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Micro- and nano-fluidics around HAB cells

The *RheFFO** Working Group

*Rheology, micro/nanoFluidics and bioFouling in the Oceans

*Ian R. Jenkinson^{1,2}, Elisa Berdalet³, Wie-Chun Chin⁴, Stephan Herminghaus⁵, Sophie Leterme⁶, James G. Mitchell⁶, Michael Orchard⁷, Ri Qiu⁸, Laurent Seuront⁹, Peng Wang¹⁰, Tim Wyatt¹¹ and Li Zhuo¹²

¹Chinese Academy of Sciences Institute of Oceanology, Key Laboratory of Marine Ecology and Environmental Sciences, 7, Nanhai Road, Qingdao, P.R. China, ianjenkinson@qdio.ac.cn, ² Agency for Consultation and Research in Oceanography, Lavergne, La Roche Canillac, France, ³Institut de Ciències del Mar (CSIC). Pg. Marítim de la Barceloneta, 37-49. Barcelona, Catalunya, Spain, ⁴School of Engineering, University of California, Merced, USA, ⁵Max Planck Institute of Dynamics and Self-Organization, Dept. Dynamics of Complex Fluids, Göttingen, Germany, ⁶ School of Biological Sciences, University of Flinders, Adelaide, South Australia, ⁷Department of Physical Ecology, University of Lincoln, UK, ⁸State Key Laboratory for Marine Corrosion and Protection, Luoyang Ship Material Research Institute, Qingdao, P.R. China, ⁹ Centre National de la Recherche Scientifique, Laboratoire d'Océanologie et de Géosciences, Université de Sciences et de Technologies de Lille, Station Marine, Wimereux, France, ¹⁰Chinese Academy of Science Institute of Oceanology, Key Laboratory for Marine Corrosion and Biofouling, Qingdao, P.R. China, ¹¹CSIC, Institut de Investigaciones marinas, Vigo, Galicia, Spain, ¹²Tongji University, College of Environmental Science & Engineering, Shanghai, P.R. China.

Abstract

Have you ever wondered how algae stay so clean? Most flowering-plant leaves also stay clean. Under air, films of water and “dirt” are repelled. Repulsion forces the water into droplets that easily roll off because these leaves are covered in hydrophobic nm- to μm - sized grooves and pillars, producing superhydrophobicity (SH) at the surface. Similarly, most algal cells bear a glycocalyx of organic fibrils that give surface structure, and are often hydrophobic. Glycocalyxes serve many functions, but whether they produce SH is poorly known. SH coatings are being developed to prevent fouling of ships and aquaculture structures without using toxins, so this technology could help understand how algae defeat fouling. Glycocalyxes are composed of exopolymeric secretions (EPS), and algae sometimes make the water more viscous using this tightly and more loosely bound EPS. EPS is also sometimes sticky. SH cuticles on copepods may change ambient fluid microdynamics by allowing slip at their surfaces, and facilitate filter feeding. By managing ambient viscosity and surface properties including slipping and sticking, algae may have the tools to engineer ambient fluidics and stay clean and unfouled.

Bioengineering of viscosity and local flow by plankton

Previous studies have shown that the viscosity of ocean water is composed of a Newtonian component due to water and salt plus a non-Newtonian one due mainly to phytoplankton as well as bacteria. Such changes have been measured at mm to cm scales (Jenkinson and Sun, 2010; Seuront et al., 2010). The exceptionally large biomasses and surface areas associated with cells and associated exopolymeric substances (EPS) in some HABs may give HAB species more potential, through quorum action, for management (bioengineering) of physical oceanographic and dispersion processes (Jenkinson and Wyatt, 1995), and may also

provide an environment where they are easier to measure *in situ*.

Micro- and nanoscale fluidics around HAB and other algal cells are important in models of secretion and uptake (Mitchell *et al.*, 1985, 2013; Lazier and Mann, 1989). By managing of ambient viscosity as well as surface properties such as slipping and sticking, algae may have the tools to engineer ambient fluidics, distributions of processes involving substances such as nutrients and allelopathic substances, and stay clean and free of fouling.

