CH-242(b) - Part 1
Lecture 1 - Surface Tension

Resources:

- *surface tension*
  - Butt et al., *Physics and Chemistry of Interfaces*, third (2013) edition, chapter 2
- *capillary action*
  - *PIC*, section 6.2.1

Summary

- *surface tension*
  - The interface between two phases is under a state of tension, characterized by a quantity γ termed the *surface tension.* Surface tension can be intepreted as a force per unit length, or an energy per unit area.
  - The phenomenon of surface tension originates from intermolecular interactions. Highly cohesive materials for example will form interfaces with the air characterised by relatively large surface tensions. Addition of surfactant molecules to a liquid will on the other hand act to reduce its surface tension.
- *Laplace pressure and the Young-Laplace equation*
  - There exists across a curved interface a pressure difference ΔP arising from surface tension. For the special case of a spherical interface of radius R we have
    $$\Delta P = 2\gamma/R$$
- *capillary action*
  - There is a length scale κ, given by
    $$\kappa = \sqrt{\frac{\gamma}{\rho g}}$$
    where the effects of surface tension and gravity are of roughly comparable importance.

  - The rise of fluid h in a capillary is related to the radius of curvature R of the meniscus formed in the capillary by the relation

$$h = -2\kappa^2/R$$

- *Kelvin equation*
  - Evaporation at a curved gas-liquid interface of radius of curvature R is characterized by a vapor pressure P'_o where

$$P'_o = P_o e^{R_o/R}$$

where

$$R_o = \frac{2\gamma V_m}{\bar{R}T}$$

where V_m is the molar volume of the liquid phase, T is the absolute temperature, and $\bar{R}$ is the universal gas constant.

  - The dependence of vapor pressure on interfacial curvature has a bearing on the phenomena of capillary condensation and nucleation of condensed phases.

1 Prelude - Heterogeneous Catalysis and Gas-Surface Dynamics

Surface (or interfacial) chemistry is a multi-disciplinary field and my own particular background is more physics-oriented. My doctoral research and my current (postdoctoral) research is in a subfield of surface chemistry known as "gas-surface dynamics"[1]. In this subfield we aim for a microscopic understanding of the mechanisms underlying chemical reactions at occuring at the solid/gas interface.

For example, we recently completed a study[2] investigating the correlation between

- the catalytic activity of a metal surface (in particular, nickel and gold) and
- the flow of energy among the different vibrational modes of a methane (CH_4) molecule induced by a collision between the molecule and the surface.

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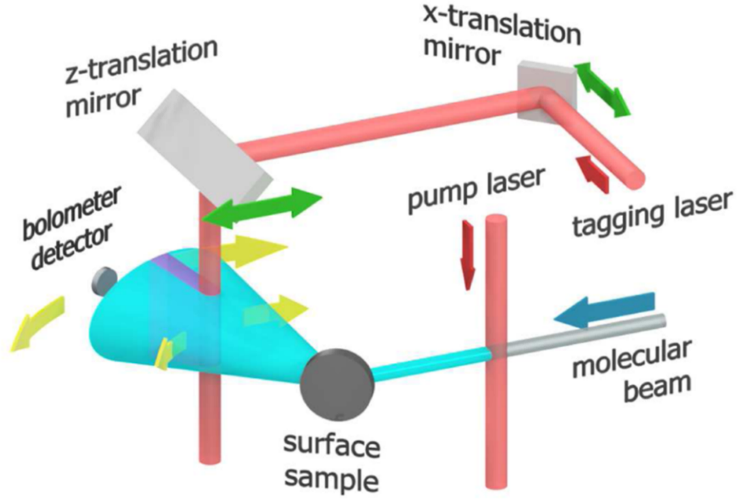
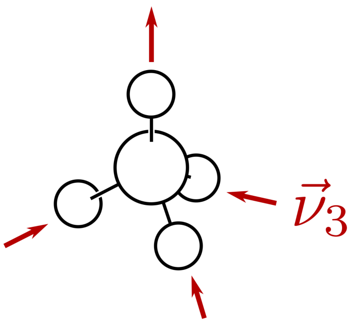
[1] For a nice broad introductory textbook on the topic, see Kolasinski, Kurt W. *Surface Science: Foundations of Catalysis and Nanoscience.* Fourth edition. Hoboken, NJ, USA: Wiley, 2020.

[2] Floß P, Reilly CS, Auerbach DJ, Beck RD. Surface-induced vibrational energy redistribution in methane/surface scattering depends on catalytic activity. Front Chem. 2023 Jul 25;11:1238711. doi: 10.3389/fchem.2023.1238711

To experimentally investigate this correlation, we prepared a beam of methane molecules that are on a collision course with a metal surface. Let's refer the following experimental diagram[3] for reference:



Before the molecules collided with the surface, we excited them using infrared-laser radiation ("pump laser" in the diagram) so that they then all had one quanta of "ν_3" anti-symmetric stretching motion, which looks like this:



with one C-H bond oscillating out-of-phase with the other three. After the molecules collided with the surface, there was a possibility that their quantum of ν_3 vibration was converted via forces exerted on the molecule by the metal surface atoms into one quanta of "ν_1" symmetric stretching vibration:

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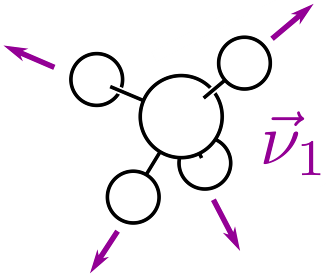
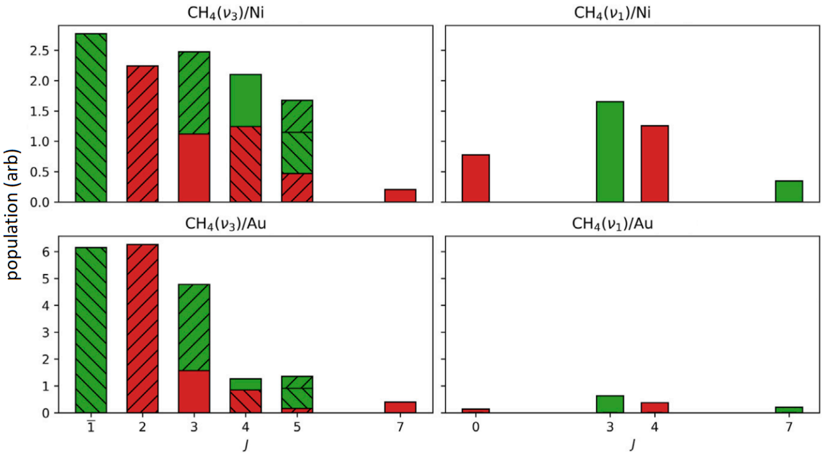
[3] Christopher S. Reilly, Patrick Floß, Bo-Jung Chen, Daniel J. Auerbach, Rainer D. Beck; Quantum state-resolved methane scattering from Ni(111) and NiO(111) by bolometer infrared laser tagging: The effect of surface oxidation. J. Chem. Phys. 7 June 2023; 158 (21): 214202. https://doi.org/10.1063/5.0150009



which has all four C-H bonds oscillating in-phase. Using a second infrared-laser ("tagging laser") in combination with a sensitive "bolometer detector", we can measure the populations of the different quantum states of the scattered molecules and thus the probability that the surface-molecule collision caused a $\nu_3 \rightarrow \nu_1$ conversion of vibrational energy. When we measured the populations over the different rovibrational states, we found a striking change in the distributions when changing the surface from nickel (Ni) to gold (Au):



Every bar plotted corresponds to the measured population of a specific rotational quantum state with one quanta of either ν_1 or ν_3 vibration. The label J indicates the rotational energy of the state, and the different shadings give further information that does not concern us here. What we want to notice rather is how weakly populated the all the ν_1 levels are after scattering from the gold surface (bottom right) compared to their populations obtained after scattering from nickel (top right). Summing up all different rotational levels associated with a specific vibrational mode, we found that molecules scattering from the nickel surface were more than ***7 times*** more likely to undergo $\nu_3 \rightarrow \nu_1$ conversion than those scattering from gold!

What is the relevant property of these surfaces that explains this stark difference in scattering behavior? Physically the surfaces share much in common, both being metals and possessing identical crystallographic surface structure. One physical difference is that the gold atoms are in fact much heavier than the nickel atoms, though this difference if anything would be expected to *promote* distortion of the CH_4 molecular motion, in the same way that a skiier is more likely to be injured colliding with a big tree than with another skiier. The surfaces however differ considerably in their *chemical* properties, and we attributed the relative effectiveness of nickel in accomplishing $\nu_3 \rightarrow \nu_1$ conversion to its status as a *catalyst* for methane "activation", i.e. dissociation $CH_4 \rightarrow CH_3 + H$.

Nickel is considered a catalyst for methane activation in the sense that the rate of methane dissociation is considerably greater in the presence of a nickel surface than it is in its absence or in the presence of a surface that is less catalytically active. On the microscopic scale, catalytic activity is related to the "activation energy" required to stretch and distort the bond sufficiently to permit bond breaking. For methane dissociation in the gas phase, this activation energy is simply the C-H bond energy, equal to 4.3 eV. At a nickel surface this energetic barrier to dissociation is just 1.1 eV, while for gold it is almost double this (1.9 eV).

