Molecular Modeling in Engineering: Methods and Applications

Lecture: Molecular origin of surface tension

Nikolai V. Priezjev

Pressure-stress 3x3 tensor: equilibrium properties

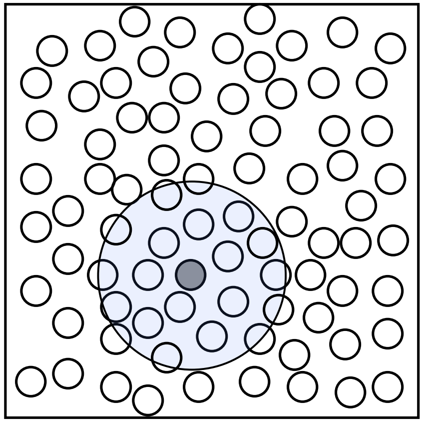
$$P_{\alpha\beta}V = \sum_i m v_\alpha^i v_\beta^i + \sum_i \sum_{j>i} r_\alpha^{ij} F_\beta(r^{ij})$$

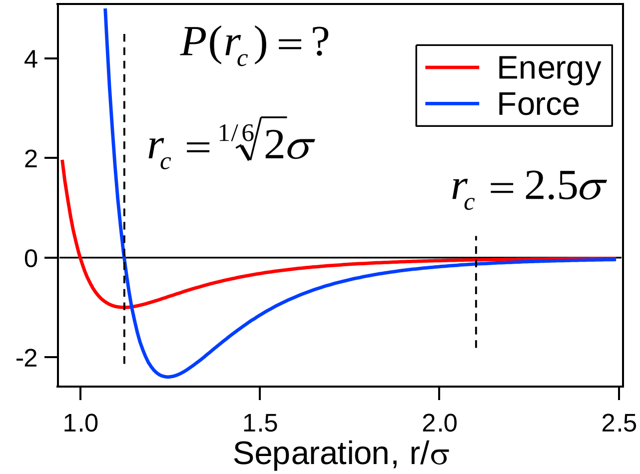
$\alpha = \mathrm{x, y, or\ z}$ and $\beta = \mathrm{x, y, z}$

$$\begin{pmatrix} P_{xx} & P_{xy} & P_{xz} \\ P_{yx} & P_{yy} & P_{yz} \\ P_{zx} & P_{zy} & P_{zz} \end{pmatrix}$$

$$\boxed{\frac{3}{2}k_B T = \frac{1}{2N}\sum_{i=1}^{N} m_i v_i^2}$$

- *At equilibrium (i.e. no shear flow or external forces) non-diagonal elements of the pressure-stress tensor are zero ($P_{xy} = P_{xz} = P_{yz} = 0$).*
- *The diagonal elements are pressures in the x, y, or z directions ($P_{xx} = P_{yy} = P_{zz}$).*
- *First term is just a sum of all kinetic energies in the x, y, or z directions (ideal gas law).*
- *Second term is the virial: sum of the product $F_x r_x$ of all pairs within the cutoff radius.*





Examples of surface tension force in nature (water striders)