The remainder of this communication concerns possible bioengineering of processes only nm to mm from plankton cell surfaces.

Wall slip

The notion of wall-slip, slipping of a sheared fluid at a wall (Fig. 1), was introduced by Navier (1823). Yet for over a century engineering manuals and physics textbooks taught “no-slip” as a quasi-universal premise for practical models of hydrodynamics (Jenkinson 2014). In the last 10-20 years, with the surge in machines, such as lab-on-a-chip, that incorporate microcapillary flow the idea of “no-slip” between liquid and solid surfaces has once again come to be regarded as “no more than a convenient approximation” (Rothstein 2010).

repelled water and “dirt”. Size of photo ~10 cm. Photo: Ian Jenkinson.

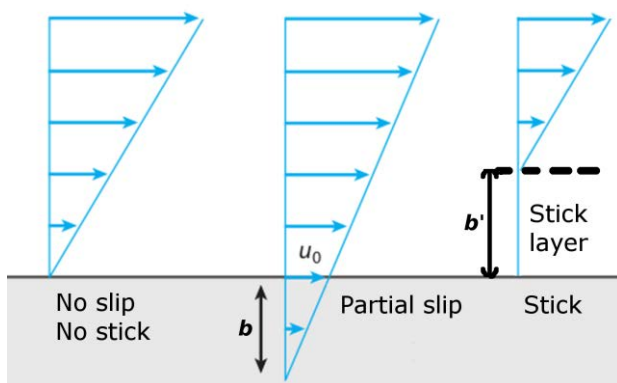


Fig. 1. Diagram of slipping and sticking and fluid-shearing at a solid interface. b is slip length; b' is sticking length; u_0 is slip velocity. b can range from nanometres to micrometres, or occasionally millimetres. Modified from Rothstein (2010).



Fig. 2. Lotus (water lily) leaf showing

The purity of the sacred lotus and plankton: slip layers, self-cleaning and anti-fouling,

Lotus leaves remain “pure”, or dry and clean, because their leaf surfaces are superhydrophobic (SH) and therefore repel water and “dirt” (Fig. 2) (Barthlott and Neinhuis 1997; Thielicke, 2015). Hydrophobic surfaces can be SH when they bear in addition nano- or micro-sculpturing (Rothstein, 2010; Koch *et al.* 2009). On many terrestrial plant leaves, SH is produced by a wax-covered surface in the form of grooves or pillars (Fig 3). This principle has recently been incorporated into products such as: non-stick frying pans; dirt-repelling household wiping cloths; “green” (i.e. non-toxic) anti-biofouling, slippery surfaces for ships and structures used in aquaculture.

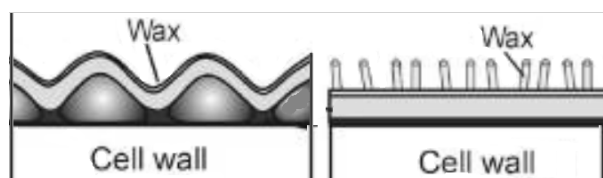


Fig. 3. Sketch of the origin of SH on leaves of flowering plants. Left – leaf with grooves; Right – micropillars. Adapted from Koch *et al.* (2009).

Anti-biofouling surfaces

Like the self-cleaning lotus leaves, many aquatic algae remain remarkably clean of “dirt”, as well as of fouling organisms. While secretion by algae of mucus can reduce fouling (Boney, 1981), the surfaces of many clean algae appear devoid of mucus. At μm scale many phytoplankton cells bear sculptured surfaces either when bare (Figs. 4, 5) or when covered with exopolymeric secretions (EPS) (Fig. 6), whether tightly bound as a glycocalyx or more loosely bound. Most algal and bacterial cells bear a glycocalyx of organic fibrils that give surface structure, and are often hydrophobic. Glycocalyxes serve many functions, but whether they produce SH is poorly known.