In a very rough sense we can explain catalytic activity by the formation of bonds between the relatively reactive atoms of the metal surface and the reacting molecule. Electrons normally participating in the formation of *intra*molecular bonds (C-H bonds in the case of methane) are recruited for the formation of *inter*molecular bonds between the molecule and the surface, thus weakening the intramolecular bonds and reducing the energy required for their dissociation. Since the ν_1 and ν_3 vibrations differ only by the relative phase of the individual C-H bond vibrations, it is then reasonable to suppose that the greater temporary weakening of a methane C-H bond (or, equivalently, reduction in its vibrational frequency) during a collision with the more catalytically active nickel surface will more effectively induce the phase-shift required for $\nu_3 \rightarrow \nu_1$ conversion. This phenomenon of collisionly-induced transfer of energy among the different modes of a polyatomic molecule serve in this sense as a kind of probe of a surface's catalytic activity.

While such experiments revealing the reflection of macroscopic chemical properties (catalytic activity) in detailed microscopic effects in molecular scattering behavior ($\nu_3 \rightarrow \nu_1$ conversion) are interesting (to me, at least), they also serve a more practical purpose of furthering our understanding of heterogeneous catalysis, i.e. of reactions catalysed by catalysts whose phase (i.e. gas, liquid, or solid) differs from that of the reactants/products. Heterogeneous catalysis is a subject with a significant impact on modern life, whether we consider the catalytic converters which eliminate harmful pollutants from car exhaust or the iron-catalysed Haber-Bosch process $N_2 + 3H_2 \longrightarrow 2NH_3$ producing the ammonia responsible for half the world's fertilizer[4]. High quality data from experiments studying interactions between molecules and surfaces are essential for the im-

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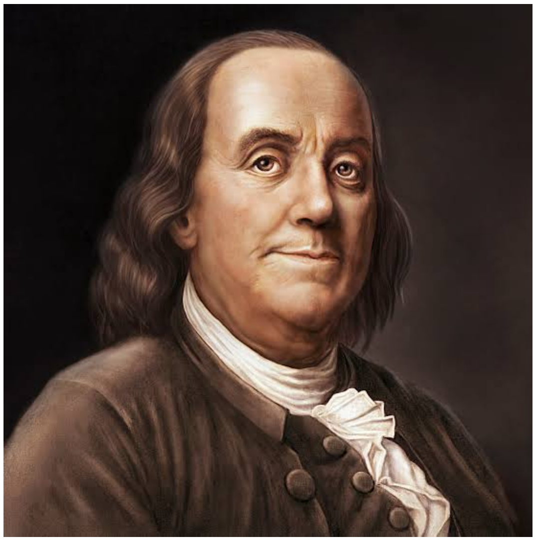
[4] Smil, V., "Enriching the Earth – Fritz Haber, Carl Bosch, and the Transformation of World Food Production," The MIT Press, Cambridge, MA (Dec. 2000)

provement and refinement of theoretical models used for the discovery of better catalysts[5].

2 Surface Tension

2.1 Introduction

The subject of surface tension, primary to the field of interfacial chemistry, we begin as one best begins any subject – that is, with a bit of American history:



Benjamin Franklin, immortalized in contemporary American music thanks to the $100 bill containing his likeness, was – in addition to businessman, philosopher, and politician – also an accomplished scientist. You might recall the famous “kite-key experiment”[6] where Franklin flew a kite with a key attached during a storm to demonstrate the equivalence of lightning and electricity.

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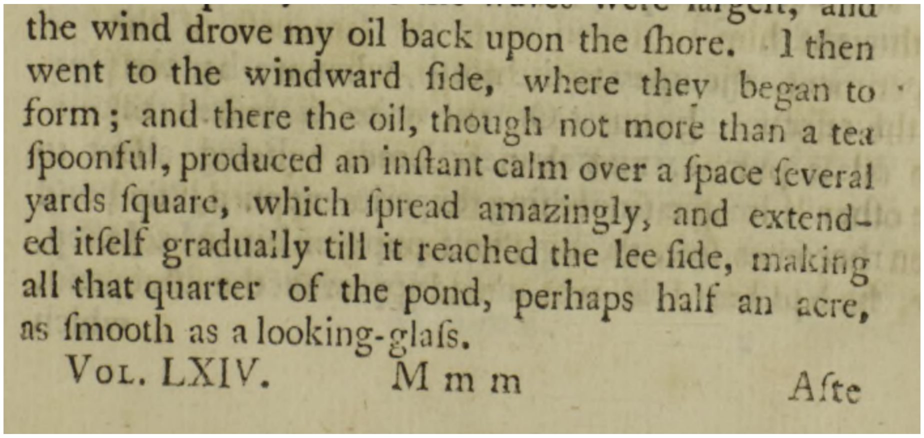
[5] C.H. Christensen and J.K. Nørskov *J. Chem. Phys.* **128**, 182503 (2008)

[6] Benjamin Franklin, *The Autobiography of Benjamin Franklin*, www.gutenberg.org/files/20203/20203-h/20203-h.htm

Franklin turns out to also have been among the first to study in a (relatively) systematic fashion the phenomenon of surface tension. Having during his trans-Atlantic voyages observed the "calming effect" of cooking oil dumped overboard on the amplitude of the sea waves, he attempted to reproduce the effect under more controlled conditions on a small pond in Clapham (London, England). Have a look at the following extract[7], where Franklin describes what happens upon placing a teaspoon ($5\,\mathrm{cm}^3$). Watch out for the old-English "long s", which is easily confused with the letter 'f':



the wind drove my oil back upon the ſhore. I then went to the windward ſide, where they began to form; and there the oil, though not more than a tea ſpoonful, produced an inſtant calm over a ſpace ſeveral yards ſquare, which ſpread amazingly, and extended itſelf gradually till it reached the lee ſide, making all that quarter of the pond, perhaps half an acre, as ſmooth as a looking-glaſs.

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See the following Youtube demo for an (even smaller-scale) reproduction of the experiment, where soap is used in lieu of oil. A couple questions immediately come to mind:

- What is responsable for this "amazing" spread of the oil across the pond surface?
- How thin is the resulting layer of oil?

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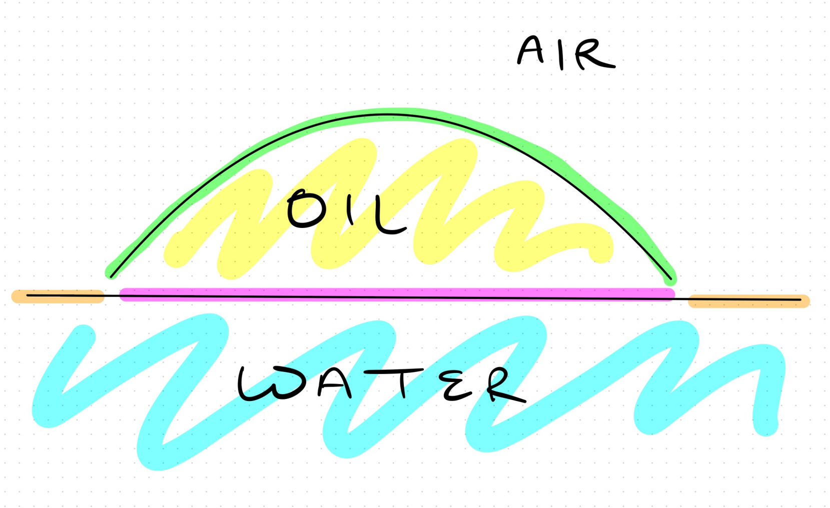
[7] Franklin et al. "Of the stilling of waves by means of oil." *Phil. Trans. R. Soc.* **64** 445–460 http://doi.org/10.1098/rstl.1774.0044

The second question is easier. Taking into account that $1\,\text{acre} \approx 4 \times 10^3\,\text{m}^2$ we have

$$t = \frac{V}{A} = \frac{5\,\text{cm}^3}{0.5 \times 4 \times 10^7\,\text{cm}^2} \approx 25\,\text{Å}$$

which is on the same order as the length of a molecule in oil, which is composed of hydrocarbon chains composed of on average ten or so carbon-carbon links of length 1.5 Å. We find then that Franklin's experiment quite likely produced a single "monolayer" of oil molecules on the pond surface, making him one of the world's first nano-scientists!

Let's turn now to the first question: what is responsable for this remarkable "spreading force" which causes the oil layer to stretch itself to atomic thinness? We limit ourselves for the moment to the following somewhat "hand-waving" argument, putting off more rigorous discussion for later. Refer to the following diagram:



The spreading of oil on the surface of water is driven by the general (ultimately thermodynamic) tendancy for the chemical systems to minimize their energy, just as energetic reactants are driven to form more stable products. Now in our case the only relevant changes to the system occurring during spreading[8] are:

- the increases in surface areas of
  - the oil-water interface (shown in purple), and
  - the oil-air interface (shown in green), as well as
- the decrease in the surface area of the water-air interface (shown in orange).