D. Hu, B. Chan, J. W. M. Bush. 2003. The Hydrodynamics of Water Strider Locomotion. Nature 424, 663-666.

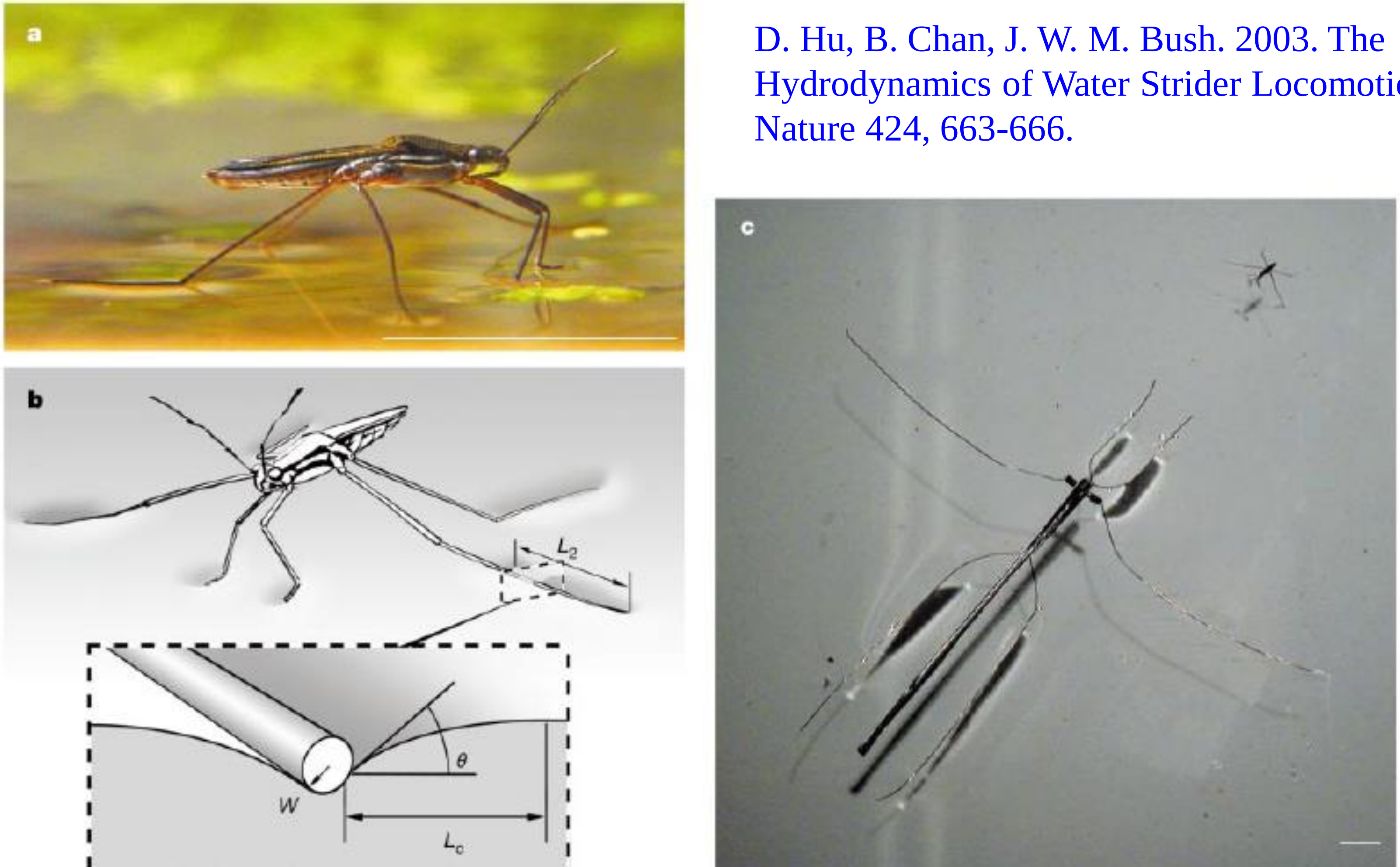
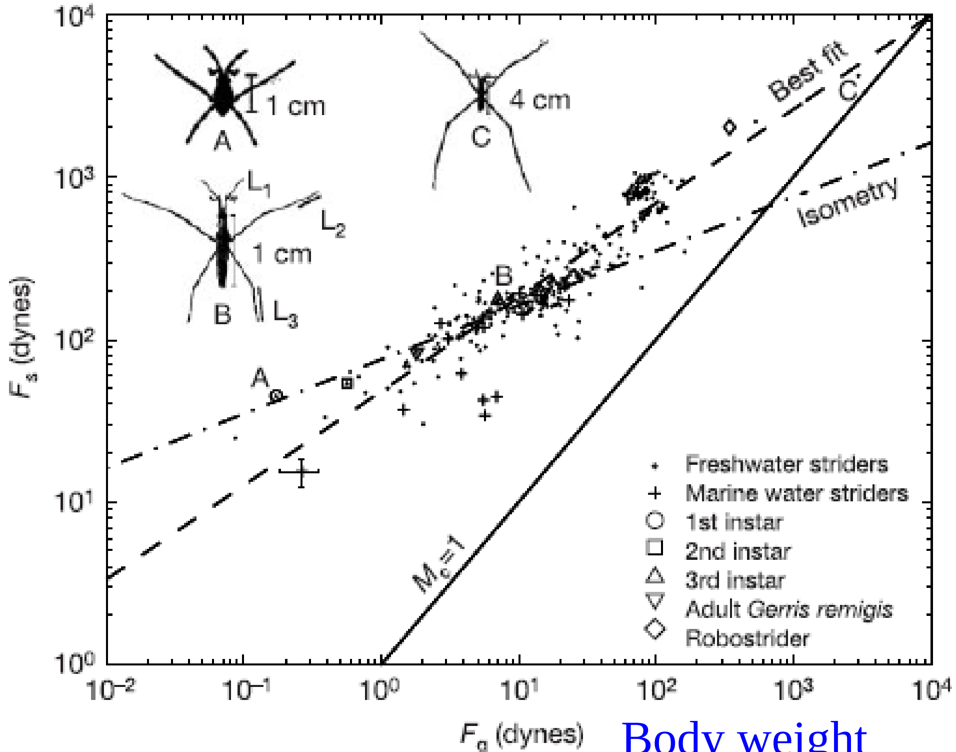


Figure 1 Natural and mechanical water striders. **a**, An adult water strider *Gerris remigis*. **b**, The static strider on the free surface, distortion of which generates the curvature force per unit leg length $2\sigma \sin\theta$ that supports the strider's weight. **c**, An adult water strider facing its mechanical counterpart. Robostrider is 9 cm long, weighs 0.35 g, and has proportions consistent with those of its natural counterpart. Its legs, composed of 0.2-mm gauge stainless steel wire, are hydrophobic and its body was fashioned from lightweight aluminium. Robostrider is powered by an elastic thread (spring constant 310 dynes cm^{-1}) running the length of its body and coupled to its driving legs through a pulley. The resulting force per unit length along the driving legs is 55 dynes cm^{-1}. Scale bars, 1 cm.

