometer friction consistently tests also yielded lower friction for hair treated with low

concentrations of CTAB compared to contacts fully wetted with water only [148]. LaTorre and Bhushan observed further that commercial hair conditioners containing cationic surfactants could effectively restore the friction coefficient of virgin hair on chemically damaged fibres [5]. The adsorption of cationic surfactants from aqueous solution onto hair can also effectively eliminate high-frequency stick-slip phenomena between hair bundles and human skin [172]. It was demonstrated in NEMD simulations of hair with adsorbed cationic model surfactants (CTAB) that a surfactant monolayer was sufficient to restore the virgin hair hydrophobic character and low average friction coefficient and oscillations on medium bleached model hair surfaces [97]. Excess surfactants on virgin hair did not significantly increase friction and would be expected to wear off when considering an open-boundary simulation setup as opposed to the semi-periodic setup chosen in Ref [97].

More complex aggregate structures of adsorbed surfactants on hair are also conceivable and could have interesting implications for hair lubrication. Nagahara et al. [161] reported that a model shampoo containing cationic surfactant vesicles provided combing force reductions on colour-damaged hair below the value of the untreated virgin hair. However, the exact structure of the deposited aggregates is not known as only the structure in solution was analysed. It is therefore unclear whether the lubrication effect was due to the vesicles breaking up into thinner layers or if *intact vesicle deposition* [289,290] was achieved. It has been shown for phospholipids (DSPC) on mica surfaces that intact vesicles could provide substantially lower coefficients of friction than lipid bilayers [291]. Softening mechanisms on textile surfaces have also been attributed to the deposition of cationic surfactant vesicles [292].

Free fatty acids have also been found to be a suitable additive for restoring a hydrophobic character and low friction properties on chemically damaged hair [160]. The addition of silicones to shampoos and conditioning products [109,164] containing cationic conditioners has also been found to provide a superior lubrication performance. This was attributed to binding of silicones to polymer backbones on the surface. Additionally, fatty alcohols and silicones are commonly used in combination with cationic compounds to form the class of lamellar gel conditioners [92–94]. A comprehensive review on the formulation, manufacturing and experimental characterization of lamellar gel conditioners including rheological insights was recently provided by

Cunningham et al. [27] LaTorre et al. [92] investigated the hair friction in the presence of conditioners containing cationic surfactants, fatty alcohols and silicones. They reported a highly heterogeneous distribution of conditioners on the cuticle of damaged hair which was attributed to the intrinsic heterogeneity of hair and distribution of anionic sites. The addition of PDMS improved the lubrication efficiency of the conditioners during sliding conditions [92]. Amino silicones were found to be similarly effective at reducing combing work even for virgin hair [158]. It was also found that the size and chemistry of the counterions for cationic surfactants in lamellar phase conditioners directly influenced the wet friction of hair tresses. A less swollen, more densely packed surfactant layer was found on hairs treated with behenyl trimethyl ammonium methyl sulfate (BTAMS) compared to behenyl trimethyl ammonium chloride (BTAC), which resulted in substantially reduced wet friction and a higher acceptance rate in sensory panel tests [93].

The deposition efficiency and structure of larger molecules such as polymers and cationic polyelectrolytes on hair will strongly depend on the architecture, polyelectrolyte charge density and salt concentration. Hössel et al. [100] compared four different quaternary polymer architectures with respect to their hair conditioning performance. While all polymer architectures yielded substantial combing force reductions, a branched polyelectrolyte (Polyquaternium 44, P44) was found to outperform the other compounds with 40%–50% force reductions at low bulk concentrations (0.1–0.5 wt-%). This was attributed to a more pronounced coiling of P44 compared to the other polymers arising from its branched vinylpyrrolidone group which would allow fast deposition on the surface and avoidance of surface ‘overcharging’. P44 was also found to desorb more easily compared to the other polymer-surfactant formulations. Wet combing force reductions due to cationic quat-based polymers were attributed to the arrangement of polymers in brush-like layers on the hair surface, where uncharged parts of the polymers would protrude in the bulk in the form of loops and tails [100]. Molecular dynamics simulations predicted that the adsorption of the homopolymer cationic guar gum with a linear backbone onto virgin hair can potentially increase hair friction due to entanglement of polymers on opposite surfaces, even though the polymers formed flat aggregates on the surfaces [275]. The use of oppositely charged surfactants in the same formulation was found to drastically change this behaviour, which will be further discussed in the next section. As an alternative to linear homopolymers, amphiphilic copolymers have shown promising lubrication properties on mica surfaces at similar flat aggregate structures [150].