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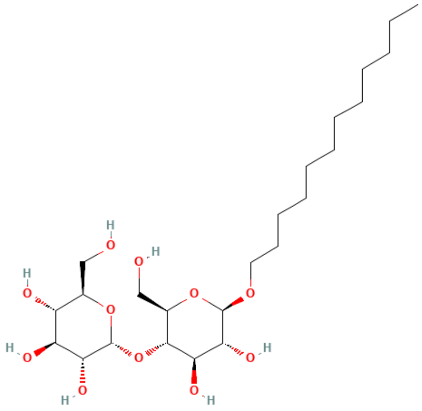
[8] we ignore here the effect of gravity, which is relatively weak in this scenario

The fact that the oil drop spreads quickly indicates therefore that the increase in energy occasioned by the increase in the oil-air interface is more than compensated by energy reduction occasioned by the replacement of water-air interfacial area by the oil-water interface.

Can we rationalize this spreading-induced energetic stabilization (i.e. energetic decrease) in chemical terms? At first glance, your intuition may tell you that such a decrease is not necessarily expected. After all, the non-polar saturated hydrocarbons making up the oil molecules are not expected to form strong bonds with the polar water molecules, so the oil-water interface should hardly be any more stable than the air-water interface. In fact, your intuition is sound: *pure* oils will **not** spread across a water surface[9]. However, all naturally obtained oils will contain to some degree various impurities. Some of these impurities will, for example, be polar and can form intermolecular bonds with the water molecules at the oil-air interface through strong polar interactions. If we add, for instance, some (polar) dodecyl-β-D-maltoside molecules to the oil:



Then our diagram becomes:

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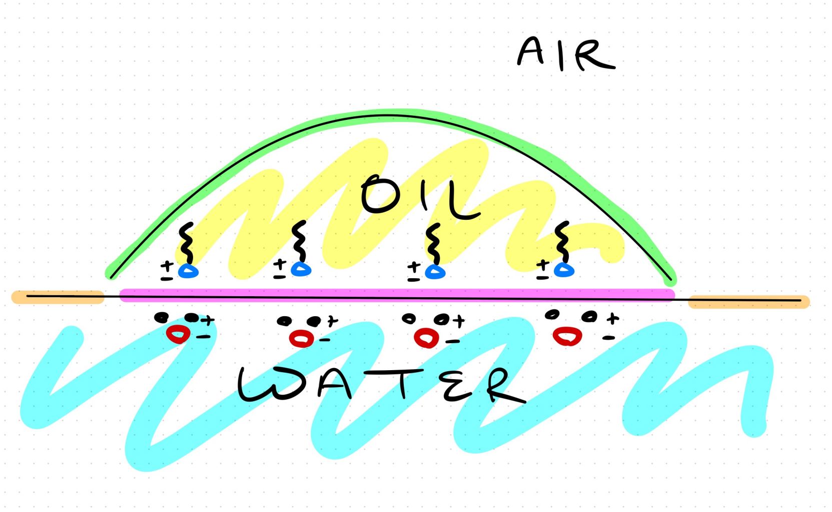
[9] Camp DW, Berg JC. The spreading of oil on water in the surface-tension regime. Journal of Fluid Mechanics. 1987;184:445-462. doi:10.1017/S0022112087002969

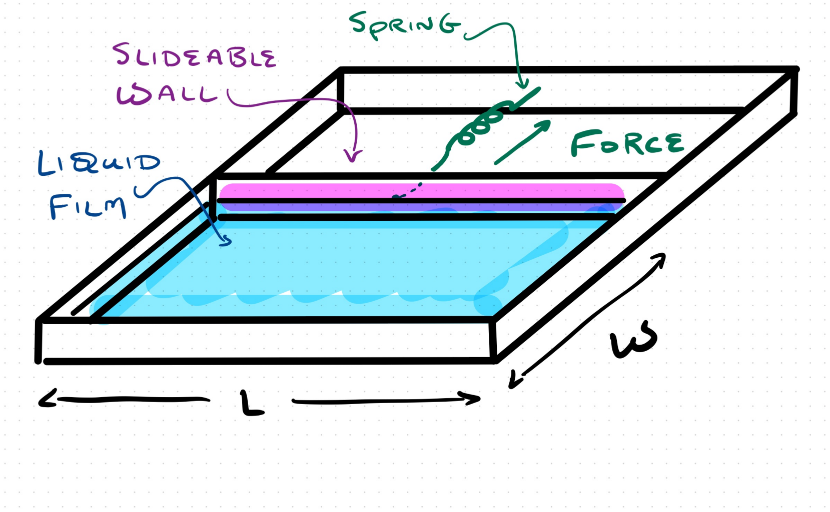


with the blue circles representing the polar head of the molecule. The addition of these molecules now presents the opportunity for strong intermolecular bonding at the oil-water interface, an opportunity not present for the water molecules at the water-air interface. The oil-water interface is thus energetically more stable than the water-air interface, and with sufficient concentration of solute this increased stability is enough to overcome the (rather weak) energy penalty associated with the growth of the oil-air interface, leading to spreading. Solutes that contribute to an increase of this spreading force are termed *surfacants*, which is a shorthand for “surface-active agent”.

2.2 Definition of surface tension

2.2.1 Force definition

As you probably have guessed, the driving force underlying the spreading of the (contaminated!) oil drop on the water surface is associated with the concept of *surface tension*. To define precisely what is meant by surface tension, we make reference to the following experimental arrangement:



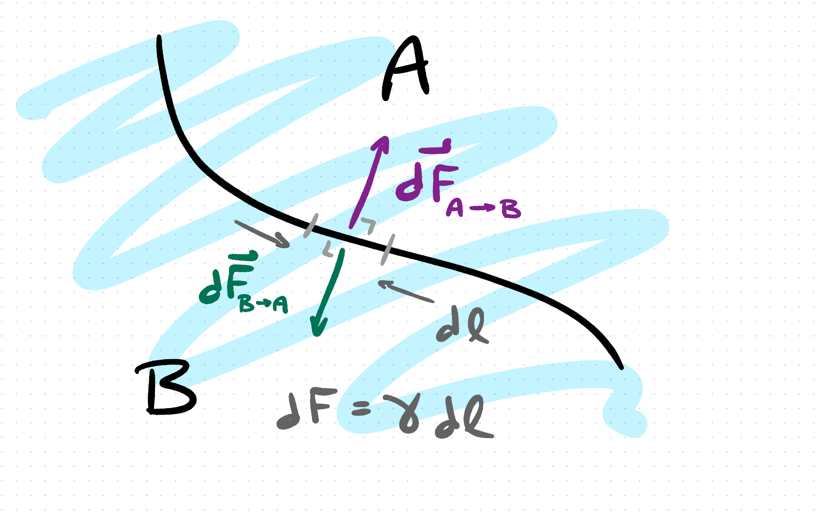
We have a very thin free-standing liquid film which spans four walls, one of which can slide freely and to which we have attached from the other end a spring. We assume that the experiment is performed in low-gravity so that we can ignore the weight of the liquid film. In equilibrium we will find that the spring is *stretched*, so that a finite force F is required to prevent the film from shrinking (i.e. to prevent a decrease in the dimension W). If you don't believe me, I refer you to the following Youtube demonstration. Repeating this experiment for different geometries, we observe that, for sufficently thin films, the force F required to stabilize the film:

- is indepedent of the width W of the liquid film,
- is indepedent of the film thickness,
- is proportional to the length L of the film, and
- depends on the *chemical composition* of the film. In particular, F is sensitive to the addition of small quantities of surfactant molecules.

to explain these observations, we advance the following general hypothesis:

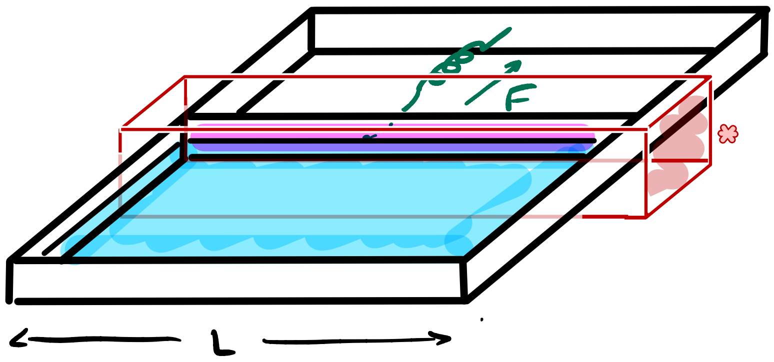
> An interface is under a state of *tension* in the sense that for some short virtual line segment $d\vec{l}$ of length dl lying on the interface there will be a force $d\vec{F}$ exerted by the surface on one side of $d\vec{l}$ on the surface on the other side. The direction of the force $d\vec{F}$ is parallel to interface and perpendicular to $d\vec{l}$ and pointing toward the side exerting the force. The magnitude $|d\vec{F}| = \gamma dl$ of the force is proportional to dl with a proportionality constant γ called the *surface tension* which is a property of the interface.