Associated with the progressive banning of toxic antifouling paints, there is much research into producing long-lasting anti-fouling and anti-corrosion SH coatings (Yang *et al.*, 2015). Research in this field is benefiting from mimicking the surfaces of organisms. In return, research on fouling and antifouling by plankton can be inspired by such industrial research. The potential exists for collaboration between

researchers on industrial antifouling coatings and those working on both fouling and antifouling by plankton organisms.

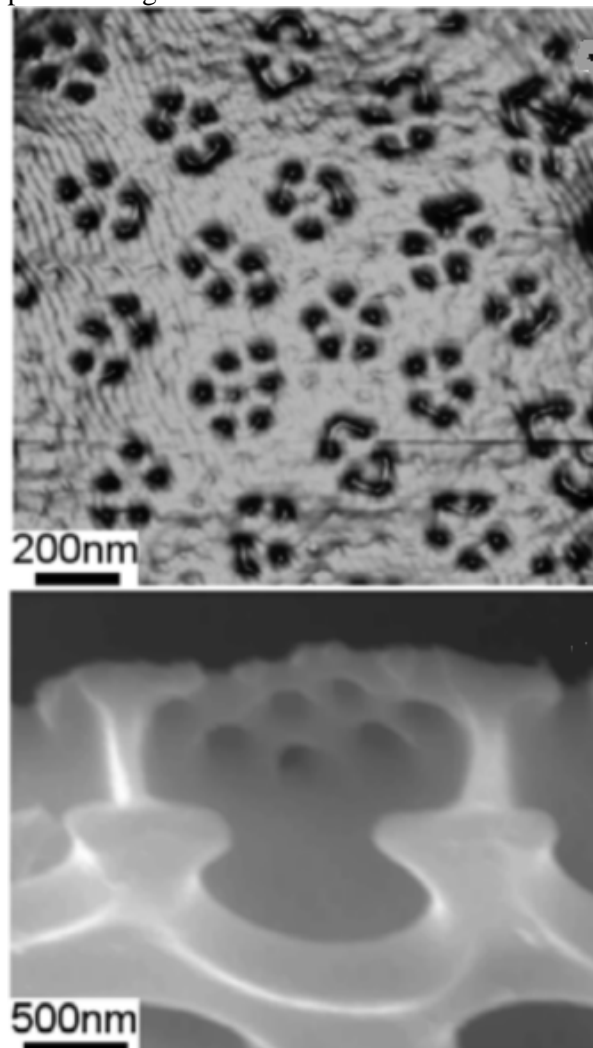


Fig. 4. Scanning electron micrograph (SEM) of detail of diatom valve Upper – *Coscinodiscus sp.*; lower – *Thalassiosira eccentrica*. Modified from Mitchell (2013).

Slippery liquid-infused porous surfaces (SLIPS)

SLIPS are SH surfaces in which the interstices between the sculptures (c.f. Fig. 3) are filled with a fluid, different from the overlying one, that is either locked in place, or constantly replaced, e.g. by secretion through pores, or both (Wong *et al.*, 2011). SLIPS can be omniphobic, that is repellent to both and hydrophilic objects, slippery and are self-cleaning. In many phyla of HAB and other algae, the potential seems available for renewal of

such fluid through pores between sculpturing. It should be investigated whether some HAB algae and protists may bear SLIPS that could modulate hydrodynamics and biofouling.

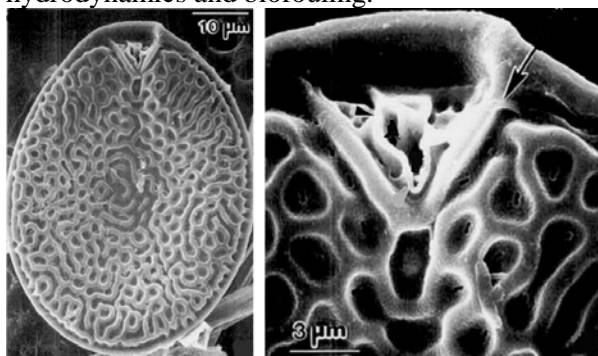


Fig. 5. SEM of the dinoflagellate *Prorocentrum reticulatum*. 55-60 x 40-45 μm. Note sculpture at different scales. Arrow (right) shows a bacterium. Detail from Faust (1997).