Friction reductions were also observed on bleached hair treated with PLL-g-PEG polymers which are known to form brush-like conformations on negatively charged surfaces [200]. Lubrication by polymer brushes is common in other biological systems such as articular cartilage, where ultralow friction is essential to the longevity and wear resistance of joints [293]. However, similar effects have also been reported recently for random zwitterionic copolymers adsorbed on virgin hair [294]. Those copolymers were described to bind to negative sites on the hair surface through their cationic blocks, while exposing anionic blocks to the wet environment where hydration shells from adsorbed counterions were hypothesized to provide hydration lubrication. This led to friction reductions comparable or lower than conventional cationic polymers as measured in a friction tester [294]. The hydration of the adsorbed layers on hair also affects the lubrication performance. Polymers can render high friction forces on dry hair by means of a soft, thick viscous film but still be effective at reducing wet combing forces as capillary effects are suppressed [58].

Treatment with conditioners can also result in adverse effects such as increases in hair-hair adhesion forces [141] and adhesion between a single hair and a contacting probe [92,219] due to the formation of a meniscus between the two contacting surfaces. It was also found that surface-normal adhesion forces increased with the molecular weight of a conditioning silicone polymers [141]. Adhesion forces

are further increased by an ‘overconditioning’ effect, i.e. the deposition of excess conditioner than required for optimum lubrication. This was found to increase capillary forces and lead to the formation of a thick, viscous film on hair [58]. By measuring hair adhesion using functionalized AFM tips, Labarre et al. reported strong differences in the structure of deposited conditioners between virgin and platinum-bleached hair. [219]

4.5.2. Oppositely charged polyelectrolyte-surfactant formulations

The importance of oppositely charged polyelectrolyte-surfactant formulations for the deposition of personal care products has been highlighted in the introduction of this work and elsewhere numerous times [22,107,295]. However, the hair friction mechanisms related to the presence of adsorbed oppositely charged polyelectrolyte-surfactant complexes are not fully understood to date. One working theory on the effectiveness of polyelectrolyte-surfactant as a lubricant is that complexes adsorb on hair as a highly swollen film which through exposure of hydrophobic polymer tails provides beneficial lubrication similar to that observed in polymer brushes or hydrogels [296].

Early experiments on hair with adsorbed synthetic cationic polyelectrolytes and anionic detergents at high charge densities reported no significant effect on the tactile perception and combing work [162]. This was explained by the desorption of neutralized complexes forming between the oppositely charged compounds. The desorption process was also further corroborated by streaming potential measurements during the titration of anionic surfactants on hair fibres with pre-adsorbed cationic polyelectrolytes [162]. Treatment of virgin hair with polymer-surfactant formulations containing the cationic polymer Merquat, anionic (SLES) and zwitterionic surfactants (CAPB) rendered significant combing work reductions [164]. Changes in the polymer concentration and therefore the solution viscosity did not have any quantifiable impact on the combing force without excess salt. Upon addition of excess salt, the solution viscosity profoundly decreased along with combing force reductions which was attributed to a decreased spreading efficiency on the surfaces [164]. The deposition of complexes from shampoos containing micrometre-sized coacervates reduced both the friction and surface roughness off perm-damaged hair, as measured by lateral force microscopy [297]. Miyamoto et al. [149] proposed an alternative explanation to friction reductions observed from the deposition of polyelectrolyte-surfactant formulations which also contained non-ionic polymers. Their results were explained by a model in which free non-ionic polymers would deposit to the hair surface, while charge-neutralization between the remaining polycations and anionic surfactants occurred in the bulk. The polyelectrolyte-surfactant complexes would then adsorb on top of the non-ionic polymers to form a multilayer structure [149]. This suggests that kinetic processes also play a role, as previously highlighted by Nylander [106].