This somewhat abstract definition, graphically summarized in the diagram below, will become clearer after working through some examples.



The vector $\vec{dF}_{A\to B}$ refers to the force exerted by side A on side B, and vice-versa.

As a first application, we can calculate the spring force F required to hold the liquid film in place in our experiment. To do this, we construct a virtual surface that is indicated by the red cage in the diagram below:



Our task is to determine the forces acting on the volume enclosed by the red cage. As we continue to ignore gravity, there is no external forces acting on in the interior of the volume. There are certainly forces due to the pressure exerted on the faces of the volume, but the forces from opposite faces will cancel[10]. We

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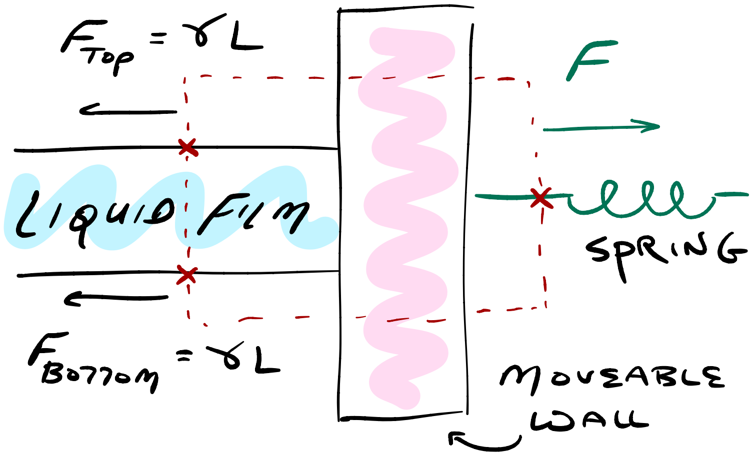
[10] You might object that, as a result of the surface tension, it is possible that the pressure

have therefore only to analyze the forces due to surface tension of the liquid film and the spring. Let's look from the perspective looking from the face shaded in light red and marked with an asterisk (*):



Our virtual surface cuts a line of length L (going into/out of the page in the above perspective) across the top and bottom surfaces of the liquid film (marked by the two red Xs on the left). Consider the line cutting across the top side of the film. For each small segment dl of the line, there is a force γdl applied by the fluid outside of the virtual volume on the fluid inside the volume. The forces all point towards the left (the fluid outside the volume "pulls" the fluid from inside the volume) so that, summing together all the small segments we obtain a force $F_{\text{top}} = \int_0^L \gamma dl = \gamma L$ due to surface tension of the top of the film, acting to the left. The force F_{bottom} is similarly γL, so that together they exert a force on our virtual volume equal to $2\gamma L$. At equilibrium this force is equal to the force F exerted by the tension due to the spring attached to the movable wall.

2.2.2 Energy definition

In our discussion on the spreading of the oil drop, we attributed the driving force of spreading to a tendancy towards lower system energies. In the previous section we quantified this driving force in terms of the surface tension γ associated with the interface. Can surface tension similarly be related to changes in system energy? Indeed it can:

> The work dW required to increase the surface area of an interface by some amount dA is equal γdA.

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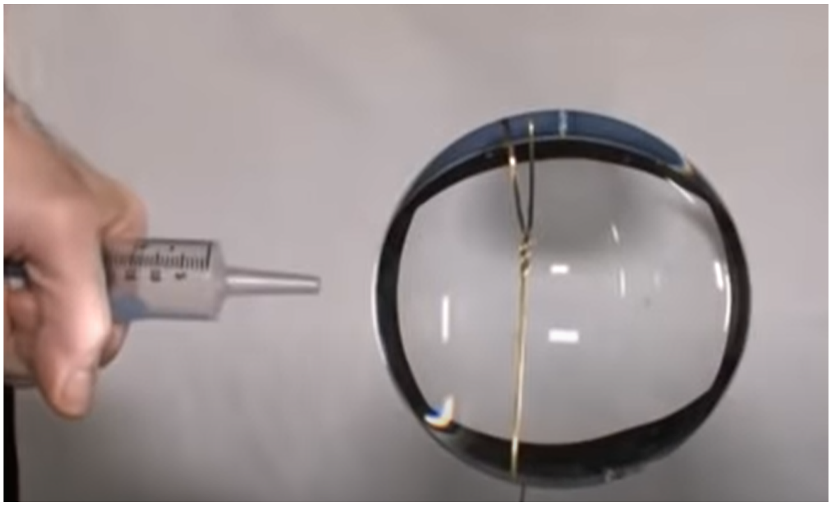
inside the liquid film may be larger or smaller than the ambient pressure. We will see later that the pressure difference across an interface is proportional to the *curvature* of the interface. Since the liquid film is *flat*, there pressure inside the liquid film is equal to the ambient pressure.

To see that this defintion is consistent with the force-based definition given in the previous subsection, we refer again back to the experimental arrangement with the sliding wall, except now replacing the force applied by the spring with an applied force $F = 2\gamma L$ required to oppose the force due to surface tension. We then increase the applied force by a tiny amount δF to $F' = F + \delta F$, so that the sliding wall is able to move in the direction of the applied force by a distance dx before we reduce the applied force back to the F and the movement stops. The change in area dA occasioned by the operation, taking into account both the top and bottom surfaces of the liquid film, is $2 \times Ldx$. The operation required a quantity of work $dW' = F'dx$ from the applied force. The minimum work dW required to stretch the film is we thus find is $\lim_{\delta F \to 0} dW' = Fdx = 2\gamma Ldx = \gamma dA$, consistent with answer one obtains using the alternative, energy-based definition of surface tension. The extra energy $\delta W' = \delta F dx$ is evidently transferred to the system as heat.

From the energy-based definition of surface tension it is immediately clear that, in the absence of gravity, an isolated quantity of liquid will, in its evolution towards its lowest energy state, tends towards the shape of a sphere, this being the shape with minimal surface area for a fixed volume. Here is a screen cap of a Youtube video showing large glob of water up in space (human hand for scale):



Surface tension also explains the more familiar phenomenon of soap bubbles forming nearly perfect spheres. Because bubbles are so thin, their surface-area-to-volume ratio of the bubble is very large so we can neglect the influence of gravity. Mathematically we have that the shape minimizing the total surface area of a volume enclosing another volume is a hollow sphere[11], so the lowest

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[11] Sullivan, J.M. (2012). Pleasing Shapes for Topological Objects. In: Bruter, C. (eds) Mathematics and Modern Art. Springer Proceedings in Mathematics, vol 18. Springer, Berlin, Heidelberg. https://doi.org/10.1007/978-3-642-24497-1_13

energy shape of a soap bubble, i.e. a fixed volume of soapy water enclosing some fixed volume of air, should be a hollow sphere. Of course, a *much* lower energy configuration for the fixed volume of soapy water would be a much tinier *solid* sphere, but to access this configuration one would need to "pop" the bubble, i.e. create an opening, which requires some "activation energy" to accomplish. In this sense the shape of a soap bubble is "topologically protected"!

2.2.3 Microscopic origin of surface tension

Simply put, surface tension is the result of breaking of intermolecular bonds that necessarily occurs when a molecule is transferred from the bulk to the surface. We explain this idea further using liquid water as an example. Imagine that we "cut" a volume of water in half, forming two surfaces. What is the ratio $\Delta E/\Delta A$ of

- the energy increase ΔE due to broken hydrogen bonds incurred in creating these two sufaces to
- the surface area ΔA created,

and how does it compare to the known value of the surface tension of the water-air interface $\gamma_{\mathrm{H_2O}} = 72\,\mathrm{mN\,m^{-1}}$?

Before we cut the surface, each water molecule at the interface was hydrogen-bonded to roughly two other water molecules. The molecules to which the molecule was hydrogen-bonded were just as likely to be on one side of the interface as the other, so that on average we break one hydrogen bond per interfacial molecule.

Now the density of water is $1\,\mathrm{g\,cm^{-3}}$, so that the each molecule occupies on average

$$\frac{1\,\mathrm{cm}^3}{1\,\mathrm{g}} \times \frac{18\,\mathrm{g}}{1\,\mathrm{mol}} \times \frac{1\,\mathrm{mol}}{6\times 10^{23}\,\mathrm{molecules}} = 3\times 10^{-23}\,\mathrm{cm}^3/\mathrm{molecule}$$

If we approximate the shape of a molecule as a cube, we then have molecular surface density of $\frac{\mathrm{molecule}}{(3\times 10^{-23})^{2/3}\mathrm{cm}^2} \times \frac{1\,\mathrm{mol}}{6\times 10^{23}\,\mathrm{molecule}} = 1.7\times 10^{-5}\,\mathrm{mol\,m^{-2}}$. Taking into account the $23\,\mathrm{kJ\,mol^{-1}}$ of energy required to break a mole of hydrogen bonds, we obtain an surface energy density $\Delta E/\Delta A$ of $1.7\times 10^{-5}\,\mathrm{mol\,m^{-2}} \times 23.3\times 10^3\,\mathrm{J\,mol^{-1}} = 400\,\mathrm{mN\,m^{-1}}$ This is remarkably close to the measured value of the surface tension of $72\,\mathrm{mN\,m^{-1}}$, considering the crudeness of our model. What modifications can you think of that we could make to make the model more realistic? In the literature one can find a significantly more sophisticated attempt[12] to compute the surface tension of water by counting hydrogen bonds, but they do hardly any better (off by a factor of two), though interestingly, in contrast to our result, theirs turns out to be an *under*estimation.