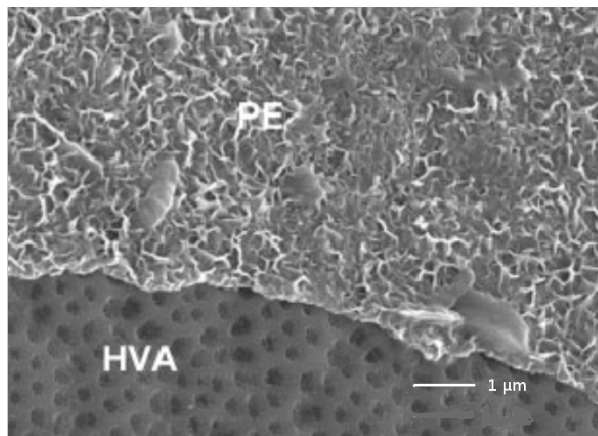


Fig. 6. SEM of *Coscinodiscus perforatus* cell to show hypovalve areolation (HVA) and overlying perfrustular envelope (PE). Reworked detail from Beninger and Decottignies (2009).

Copepods as predators of algae: their surfaces

Copepods are important in controlling HAB and other algae. However, HAB species may benefit from being able to defeat such predation. Like lotus leaves, copepods are believed to have waxy cuticles, often with surface sculpturing. Copepod feeding appendages bear two rows of setules typically 2 to 10 μm apart (Marshall and Orr, 1966) (Fig. 7). Whether these setules are used to filter phytoplankton is much debated, as observations of feeding, that apparently included filter feeding (Paffenhöfer *et al.*, 1982) have been challenged by hydrodynamic models (Jørgensen, 1983) with which it has been difficult to reconcile

observations. The models have all used the no-slip assumption, however. New observations using better optics and higher-speed video have led to the total absence of filter-feeding being re-questioned (Kiørboe, 2011). A slip length at the surface of setules of 1 μm or more may allow hydrodynamic models to be reconciled with filter feeding, which needs to be investigated, with and without viscosity changed by more-or-less sticky algal mucus.

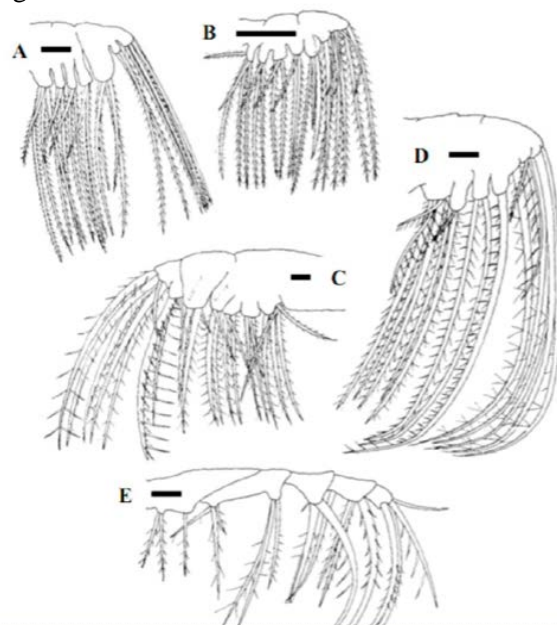


Fig. 7. Copepod feeding appendages, to show setae and setules. A – *Pseudocalanus*; B- *Temora*; C – *Centropages*; D – *Acartia*; E – *Oithona*. Scale bars – 20 μm. Modified from Marshall and Orr (1966). Reproduced with kind permission.

The RheFFO Working Group

RheFFO stands for Rheology, micro/nanoFluidics and bioFouling in the Oceans. The aim of the working group (WG) is to associate a corpus of researchers in the physical and biological ocean sciences, rheology, surface science and fouling/antifouling research, development and innovation. Harmful algae are a key part of it. It brings together science in modelling the environment with innovation of commercial products. Interested scientists may ask to join, or just associate, with this WG.

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