Thin-film coating experiments were used to evaluate both pure cationic polymer formulations and polymer-surfactant formulations with SDS with respect to gloss, opacity and film-on-film friction [298]. It was observed that strong friction reductions were observed with SDS for polyquaternium polymers in particular. For cationic guar, friction was relatively constant between purely polymeric and polymer-SDS formulations, with little dependence on the molecular weight of guar [298]. This once more suggests that the frictional response of such polymer-surfactant layers might be highly sensitive to the polymer architecture. It has indeed been shown in self-consistent field theory calculations that the structure of polymer-surfactant layers on biomimetic hair surfaces strongly depends on the polymer architecture [117,248].

Interfacial friction NEMD simulations of hydrodynamic hair-hair contacts containing self-assembled oppositely charged polyelectrolyte-surfactant complexes [18] suggest that shear-induced polymer stretching and detachment might contribute to strong temporal fluctuations in friction forces. These simulations were performed under hydrodynamic lubrication conditions, which will only occur at low normal loads in

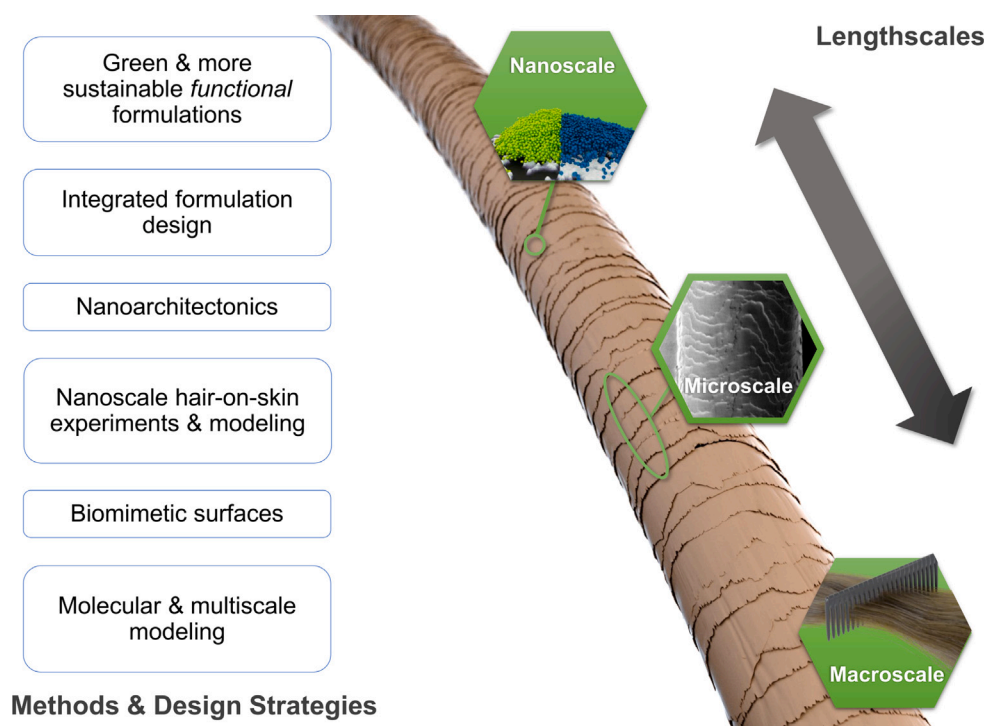


Fig. 15. Methods, design strategies and lengthscales for consideration in future hair tribology research.

aqueous films [299] or for highly viscous lubricants. NEMD simulations of virgin and bleached hair under boundary lubrication conditions showed that a swelling of strongly adsorbed short polyelectrolytes with anionic surfactants might not be necessary to provide a lubricating effect [275]. It was reported that the existence of anionic surfactants in the contact was required to sustain an effective lubrication. Polymer detachment was not observed in this study which is probably due to a significantly higher polymer charge density leading to higher resistance to shear-off. On another note, there are also indications of kinetically trapped states of adsorbed polymer-surfactant complexes, [106, 111, 249, 295] which are deemed difficult to be accurately captured in either equilibrium SCFT or molecular dynamics. Advanced sampling techniques [300, 301] might be suitable accelerators for molecular simulations allowing to screen a higher fraction of the extremely intricate energy landscape of large polyelectrolyte-surfactant complexes on interfaces.