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[12] A. Luzar, S. Svetina, B. Žekš, The contribution of hydrogen bonds to the surface tension of water, *Chem. Phys. Lett.*, **96** 4 (1983), 485-490, https://doi.org/10.1016/0009-2614(83)80737-4

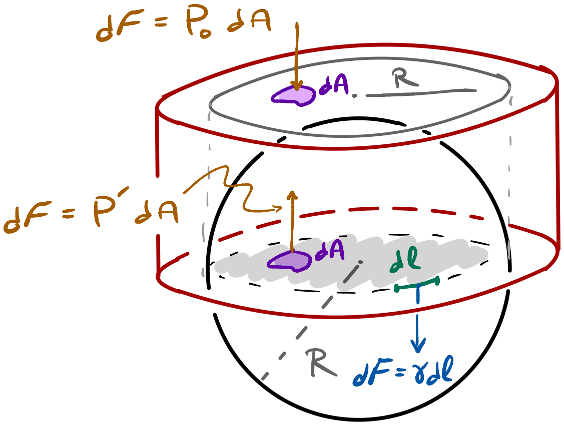

Figure 1: Force analysis on a cylindrical virtual volume enclosing the upper hemisphere of a spherical interface.

3 Laplace pressure

In this section we see how the *curvature* of an interface gives rise to a pressure differential, known as the *Laplace pressure*[13] across the interface.

3.1 Derivation of Laplace pressure ΔP

We derive here the Laplace pressure here for the simplified case of a spherical surface, and give the general rule without proof after. Consider a spherical interface of radius R, and a cylindrical virtual volume enclosing the top half of the sphere (figure 1). For this system we repeat the same force analysis that we performed earlier for the rectangular liquid film attached to the moveable wall. We still ignore gravity so that there are no external forces acting within the virtual volume. The volume cuts the sphere at the equator, so that the force applied on the volume due to surface tension from a segment of length dl running around the equator will again be of magnitude γdl but will now point straight down for all line segments, resulting in a net downwards force $F = 2\pi R\gamma$ equal to γ times the circumference $2\pi R$ of the equator.

Now suppose the ambient pressure P_o outside the surface and the pressure P' are the same (i.e. $P = P'$) so that the forces due to the pressure applied on the walls of the virtual volume all cancel each other. In this case we find there will be an overall net force F pushing down on the upper hemisphere. By symmetry we would similarly deduce the same force acting up on the lower hemisphere, acting right on the left hemiphere, acting left on the right hemisphere, etc., so

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[13] Named after French scientist Pierre-Simon Laplace (1749-1827).

that overall we would conclude that there should be a net *inwards* force from surface tension acting to compress the sphere.

Some small amount of compression will then lead to a pressure increase ΔP in the sphere. With this pressure differential $P' - P_o = \Delta P$, there will now be a greater upwards force $P'dA$ due to pressure exerted by the sphere on some small patch dA in the region of the bottom cap inside the sphere (colored grey) than the downwards force $P_o dA$ exerted by the amibient pressure on the corresponding region on the upper cap.

Summing up the contributions from each small patch we get a net force due to the pressure differential equal to $\pi R^2 \Delta P$ due to the pressure differential ΔP across the interface. Evidently the sphere will compress until the pressure differential $P' - P_o = \Delta P$ is large enough that the upwards force due to the pressure differential equals the downwards force due to surface tension. This occurs when

$$\Delta P = \frac{2\gamma}{R} \quad \text{(Young-Laplace equation)} \tag{1}$$

This is the famous Young-Laplace equation[14] for a spherical interface. In general a point on a non-spherical surface will not necessarily have the same radius of curvature in all directions. Think for example of an ellipsoid (i.e. a rugby ball) which is more curved in one direction than along a direction perpendicular. The more general Laplace equation states that the pressure difference ΔP across an interface is given by

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad \text{(Young-Laplace equation, generalized)} \tag{2}$$

where R_1 and R_2 are the radii of curvature at measured in any two orthogonal directions at a point on the surface. The sign (±) conventions are the same as for the spherical case: the side of the interface which the surface curves more towards will have the greater pressure.

3.2 Gravity and the capillary constant

This is maybe a good point to stop and address the influence of gravity, which we have up to this point been excluding, on the forces governing the equilibrium geometry of interfaces. Returning to our spherical interface (figure 1), we can include the influence of gravity on our cylindrical virtual volume by adding an additional downwards force

$$F_g = m \times g = (\rho \times V) \times g = \left(\rho \times \left(\frac{1}{2} \times \frac{4}{3} \pi R^3 \right) \right) \times g = \frac{2}{3} \pi R^3 \rho g \ ,$$

where

- $g \approx 9.8\,\mathrm{m\,s^{-2}}$ is the acceleration due to gravity,

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[14] Named respectively for British and French scientists Thomas Young (1773-1829) and Pierre-Simon Laplace (1749-1827).

- $m = \rho \times V$ is the mass of the upper hemispherical volume enclosed by the virtual volume (we ignore the mass of the surrounding medium, which we presume for this exercise to be air),
- ρ is the mass density of the medium composing the sphere, and
- $V = \frac{1}{2} \times \frac{4}{3}\pi R^3$ is the volume of the hemisphere.

Evidently this gravitational force acting on the virtual volume can be neglected to the extent that it is much smaller than the force $2\pi R\gamma$ arising from surface tension at the interface. The forces are equal when $R = \sqrt{\frac{3\gamma}{\rho g}}$. Check for yourself that at smaller radii the gravitational force becomes weaker than the force due to surface tension. We conclude then that, as a rule of thumb, gravity can be neglected so long as the size of the system is smaller than the "capillary length"[15] κ given by

$$\kappa \equiv \sqrt{\frac{\gamma}{\rho g}} \,. \tag{3}$$

For water the capillary length turns out to be 2.71 mm. So on the length scale of an ant abdomen, we don't expect gravity to play an important role in determining the shape of water droplets. This means that the pressure inside the droplet is essentially the same everywhere, which in turn implies the radius of curvature is essentially constant across the interface, i.e. the droplet is essentially spherical:

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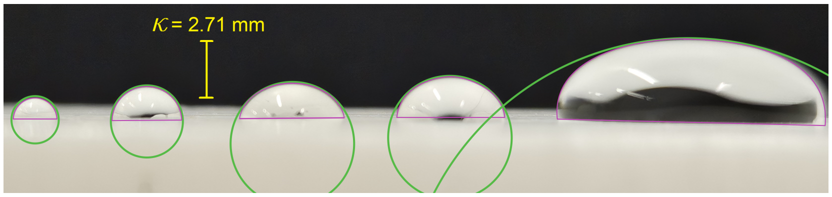
[15] Depending on who you ask, κ might also be defined to be $\sqrt{\frac{2\gamma}{\rho g}}$, i.e. a factor $\sqrt{2}$ longer.

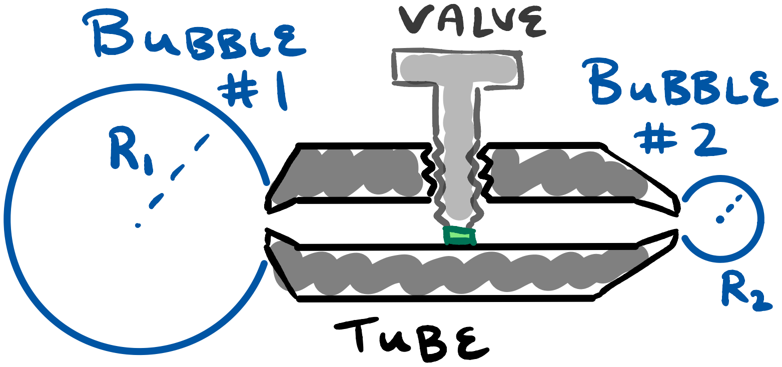
As the droplet size becomes comparable to the capillary length, the shape of the droplet begins to distort under the force of its own weight. Here we show a series of water droplets of increasing volume, desposited on a teflon surface[16]:



As you can see, the shape of the droplets (outlined thinly purple) conforms closely to a circle (thicker green outline) for droplets significantly shorter than the capillary length (yellow bar), while taller droplets show significant flattening towards the top.