Examples of surface tension force in nature (water striders)

Maximum Curvature Force



Body weight

Figure 2 The relation between maximum curvature force $F_s = \sigma P$ and body weight $F_g = Mg$ for 342 species of water striders. σ is the surface tension of either pond water (67 dynes cm^{-1}) or sea water[17] (78 dynes cm^{-1}) at 14 °C and $P = 4(L_1 + L_2 + L_3)$ is twice the combined lengths of the tarsal segments (see strider B). Anatomical measurements were compiled from existing data[20,26–29]. Open symbols denote striders observed in our laboratory. Insets show the adult *Gerris remigis* (B) and extremes in size: the first-instar infant *Gerris remigis* (A) and the *Gigantometra gigas*[20] (C). The solid line represents $M_c = 1$, the minimum requirement for static stability on the surface. The surface tension force is more than adequate to support the water strider's weight; however, the margin of safety (the distance above $M_c = 1$) decreases with increasing body size. If the proportions of the water strider were independent of its characteristic size L, one would expect $P \sim L$ and hence $F_s \sim L$, and $F_g \sim L^3$: isometry would thus suggest $F_s \sim F_g^{1/3}$, a relation indicated by the dash-dotted line. The best fit to the data is given by $F_s = 48F_g^{0.58}$ (dashed line). Characteristic error bars are shown.

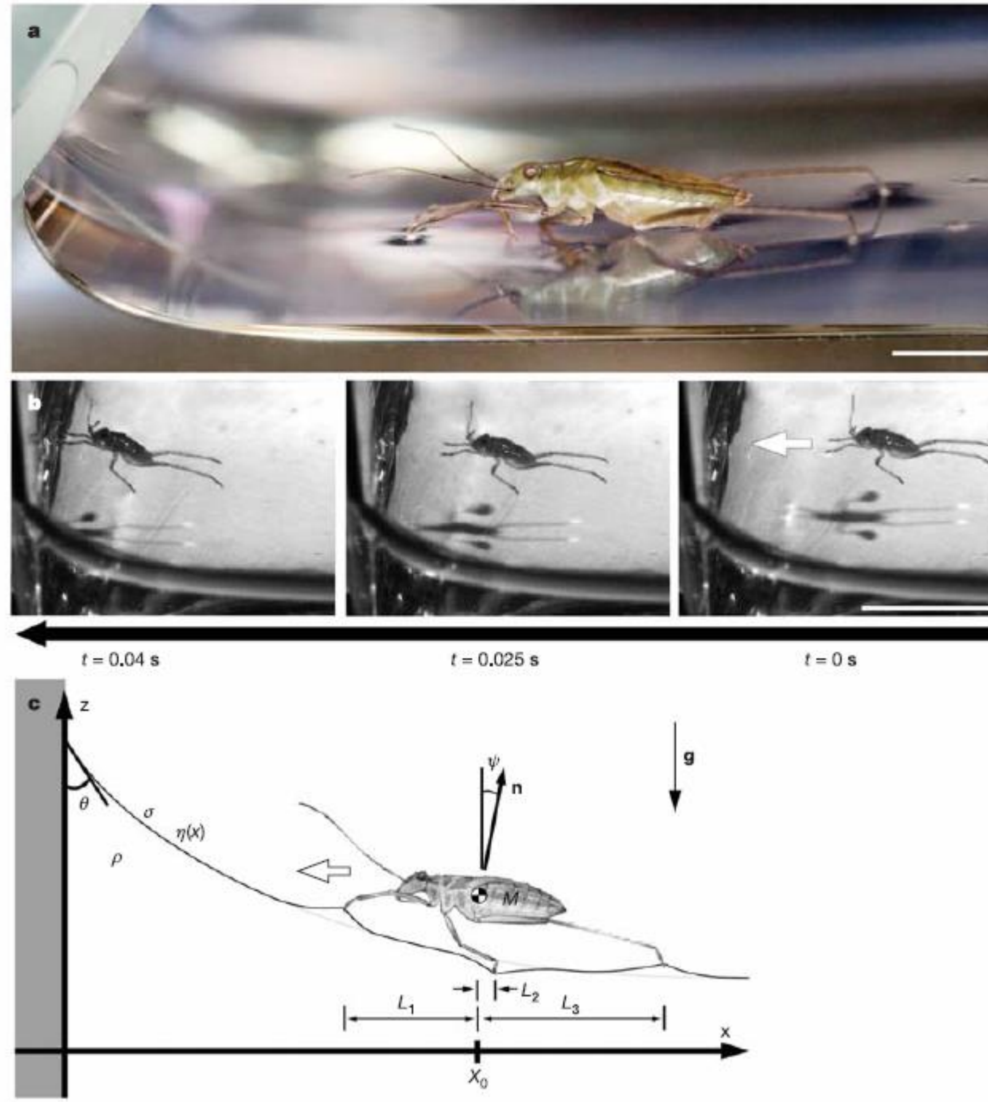
D. Hu, B. Chan, J. W. M. Bush. 2003. The Hydrodynamics of Water Strider Locomotion. Nature 424, 663-666.