4.5.3. Relationship between bulk properties and hair friction

The capability of linking bulk properties to the expected behaviour on surfaces is an intricate idea for accelerating formulation development. Some studies have attempted to draw a direct link between the rheology of hair care formulations and their lubrication or tactile performance [94, 100, 164, 302–304]. Ozkan et al. [302] coupled non-linear rheological measurements with expert sensory perception panel test on hair to demonstrate that ‘rheological fingerprinting’ would be suitable to predict the tactile performance of cosmetic products. A high viscosity is generally beneficial for forming a consistent film on the substrate, [94, 164] as capillary droplet formation is suppressed. This aligns with the classical Stribeck curve: a shift towards higher Hersey numbers ($He = \mu \cdot v_s / \sigma$) with higher viscosities leads to hydrodynamic lubrication where surfaces are fully separated by lubricants [164]. Davies et al. consistently reported that a higher viscosity in lamellar gel conditioners containing cationic surfactants and fatty alcohols resulted in a more even distribution of a conditioning film on hair and as a result yielded lower combing work [94]. Conversely, Iwata et al. highlighted that friction reductions observed on hair treated with lamellar gel conditioners were not due to an increased deposition efficiency of a

formulation with a higher storage modulus but rather due to superior structural properties after adsorption, thus a higher resistance against breaking [93]. A direct causality of rheology of polymeric solutions on hair friction is in fact not always apparent. For soft matter systems, the traditional Stribeck curve behaviour is in fact not universally applicable [305]. Other works also did not find a direct correlation between hair combing work and the formulation viscosity [303, 304].

This suggests that predictions of the tribological response of hair by treatment with hair care formulations based on rheology are not always adequate. One factor is probably the sheer number of morphological transitions that aggregates can be subjected to during adsorption and rinsing (dilution). The link between viscosity and lubrication might indeed be highly non-linear beyond what is predicted by a typical Stribeck curve and subject to a vast number of variables (hair damage, water hardness, dilution factor) which are hard to control in real application. Surface overconditioning might also affect the tactile perception of overly viscous conditioners, while sufficient spreadability might not be obtained at low formulation viscosities. To date, no openly available theoretical or computational models have been applied to investigate the link between formulation viscosity and hair tribology to the authors’ knowledge. Additionally, in the case of shampoos, water is almost always either an integral part of the applied formulation or indirectly present on the hair surface due to a humid environment or explicit wetting. This complicates conclusive predictions from the bulk, as additional mechanisms such as phase separation and dilution-deposition occur, often by design, as discussed above.

As a consequence, we recommend not solely relying on rheology for formulation design, especially when the deposition and lubrication performance on the hair surface is of interest. In fact, rheology is typically only one puzzle piece. Instead, both the deposition process and its resulting surface properties should be part of an early-stage screening. Given that a high throughput is usually key in the early stage of product design, suitable methods could be macroscopic wetting measurements, hair combing and if accelerated further also numerical approaches.

5. Perspectives in hair tribology

Traditionally, the development of personal care products in the context of surface sciences has been driven by experts in chemistry and physics. In this section, we aim to make the case for including more engineering-based approaches in the early-stage formulation process, including highlighting the dedicated role of tribologists. We will consider how the status quo in hair tribology can be leveraged to further advance the development of hair care formulations in the future. We also address open questions and challenges in the development of hair care products and highlight how the field of hair tribology could help address them in the future. Fig. 15 shows an overview on future directions in hair tribology as deemed important by the authors.