3.3 Lung surfactant

Take a look at the following diagram:



We have two soap bubbles, one big and one small, that are connected to a common tube but sealed off from one-another by a valve. The question is: what will happen when we open the valve? Intuitively we have some sense that initially the pressures on each side of the tube will be different because the bubbles are of unequal size, and perhaps we are tempted to conclude that the larger bubble will shrink and the smaller one will grow until they both are the same size at which point their pressures will be equal and equilibrium will be established. However, when we perform the experiment (Youtube demonstration),

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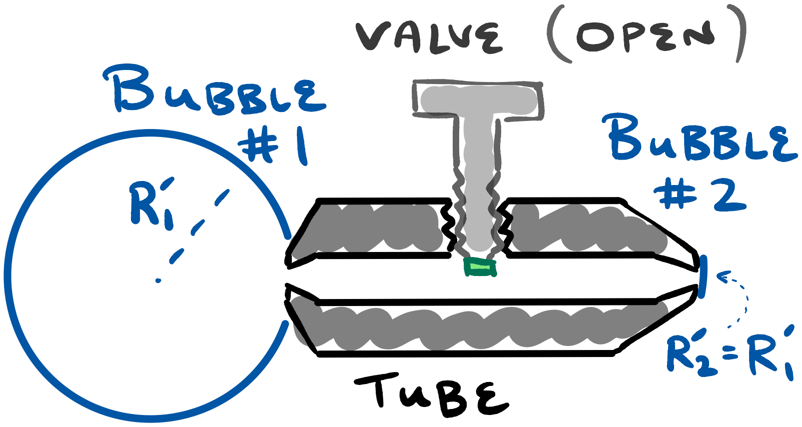
[16] Photographer credit: Léa Zupan

we find, counter to this intuition, that it is the smaller bubble that shrinks and the larger that grows.

This of course is in perfect keeping with the Laplace equation for spherical interfaces, which asserts that the pressure inside a bubble is inversely proportional to its radius of curvature. Therefore before we open the valve the pressure will be larger on the right side of the tube, and when we open the valve air will flow from right to left, deflating the right bubble and inflating the left. The system reaches equilibrium when the pressure is equal throughout the tube, but this will only occur when the radii of curvature of the two bubbles are equal. This occurs when we have a smaller bubble shrinks so that it is a *slightly* curved (i.e. nearly flat) film spread over the end of the tube:



This tendency due to the Laplace pressure for smaller cavities to shrink and larger ones to grow poses a potential problem for our lungs, which contain almost a billion little air sacs called *alveoli* where gas is exchanged between our bodies and the outside world. Here we show two such alveoli, one larger than the other[17]:

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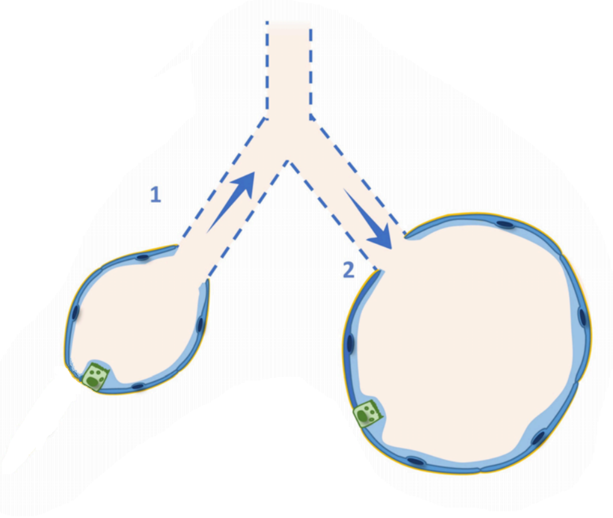
[17] Adapted from Sehlmeyer et al., Alveolar Dynamics and Beyond – The Importance of Surfactant Protein C and Cholesterol in Lung Homeostasis and Fibrosis. *Frontiers in Physiology* **11**, (2020).



These air sacs are lined with fluid, forming a gas-liquid interface that is subject to the effects of surface tension. If the fluid were composed of pure water, then differing Laplace pressures would for reasons just discussed lead to the collapse of the smaller alveoli, presumably prohibiting gas exchange at this location. In reality however the fluid is a complex solution containing a variety of surfactant molecules in sufficient concentration that the surface tension of the fluid *decreases* as the alveoli shrinks. This is reflected in the fact that, at the end of an exhale when your alveoli are at their smallest, the average surface tension is only $0.5\,\mathrm{mN\,m^{-1}}$ (compare this to the $72\,\mathrm{mN\,m^{-1}}$ of pure water), which is more than twenty times less than the average surface tension at higher levels of inflation[18]:

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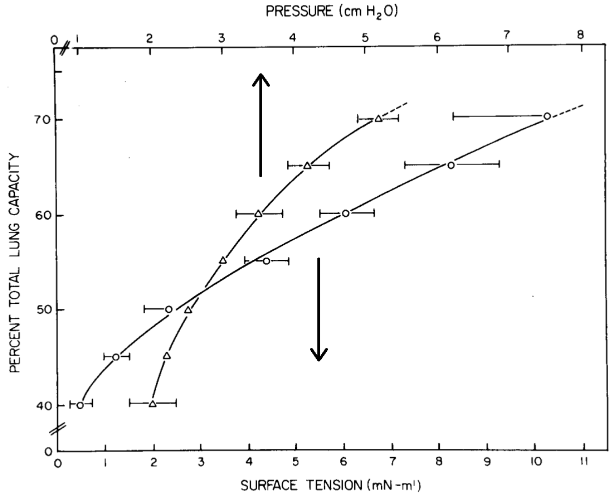
[18] Schürch, S. Surface tension at low lung volumes: Dependence on time and alveolar size. *Respiration Physiology* **48**, 339–355 (1982).

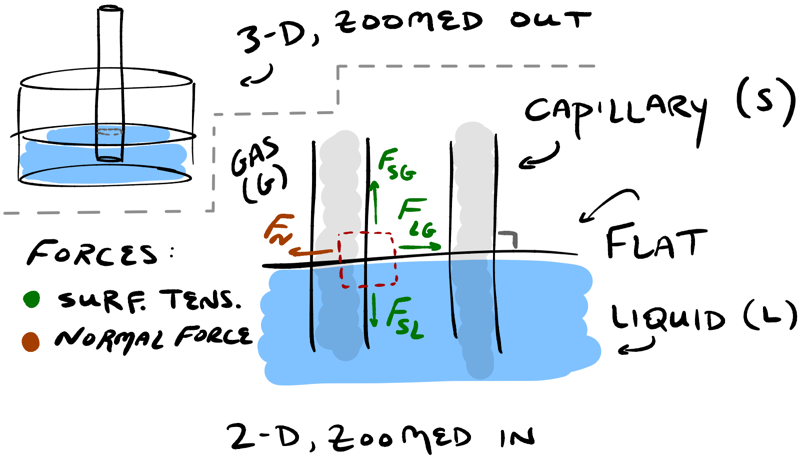


Lung surfactant therefore has the effect of stabilizing the sizes of alveoli, since the increase in Laplace pressure due to decrease in the alveoli size is compensated by a corresponding decrease in surface tension.

Lung surfactant incidentally has the additional benefit of reducing the work required for lung inflation (recall $\Delta W = \gamma \Delta A$). Infants born sufficiently prematurely will lack the necessary concentration of surfactant and will be unable therefore to summon the necessary strength to breathe. In such cases doctors will employ ventilator to assist the infant in respiration.

4 Capillary action

One phenomenon commonly associated with surface tension is capillary action, which is the rise (or in some cases descent) of fluids in narrow channels (i.e. "capillaries") against the opposing force of hydrostatic pressure. The mechanical origin of the rise / fall of fluid in capillaries is the same as that underlying the spreading of oil across the surface of water: a competition between the surface tensions of the different interfaces at play. To articulate this more precisely, let's take a look at the following diagram which captures the situation at the moment of insertion of a capillary into a fluid, before the forces of surface tension have had any time to act:



Similar to previous examples, we construct as a virtual volume (outlined in dotted red) a tiny cube of side length dl enclosing simultaneously all three interfaces: liquid-gas (LG), solid-liquid (SL), and solid-gas (SG). In this case it suffices to consider only the forces due to surface tension, since these forces, which scale with the side-length dl, will dominate over the forces due to pressure or gravity, which scale as dl^2 and dl^3 respectively. At the moment of insertion, the liquid-gas interface is flat, so that force $F_{\mathrm{LG}} = dl\gamma_{\mathrm{LG}}$ due to the surface tension γ_{LG} from this interface will act horizontally and will therefore not contribute towards any rise or fall of the fluid inside the capillary[19]. As mentioned, there is in addition to this interface a solid-gas and solid-liquid interface, which will exert upwards and downwards forces $F_{\mathrm{SG}} = dl\gamma_{\mathrm{SG}}$ and $F_{\mathrm{SL}} = dl\gamma_{\mathrm{SL}}$ respectively on the virtual volume. Evidently whether the net vertical force $F_{\mathrm{SG}} - F_{\mathrm{SL}} = dl\,(\gamma_{\mathrm{SG}} - \gamma_{\mathrm{SL}})$ will be up or down depends on whether γ_{SL} is smaller or greater than γ_{SG}. This is equivalent to asking whether the energy change $dW = (dh \times dl) \times (\gamma_{\mathrm{SL}} - \gamma_{\mathrm{SG}})$ in raising the fluid a height dh is negative or positive. If the liquid is able to bond strongly to the capillary surface, then this energy change will be negative and the liquid will rise. In this case we say that the surface is *wetting* with respect to the liquid, or if the liquid is water we say the surface is *hydrophilic*. Dangling silicon bonds, for example, at a (clean!) glass surface can interact attractively hydrogen atoms in water making this surface strongly hydrophilic. Conversely, if the liquid is repelled by the capillary surface then the liquid will fall and we say the surface is *non-wetting* with respect to the liquid or equivalently is hydro*phobic* if the liquid is water. A teflon surface, being composed of fluorine-substituted saturated hydrocarbons, does not exhibit strong attractions with water molecules, rendering it relatively hydrophobic.