Examples of surface tension force in nature (water striders)

Meniscus-climbing insects

David L. Hu[1] & John W. M. Bush[1], MIT

Water-walking insects are generally covered with a mat of dense hair that renders them effectively non-wetting[4,21], but some have developed specialized feet with retractable hydrophilic claws or 'ungues' that allow them to raise the free surface[2,4], an adaptation critical for meniscus-climbing. Water-walking insects such as *Mesovelia* (Fig. 1) ascend menisci by assuming a static posture in which they pull up on the free surface with the wetting tips of their front and rear tarsi and push down with their middle tarsi.



The deformation of the water surface near the head and tail of the larva is clearly visible. In these images, it approaches an emerging wetted leaf.

http://www-math.mit.edu/~dhu/Climberweb/climberweb.html

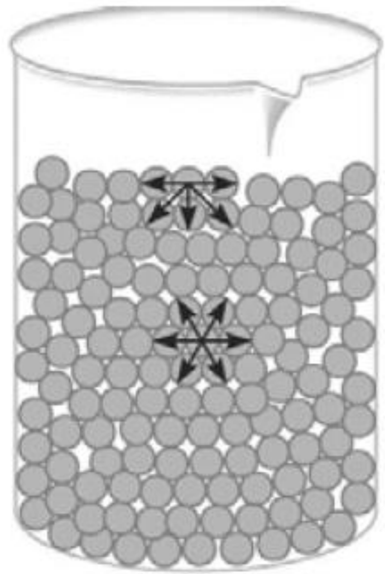
Net forces at the liquid-vapor interface

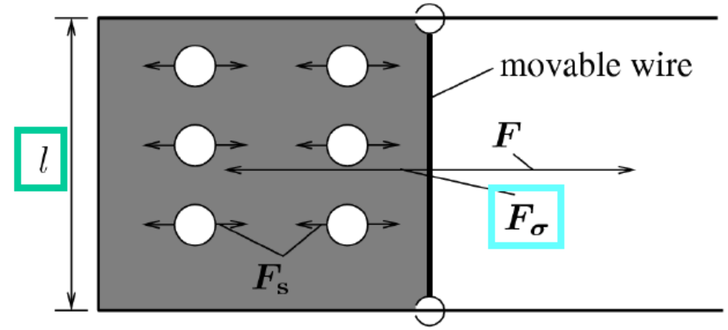
Surface tension is the amount of energy required to stretch or increase the surface of a liquid by a unit area.