5.1. Sustainability & functionality

The most pressing issue in the hair care industry as a whole is probably the need for more sustainable and biocompatible ingredients and for a more responsible and eco-friendly product lifecycle. Recently, Luengo et al. [20] provided a comprehensive review on the matter of green chemistry in hair care products. The authors stressed the importance of replacing petroleum-based ingredients, phosphates, silicones and even cationic components by sustainable alternatives without compromising product performance [20]. Picken et al. [306] and Kelly [307] recently highlighted similar problems for polymers for home care and beauty product formulations. Numerous works already studied the deposition mechanisms of biocompatible ingredients on hair [102,111,308]. Some studies have already focused on hair tribology in this area to some extent. For example, the friction response of bio-sourced polysaccharides such as guar gum and cellulose derivatives on hair has been subject to research for more than two decades [18,275,298,304]. Additionally, biosurfactants are also regarded as a promising surrogate and have therefore been focus in formulation research [309–311]. Specifically, glycolipids such as mannosylerythritol lipids (MEL) [309,310] acidic sophorolipid (ASL) and alkyl polyglucoside (APG) [311] have shown promising lubricating properties on hair in macroscopic friction experiments. However, a large fraction of today's hair care products typically contain some of the problematic components mentioned above. Cationic surfactants and silicones are in fact essential for the conditioning performance of many products.

The introduction of new ingredients with minimal environmental impact must avoid degradation in durability and cosmetic performance or should ideally exceed that of the baseline compounds. The search for novel components that are responsibly sourced and biocompatible should therefore integrate tribological hair screening to ensure a reliable performance with respect to hair-on-hair, skin-on-hair and comb-on-hair friction as well as hair detanglement.

5.2. Integrated formulation design

Formulators are presented with a number of function optimization parameters for hair care products going beyond the reduction of hair friction, for instance product degradation performance, handling (rheology) and perfuming performance. This calls for the use of an integrated design approach rather than only tuning one of such formulation properties at a time. It might for instance be practical to link some tribological properties of hair care formulations to formulation bulk properties. However, we have discussed in the context of rheology that there is no convincing evidence that such predictions can be made universally and therefore expect surface sciences to remain essential to the formulation process. There are also situations in which low friction or adhesion, generally perceived as a handle for hair slipperiness and softness, might be counterproductive. For instance, it could be sensible to avoid ultralow friction of shampoos on skin for the sake of practicality as the user might otherwise spill the product during the washing process before it can even be transferred to the head.

Bhushan [13,91] also highlighted that some hair styles for curly hair might actually benefit from a certain degree of hair adhesion. This highlights another challenge that formulators are faced with: one the one hand, the universality of a care product will likely drive its success. On the other hand, more specialized products might be required, also to appeal to regional differences in hair styling preferences and variations in hair damage mechanism among different ethnic groups [74]. Some research has already focused on highlighting more refined regional and ethnic differences in hair structure and surface chemistry, including Brazilian [77] and Mongolian hair [78]. While the industry will likely have to maximize their consumer target groups with their key products, they could also reach new customers by providing functional hair care products with a lubrication performance tailored to specific target groups' needs.

5.3. Nanoarchitectonics

Due to the multiscale nature of hair and the need for new chemistries as well as high-throughput friction screening, it is conceivable that tribological investigations from the nanoscale to the macroscale will be important. Nanoscale experiments and simulations are expected further prove their value in the search for novel and yet unclear lubrication mechanisms. Recently, Guryanov et al. highlighted the potential of nanoarchitectonics of hair [312]. The deposition of lubricants and conditioner molecules by nanomaterials is a promising alternative to the equally complex dilution-deposition mechanism. The deposition of compounds from structures such as vesicles, liposomes or liquid crystals is already used in other cosmeceutical applications [313] and homecare products [314] and to some extent even in hair care [315]. However, the implications of colloidal delivery structures on hair friction are yet to be explored.

5.4. Skin-on-hair friction

The majority of experimental studies in hair tribology have focused on either combing, atomic force microscopy or hair-on-hair friction. Earlier in this work, we reviewed the available literature on hair-skin friction, which is important for quantifying and understanding the mechanisms associated to the tactile perception of hair. Most quantitative studies in this area have been focusing on either *in vivo* or artificial skin macroscopic investigations. Sensory panel tests are likely still required at a later stage of the formulation design process for subjective evaluations of tactile perception [22]. However, they are not ideally suited for the early development stage and identification of mechanistic insights into lubrication. Nanoscale experiments as well as molecular models of hair-skin contacts have not been explored in the literature to the best of the authors' knowledge. This might be due to the multiscale structure, highly non-linear elasticity and high deformability of human skin which is difficult to model at the small scale. Some coarse-grained molecular models of the stratum corneum (SC) of the epidermis in human skin have been developed recently, [316–321] which provide a suitable basis for molecular hair-skin tribology studies. We deem such small-scale models a promising extension to macroscale experiments and/or models from both a mechanistic and formulator's perspective.