After insertion of the capillary into the liquid, the liquid will then either rise

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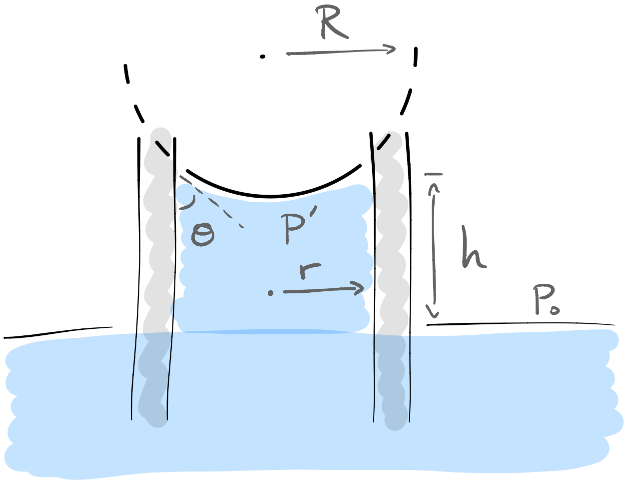
[19] This force will in fact be opposed by a normal force F_{N} exerted by the capillary walls.

or fall depending on the "wettability" of the surface and after some time the fluid level will come to rest. If we look closely at the surface of the liquid in the capillary, we will notice that it is curved (we say there is a "meniscus"):



What is the origin of this curvature? Well, because the liquid below the meniscus is a height h above the surrounding fluid, there will be a hydrostatic pressure difference $P_o - P' = \Delta P = \rho g h$ (recall intro physics) due to the influence of gravity on the column of liquid in the capillary, where ρ and g are again the density of the liquid and the acceleration due to gravity, respectively. The Laplace equation then tells us that the gas-liquid interface must curve to accomodate this pressure difference. In equilibrium therefore we have

$$h = -\frac{2\gamma}{\rho g R} = -2\kappa^2/R \tag{4}$$

where

- κ is the capillary length (equation 3), and
- R is the radius of curvature of the meniscus.

We require the negative sign to account for the fact that the radius of curvature R is *negative* according to our established convention since the surface curves *away* from the liquid surface. The above equation can be equivalently stated in the form of "Jurin's[20] law" for capillary action:

$$h = 2\kappa^2 \cos\theta / r \quad \text{(Jurin's law)}\ , \tag{5}$$

where:

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[20] James Jurin (1684-1750), English scientist and physician

- r is the radius of the capillary,
- $\theta = \cos^{-1}\left(-\frac{r}{R}\right)$ is the "contact angle" between the meniscus and the capillary

Question for the leader: what do we expect to find in the case of a non-wetting surface-liquid interaction?

5 Kelvin equation

The particularly observant reader will have remarked a small flaw in the analysis underlying our derivation of Jurin's law (equation 5) in the previous section. Because of the finite density of air, atmospheric pressure is not constant with elevation, so that the pressure P_o' above the meniscus is not exactly equal to the pressure P_o at the (flat) surface of the liquid surrounding the capillary. This pressure gradient with elevation is, for instance, why water boils at a lower temperature at higher altitudes. Because gases are, in contrast to liquids, compressible, the pressure difference is *not* given by $\rho g h$, with ρ now being the density of air, which is itself also not a constant function of elevation. Instead we have, for ideal gases,

$$P_o' = P_o e^{-\frac{Mgh}{\bar{R}T}} \tag{6}$$

where M is the molar mass of the gas, T is the temperature, and $\bar{R}$ is the ideal gas constant. Jurin's law is evidently valid to the extent that the difference $P_o' - P_o$ in the atmospheric pressure of the surrounding gas across a certain change in elevation is much smaller than the corresponding change in hydrostatic pressure in the liquid. This is of course simply the requirement that the gas be much lighter than the liquid, which holds true in nearly all practical cases of interest (air is for instance more than a thousand times lighter than water). We can then without risk of significant error apply Jurin's law to equation (6) to get an expression for the pressure above a meniscus in terms of its radius of curvature R. We obtain

$$P_o' = P_o e^{R_o/R} \quad \text{(Kelvin's law)} \tag{7}$$

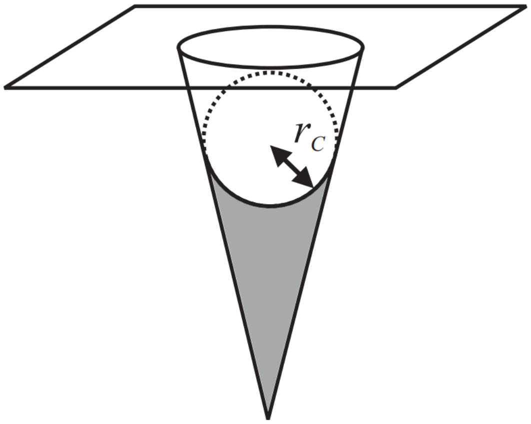
where

$$R_o \equiv \frac{2\gamma V_m}{\bar{R}T} \tag{8}$$

R_o in most practical circumstances is microscopic; for water at room temperature for instance it is just 10.5 Å. Note that equation (7), known as the Kelvin equation, still applies should we assume that the molecular composition of the gas and liquid are the same (e.g. liquid water and water vapor), in which case the pressure P_o' and P_o now represent respectively the *vapor pressure* of the liquid above the meniscus and the flat region surrounding the liquid. Further, one may notice that the result, derived by essentially comparing gravity-driven pressure gradients across liquid and gaseous fluids and applying the Laplace equation, has no dependence on the gravitational acceleration constant g. Indeed equation (7), known in this context as the Kelvin equation[21], describes the *general* influence of curvature on the vapor pressure above a gas-liquid interface and applies not only to menisci in capillaries but rather to any curved[22] gas-liquid interface. We explore some consequences of this relation in the remaning sections of this lecture.

5.1 Capillary condensation and pore-size determination

The Kelvin equation explains why some materials like cotton or silica gel can retain significant quantities of moisture at relative humidities well below the dew point. These materials are both hydrophilic and are microscopically rough. To gain a rough understanding of this effect, we model this microscopic roughness in terms numerous small conical voids at the surface of the material. Here we show one such void[23]:



Because of the surface's hydrophilicity, a meniscus with the minimal contact angle $\theta = 0°$ is able to form on the walls of the void (we say in this case that the surface is "perfectly wetting"). For very small menisci radii $|R| = r\cos\theta = r$ the vapor pressure P_o' of the interface is lower than the ambient vapor pressure αP_o, where α is the relative humidity and P_o is the vapor pressure in limit $|R| \to \infty$ (i.e. for a flat interface). The rate of absorption of water from the ambient water vapor is thus stronger than the rate of evaporation, so the fluid will continue to accumulate until the meniscus reaches a critical radius r_c where $r_c = R_o \ln\alpha$ at which point the evaporation rate equals the absorption rate. For water at 25 °C you can check that in order to achieve a critical radius of just

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[21] Named after British scientist and mathematician William Thomson, 1st Baron Kelvin (1824-1907)

[22] In the general case of a non-spherical surface with orthogonal radii of curvature R_1 and R_2 (see equation (2) and surrounding discussion) one simply makes the replacement $R \to 2/(1/R_1 + 1/R_2)$ in equation (7).

[23] Adapted from PCI, section 2.6

1 µm we need *very* humid air, $\alpha \approx 99.9\,\%$. At 75 % humidity we have a critical radius of only 4 nm! At sizes much smaller than this, the macroscopic nature of the thermodynamic and hydrostatic concepts employed in the derivation of the Kelvin equation render its application questionable.