Strong intermolecular forces

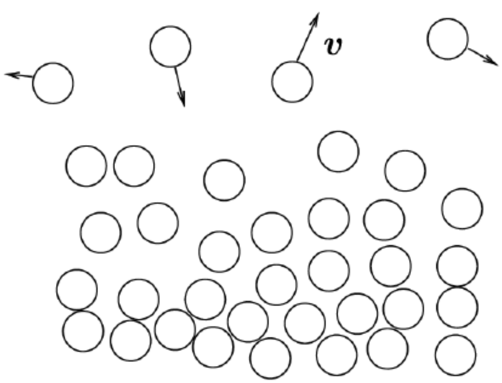
||

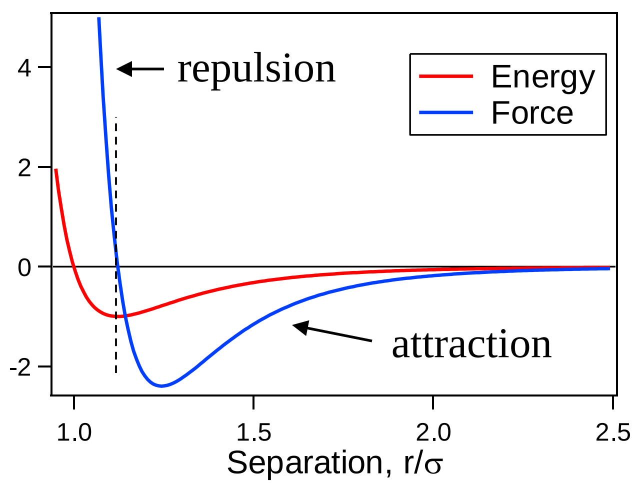
High surface tension

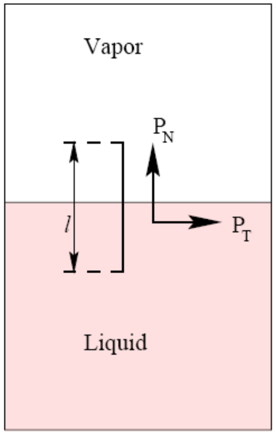




Force per unit length $\sigma = \dfrac{F_\sigma}{l}$

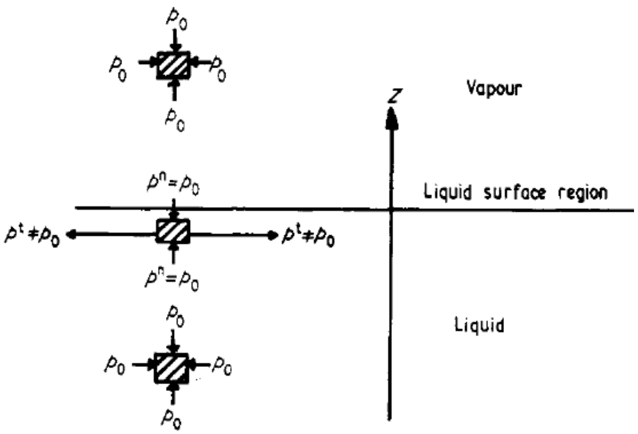




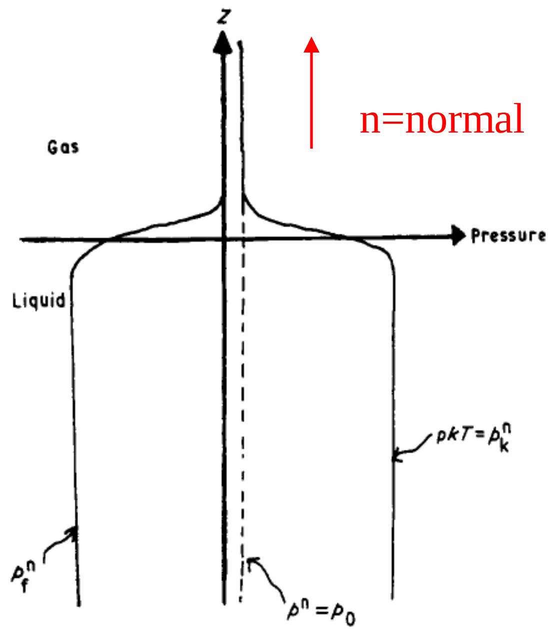


$$P_{\alpha\beta}V = \sum_i m v_\alpha^i v_\beta^i + \sum_i \sum_{j>i} r_\alpha^{ij} F_\beta(r^{ij})$$

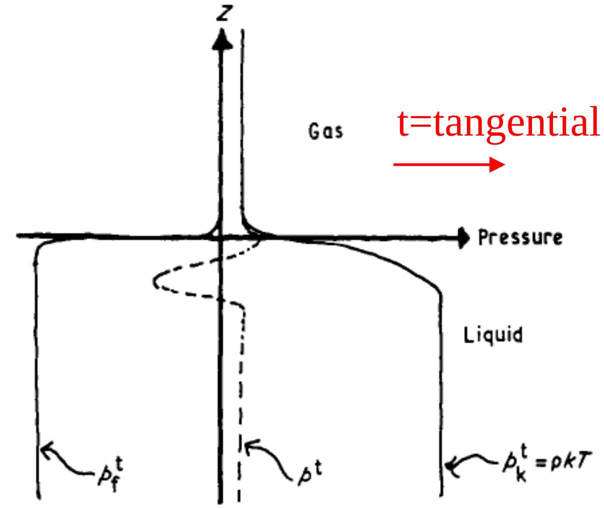
Why is surface tension a force parallel to the interface?



Equilibrium of elementary fluid cubes in liquid, vapour and surface.



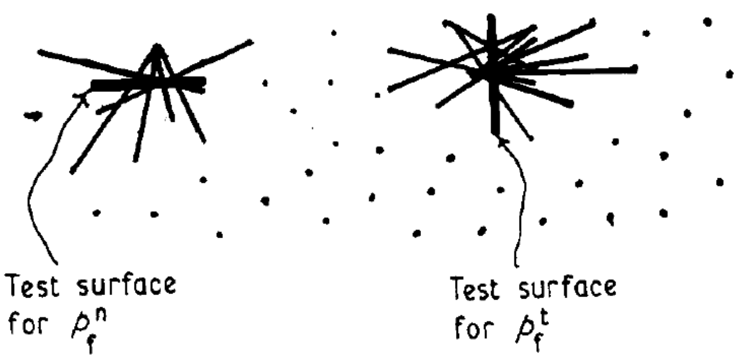
Contributions to normal pressure.



Contributions to tangential pressure.

The total pressure p:

p	$=$	p_k	$+$	p_f
(usually positive)		(always positive)		(usually negative)



Greater number of interactions contributing to p_f^t than to p_f^n near liquid surface.

The *surface tension*, γ, defined in an elementary way as the total force exerted between the portions of liquid on opposite sides of a line of unit length in the surface, is simply the integral of the underpressure through the surface layer, i.e.

$$\gamma = \int_{-\infty}^{\infty} (p_0 - p^t(Z))\,dZ.$$

The molecular mechanism of surface tension. M. V. Berry 1971 Phys. Educ. 6, 79

Why is surface tension a force parallel to the interface?

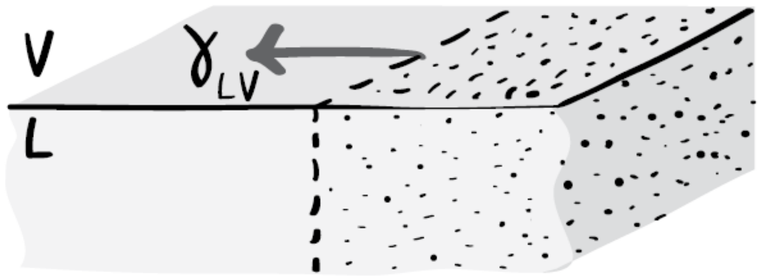


FIG. 2: Sketch showing surface tension as a force per unit length exerted by one sub-system on the other. It is parallel to the interface and perpendicular to the dividing line.