5.5. Biomimetic surface experiments

Biomimetic surface experiments lend themselves as a suitable alternative to direct tribological measurements on hair, skin or other soft substrates. Macroscopic hair mimic surfaces imitating the cuticle scale structure for tactile evaluations against skin were used in past hair tribology studies [168,179]. PDMS and polyurethane skin mimics are candidate materials for measuring skin-on-hair friction at macroscopic scales [3,8,168,170,172,180].

Coated AFM tips, [207] bare [150] and monolayer-functionalized mica surfaces and colloidal probes [10,322,323] have already been

used to mimic the surface chemistry of hair at various degrees of chemical damage. Recently, Cozzolino et al. [323] developed biomimetic hair surfaces for considering pristine and fully-damaged F-layers, [322] but most notably also partially damaged F-layers. These intermediate degrees of damage were used to investigate the adsorption of surfactants and polymers. We expect that considering biomimetic models of partially damaged hair could be highly beneficial for tribological purposes such as colloidal probe AFM friction experiments as this typically resembles the real hair surface more closely. A key advantage of using biomimetic surfaces over real hair is the increased control over repeatability and surface roughness. Colloidal probe AFM either with or without chemical functionalization further allows for capturing the soft nature of the hair substrate, as opposed to sharp AFM tips. Further advances in the manufacturing process of such probes is expected to allow for more controllable bulk probe properties and surface roughness features. [284]

5.6. Molecular & multiscale modelling

Molecular models are expected to play an even more important role in hair surface science and care product development. Such models are already capable of capturing nanoscale hair friction under both boundary lubrication [10,97,275] and hydrodynamic lubrication regimes [18]. One challenge in these simulations has been the determination of accurate formulation concentrations for different levels of surface charges and more importantly as a function of the normal load. It is conceivable that the contact thickness and composition will vary depending on the external load. So-called preliminary squeeze-out simulations [272] were introduced to establish a more realistic contact composition for systems containing water and other small molecules confined between two surfaces for a given contact pressure [10,324]. The squeeze-out technique has been applied successfully for hair contacts with water, [10] with ionic surfactants [97] and for systems of hair surfaces with pre-adsorbed larger polyelectrolytes and anionic surfactants [275]. However, the finite simulation system size limitation and the requirement for a large surrounding water bath make this technique computationally expensive for cases in which aggregates are freely distributed in solution or are subjected to partial squeeze-out. An alternative approach to capturing the realistic contact composition for such systems includes the use of grand-canonical molecular dynamics (GCMD) [325–330]. A drawback of GCMD has been its poor computational efficiency, [269] which can limit use of the approach in larger systems and with large molecules. The exchange of entire molecules such as surfactants, let-alone polymers is not expected to be realizable through grand-canonical MD in the near future. However, small and intermediate sized systems are still deemed suitable for enabling squeeze-out in hair and other soft tribological contacts.

We expect coarse-grained models such as MD and DPD to continue to play a fundamental role in hair tribology and hair care formulation design. Both bulk and interfacial simulations will be required. There is already a wide range of existing coarse-grained MD and DPD simulations of surfactants and polymers in bulk and at interfaces [331–359] which are not necessarily related to tribology but could serve as inspiration for tribological modelling. Abdelbar et al. recently provided a review of coarse-grained MD and DPD simulations that have studied the friction polymer brushes [360]. This further supports the suitability of CG molecular models for studying hair friction in the presence of macromolecules. Simulations of organized structures of deposited polymers on hair are yet to be conducted but could help explaining previous observations of enhanced lubrication by adsorbed polymer brushes [200].