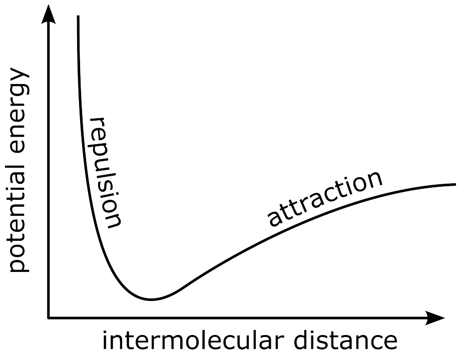
6 Aside: phase coexistence

Implicit in the discussion of interfaces is the notion of *phase coexistence*. One may naturally one why, for example, in some circumstances a pure substance will simultaneously assume two different phases of drastically different physical properties (e.g. density, compressibility, heat capacity, etc.). Evidentally in these circumstances the coexistence of two phases is thermodynamically more stable than the existence of a single phase with physical properties intermediate to the two. The general theory of phase coexistence is beyond the scope of this course, but to convince the reader that phase coexistence is not inconsistent with the principles of thermodynamics we give in this section an argument explaining how for a pure substance it happens that the competing microscopic effects of long-range attraction and short-range repulsion between molecules can lead to the thermodynamic stability of coexisting phases.

A universal feature of interactions between neutral molecules is a mutual attraction prevailing at large intermolecular distances followed by a strong mutual repulsion at intermolecular distances approaching the size of the molecules. The strength of the attractive interaction will of course depend on the molecule. Polar molecules will for example typically attract each other more strongly than non-polar molecules, though even non-polar molecules will attract one another through "dispersive" dipolar forces resulting from spontaneous distortion of the intra-molecular electronic charge distribution.

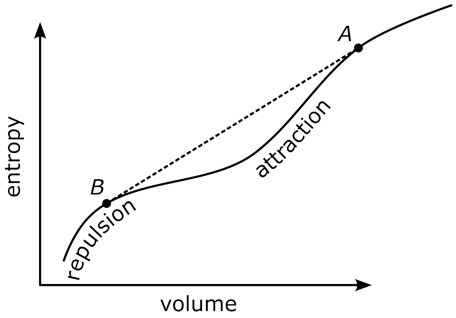
On the other hand, at shorter distances where intermolecular wavefunction-overlap is significant, molecules will feel a "Pauli repulsion" force arising from the energy cost associated with the necessary transfer of electrons from low to high energy orbitals when things begin to get too crowded.

The interplay between long-range attraction and short-range repulsion leads to a interaction potential with the following general form:



At large intermolecular separations we see the potential decreases with decreasing distance, reflecting attraction, while at short intermolecular distances the potential increases with decreasing distance, reflecting repulsion.

Given such a potential, one can apply the laws of statistical mechanics to determine the theoretical thermodynamic properties of a *homogeneous* fluid (i.e. gas or fluid) comprised of molecules mutually interacting according to a given potential. One can, for example, compute the fluid's entropy $S(U, V, N)$ as a function of the fluid volume V for a fixed total energy U and mole number N. At sufficiently low energies the particles will be moving slowly enough that the competing influences of attraction and repulsion will dramatically influence the form of entropy-volume ($S - V$) curve, so much that the curve can develop a *concavity*:



We indicate along the curve the rough range of volumes corresponding to average intermolecular distances associated with primarily attractive or primarily repulsive interactions. The concavity is located between the points marked A and B corresponding to volumes V_A and V_B respectively.

Suppose we perform an experiment, measuring various thermodynamic properties of the fluid as reduce the volume V in incremental steps. We suppose additionally that the box is closed and composed of insulating walls so that the mole number N is fixed and the energy U does not change in between compression steps. Now the potential may be as accurate as we like, so that at least for volumes *outside* the concavity we find perfect agreement between the fluid's predicted and measured thermodynamic properties. Inside the concavity however there is strong disagreement between experiment and theory, and it is in this region as well that experimentally we observe separation of the fluid into two coexisting phases: one with properties equal to that of fluid in with state variables (U, V_A, N) and the other equal to that with state variables (U, V_B, N).

Evidently for state variables U, V_C, N with V_C lying within the concavity of the $S - V$ curve the system can stabilize itself via phase separation. Now for any particular measurement the total energy, volume, and mole number are constrained to be fixed, but the manner in which the energy and molecules are distributed within the volume is unconstrained. The second law of thermodynamics (discussed in the following lecture) tells us that in this case the system will spontaneously evolve towards distributions of these fixed quantities of energy and molecules which act to increase the total system entropy.

We give now one such "partitioning" of the system into two subsystems which we show to have a larger combined entropy than the entropy $S(U, V_C, N)$ of the homogeneous (i.e. single phase) fluid. Let $V_C = \alpha V_A + (1-\alpha)V_B$, so that $0 < \alpha < 1$. We then take a fraction α of the energy and molecules and place them into a region of volume αV_a. The remaining fraction $1-\alpha$ of energy and molecules we place into the remaining volume $V_c - \alpha V_A = (1-\alpha)V_B$. The region of volume αV_a will of course correspond to the more dense phase, and the region of volume $(1-\alpha)\,V_B$ to the less dense phase. The combined entropy $S'(U, V_C, N)$ of the partitioned system[24] is given simply by the sum of the individual entropies of the individual subsystems:

$$S'(U, V_C, N) = S_A + S_B = S(\alpha U, \alpha V_A, \alpha N) + S\left((1-\alpha)U, (1-\alpha)V_B, (1-\alpha)N\right)$$

At this point we note that the entropy function is *homogeneous*[25] in the extensive variables, i.e. $S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N)$. Therefore:

$$S'(U, V_C, N) = \alpha S(U, V_A, N) + (1-\alpha)S(U, V_B, N)$$

This expression the reader can easily verify corresponds precisely to the dotted line joining points A to B, which, by the definition of concavity, lies above the curve $S(U, V_C, N)$ for the homogeneous fluid for all volumes V_C inside the concavity, i.e. $S'(U, V_C, N) > S(U, V_C, N)$ for $V_A < V_C < V_B$.

We therefore have demonstrated that the coexistence of multiple phases is not only consistent with the principles of thermodynamics but is in fact even for pure fluids a necessary consequence of them. In case the somewhat complex of the argument has it so that the "forest got lost through the trees", we summarize briefly the line of reasoning:

- The competing influences of attractive and repulsive interactions lead to thermodynamic instabilities in the properties of homogeneous fluids, one manifestation of which is the appearance of concavities in the $S-V$ curve relating the fluid entropy and volume.
- In the concave regions of the theoretical $S-V$ curve, one can take a homogeneous fluid and repartition it into two distinct coexisting phases that together yield a higher entropy than the homogeneous fluid. The homogeneous phase is therefore in these regions unstable with respect to spontaneous phase separation.

7 Condensation and nucleation

If we increase the pressure being applied to a volume of gaseous water vapor being maintained a constant temperature of 25 °C, then we will naturally ex-

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[24] We ignore here effects associated with the interface, which we can presume to be small for typical systems with large volume-to-surface-area ratios. In any event we address the subject of the thermodynamics of interfaces in the next lecture.

[25] A homogeneous function is of course to be distinguished from a homogeneous *fluid*, i.e. a fluid existing in just a single phase.

pect a phase transition to the liquid state once the applied pressure goes above 3170 Pa, which is the vapor pressure of water at 25 °C. However, this is the vapor pressure corresponding to a *flat* interface, or in other words the vapor pressure at the interface of a very large spherical drop (i.e. $R \to \infty$). For a pure fluid however, condensation from the vapor from a gas to a liquid must occur through the process of *homogeneous nucleation*, whereby individual molecules accumulate first into microscopically small clusters and then gradually grow into larger droplets. If the pressure of the gaseous vapor is only slightly above the vapor pressure P_o of flat interface, then, even should small drops somehow form, they should quickly evaporate thanks to their enhanced vapor pressure (recall the Kelvin equation, section 5).

We expect therefore for pure fluids a *kinetic stability* of the gaseous phase at pressures above the vapor pressure P_o. Fluids in such a state are termed *supersaturated*. Indeed in laboratory conditions one can straightforwardly produce water vapor with supersaturation ratios $P/P_o \equiv S$ in excess of 200 %[26].

If one however introduces impurities into a supersaturated fluid, the situation changes qualitatively. Even in the cleanest air, for instance, there will be a significant concentration of dust-like particles termed *aerosols* that are small enough to remain in the air but large enough to, say, scatter light (i.e. $\gtrsim$ 100 nm). Common aerosols include eroded soil, sea salt, and ash[27].

Aerosols can serve as sites (or "seeds") for nucleation of water droplets. At supersaturation ratios S a stable film of water can grow around aerosol particles of sizes exceding a critical radius

$$R_c = R_o / \ln S$$

where R_o is again the length scale relating interface radius of curvature R to vapor pressure P'_o (see equation (8)). One University of Bern master's thesis project[28] measured the supersaturation ratio in the air above the Jungfraujoch, arriving at a mean value of $S \approx 0.25\,\%$, suggesting that aerosol particles present had dimensions no larger than roughly

$$R_c = 1\,\mathrm{nm} / \ln\left(1 + 2.5 \times 10^{-3}\right) \approx 1\,\mathrm{nm}/2.5 \times 10^{-3} = 400\,\mathrm{nm} \ .$$

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[26] Wlasits et al. *Environ. Sci. Technol.* **57**, 4, (2023) pgs. 1584–1591

[27] meteoswiss.admin.ch/climate/climate-change/monitoring-the-atmosphere/aerosols-and-climate.html

[28] Emanuel Hammer (2011)