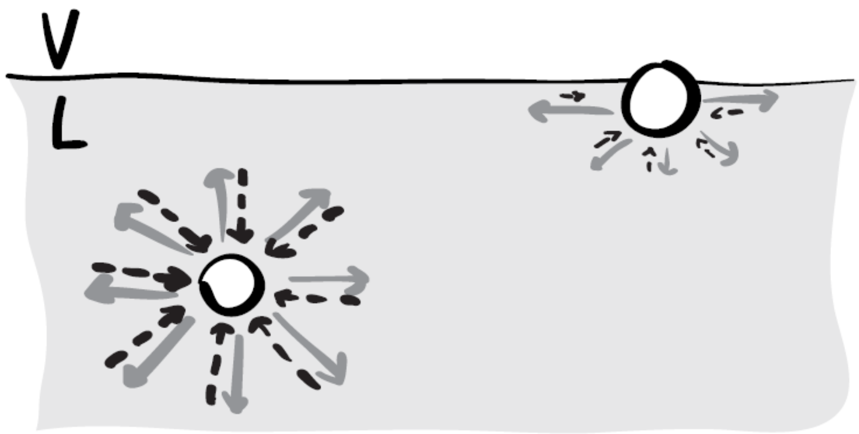


FIG. 7: Sketch showing repulsive (dashed black arrows) and attractive (gray arrows) forces in the bulk and at the surface.

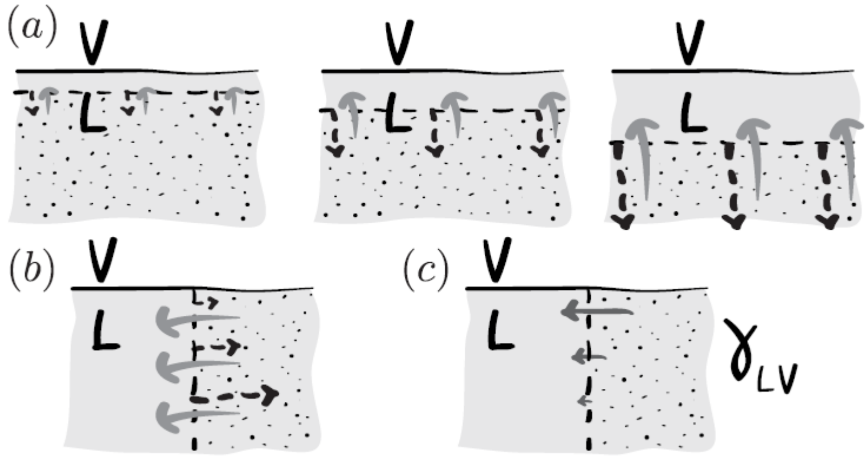


FIG. 8: (a) Vertical force balance in the liquid-vapor interface. The bulk of the liquid (dotted region) is submitted to an attractive force (gray arrows) and a repulsive force (dashed black arrow) from the interfacial zone (gray region). They must balance each other. (b) Horizontal force exerted by the left part of the liquid (gray region) on the right one. The attractive force is very anisotropic and remains almost unchanged close to the surface. On the contrary, the repulsive force is isotropic and decays close to the surface. (c) This leads to a net attractive force from one side on the other.

Antonin Marchand, Joost H. Weijs, Jacco H. Snoeijer, Bruno Andreotti, Am. J. Phys. **79**, 999 (2011).