A key pathway for improving the accuracy of molecular models and coupling to macroscopic properties and sensory perception is the use of multiscale frameworks. Such approaches have only been employed for hair in a few instances [56,243,245,361] which did not directly

consider tribological properties. One conceivable solution to capturing larger structures of polymer-surfactant complexes on hair would be to couple existing self-consistent field theory (SCFT) calculations, e.g., Ref. [116–118,248] to either all-atom or coarse-grained molecular dynamics. Equilibrium SCFT density profiles could then be used to generate an initial conformation of compounds on hair or in the bulk. Experiment-supported multiscale simulations of kerateneous filaments within the human body [244–246,362] successfully demonstrated the capability to predict tensile properties and observe new structural mechanisms. Recently, atomistic, coarse-grained and finite element method simulations were combined in multi-scale modelling studies on the adhesion of gecko feet [363–369]. The underlying surface chemistry of gecko feet is indeed loosely comparable to that of human hair, so future multi-scale approaches on hair tribology might draw inspiration from these studies. The use of machine learning for rapid force field tuning [368] in surface sciences is a further promising perspective to reducing the computational workload of multi-scale models. Hair multiscale approaches considering mesoscale particle or continuum models could bridge the gap between the nanoscale friction mechanisms and friction mechanisms associated with macroscopic surface roughness features on hair such as cuticle scales and striations. Full hair filament interaction models [233,234] could also be extended to incorporate fibre-fibre friction and adhesion forces obtained from smaller-scale models. Overall, multiscale models are expected to significantly reduce simulation times if computational load can be reduced on the smallest (nanoscale) part of the chain and shifted to the generally faster-performing, although potentially more inaccurate, larger-scale continuum models. Faster models would in fact be highly beneficial to further driving the emergence of high-throughput and virtual screening approaches [240,241] for the development of hair care formulations. [242]

6. Conclusions

Understanding hair tribology is essential to control tactile perception and detangling performance and therefore the success of hair care products. In this work, we discussed the different approaches to quantifying hair tribology with a main focus on friction and adhesion. Hair tribology covers span a wide range of length scales ranging from nanoscale experiments and simulations to macroscopic studies on hair bundles.

Macroscopic hair friction studies are well-suited for high-throughput screening of many different care formulations. We expect that formulators will continue to rely on macroscopic evaluation techniques despite their more qualitative nature. In contrast, the majority of tribological mechanisms on hair are best resolved by resorting to micro- and nanoscale screening techniques such as AFM and more recently computational models. Molecular models are a suitable basis for preliminary screening of hair care formulations with respect to hair tribology and other relevant handles in an integrated approach. They are also suitable for early-stage development of greener as well as previously untested chemistries that are otherwise difficult to synthesize in the laboratory. At the same time, controlling hair friction and sensory perception at the macroscale depends on additional factors like the hair diameter and its distribution, hair morphology and macroscale damage. In reality, hair exists in a ‘complex three-dimensional network’ [3] where a large number of hair-on-hair contacts exist at the same time. The use of multiscale approaches by means of coupling molecular simulations to larger-scale continuum models, experiments or sensory panel tests may ultimately resolve the limit of being able to fully capture macroscopic phenomena with molecular simulations [269]. Integrated multiscale approaches could ultimately connect macroscopic handles such as hair fineness, roughness and slipperiness to the respective tribological mechanisms from the nano- to the mesoscale.

Some hair friction mechanisms are also not yet fully understood. This includes the relative importance of surface roughness and surface

chemistry as well as the lubrication mechanism of polymer-surfactant complexes on hair. Recent nanoscale experiments and simulations seem to suggest that surface chemistry can account for the majority of the increase in hair friction when chemically damaging the hair. It is expected that both small-scale experiments and numerical studies will contribute to shed light on these areas. The authors deem it essential to couple these small-scale methods to the larger length scales to inform on how certain mechanisms translate to both hair entanglement and sensory perception.

CRedit authorship contribution statement

Erik Weiland: Writing – original draft, Methodology, Data curation, Conceptualization. **Francisco Rodríguez-Ropero:** Writing – review & editing, Project administration. **Yuri Roiter:** Writing – review & editing, Methodology, Data curation. **Stefano Angioletti-Uberti:** Writing – review & editing, Supervision. **Daniele Dini:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition. **James P. Ewen:** Writing – review & editing, Supervision.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

No data was used for the research described in the article.

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