Pressure and density profiles at the liquid-vapor interface

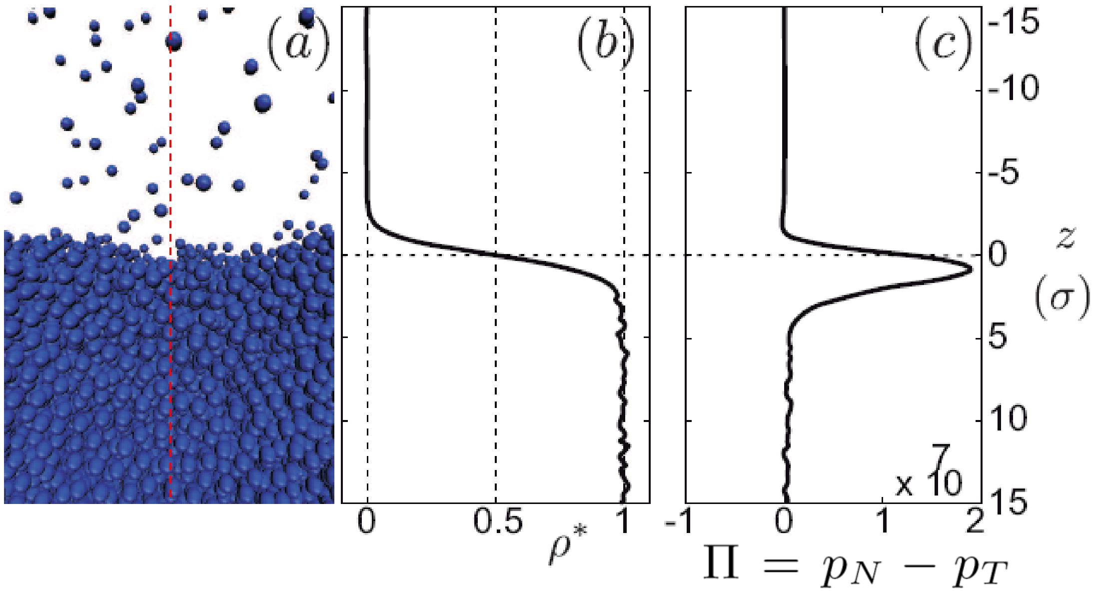


FIG. 6: The liquid-vapor interface. (a) Snapshot of Lennard-Jones simulation of a liquid-vapor interface. (b) Time-averaged density profile $\rho(z)$ across the interface. (c) Tangential force per unit area exerted by the left part on the right part of the system. Technically speaking, the plot shows the difference $\Pi = p_N - p_T$ between the normal and tangential components of the stress tensor.

The transition from the high density liquid to the low density gas takes place in a very narrow region that is only a few molecules wide.

Surface tension (ε/σ^2):

$$\gamma = \int [P_N(z) - P_T(z)]dz$$

$$\gamma = \int_{-10\sigma}^{10\sigma} [P_{zz}(z) - \frac{1}{2}(P_{xx}(z) + P_{yy}(z))]dz$$

Surface tension is very sensitive to the **cut-off radius** of the LJ potential. Rule of thumb: $r_c \geq 6\sigma$ to avoid dependency on r_c.
N molecules > 1000

Antonin Marchand, Joost H. Weijs, Jacco H. Snoeijer, Bruno Andreotti, Am. J. Phys. **79**, 999 (2011).

Temperature dependence of density profiles and surface tension

Ultra-thin Lennard-Jones film:

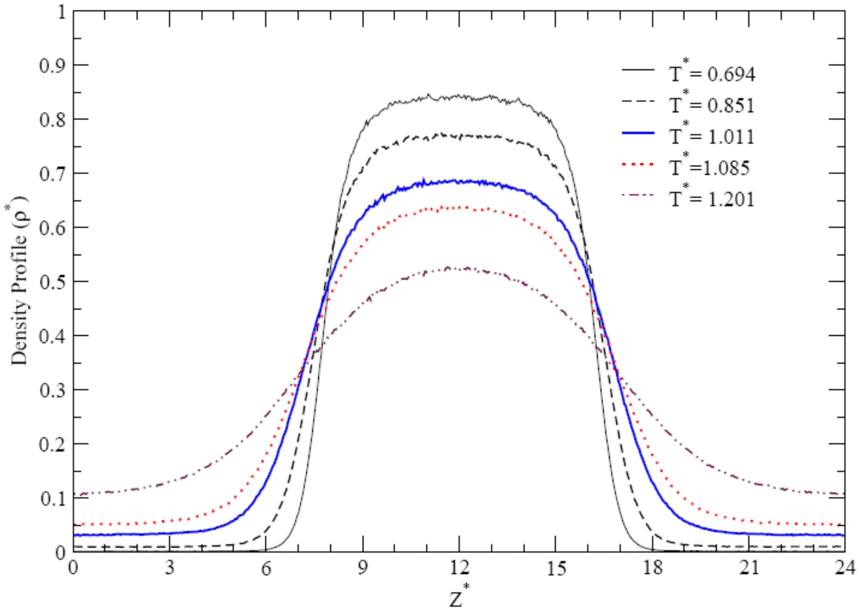


Figure 5.13: Density profiles at various temperatures

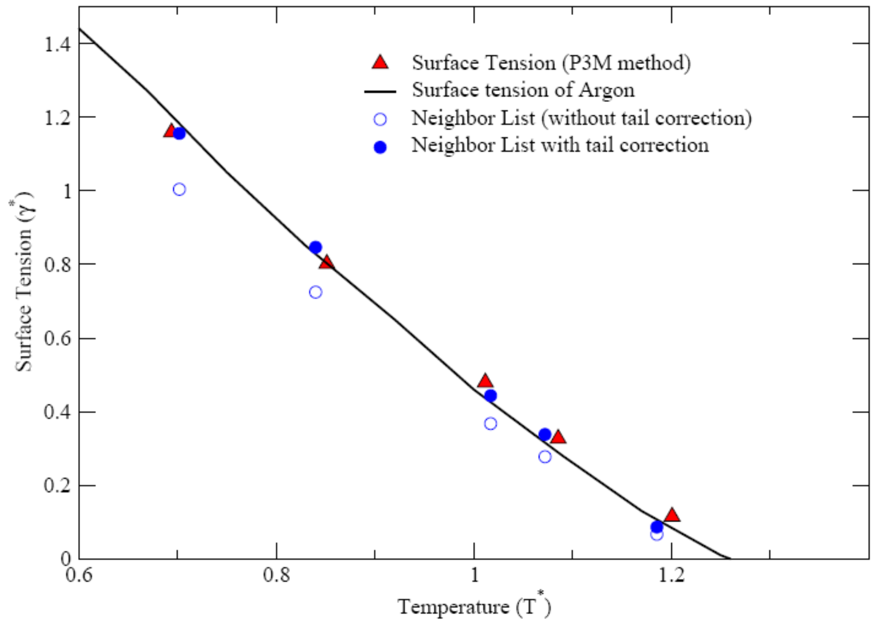
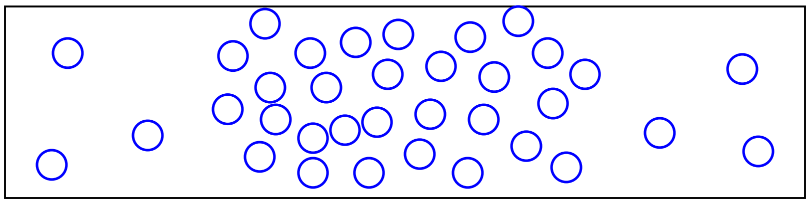


Figure 5.15: Comparison of the surface tension



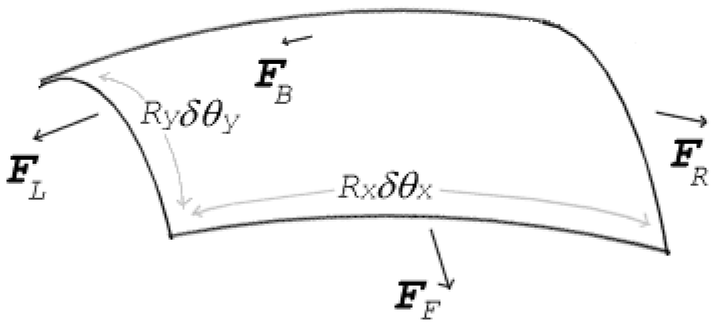
$$\gamma = \int_{0\sigma}^{24\sigma} [P_{zz}(z) - \frac{1}{2}(P_{xx}(z) + P_{yy}(z))]dz$$

and then divided by 2 interfaces

Etomica module: Interfacial tension

Ph.D. thesis by Shashank Sinha, 2004. UCLA. Molecular Dynamics Simulation of Interfacial Tension and Contact Angle of Lennard-Jones Fluid

Laplace pressure or why do soap bubbles break?



Surface tension forces acting on a tiny (differential) patch of surface. $\delta\theta_x$ and $\delta\theta_y$ indicate the amount of bend over the dimensions of the patch. Balancing the tension forces with pressure leads to the Young-Laplace equation:

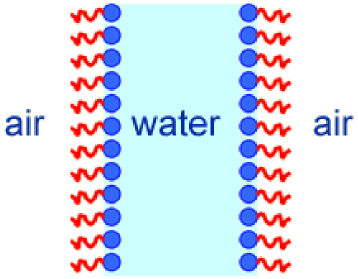
$$\Delta P = \gamma\left(\frac{1}{R_x} + \frac{1}{R_y}\right)$$

where R_x and R_y are radii of curvature in each of the axes that are parallel to the surface, γ is the surface tension, and ΔP is the pressure difference across the interface.

For a spherical bubble R_1 is being equal to R_2 and the Laplace pressure difference becomes

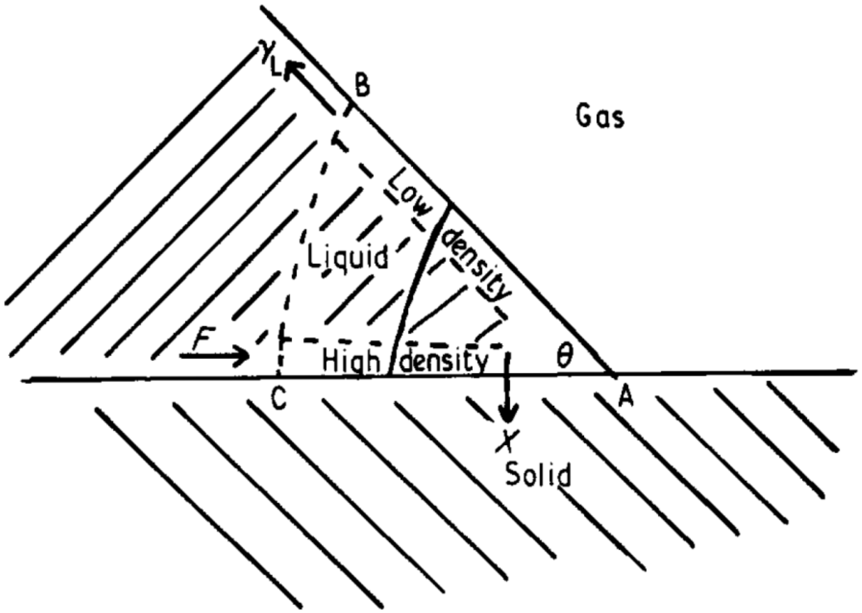
$$\Delta P = \frac{4\gamma}{R}$$

Pressure inside the bubble is equal to the atmospheric pressure plus the Laplace pressure (note 2 interfaces!)



Surfactants lower surface tension of water, increase elasticity and reduce evaporation. Bubbles last longer on a rainy day: reduced evaporation.

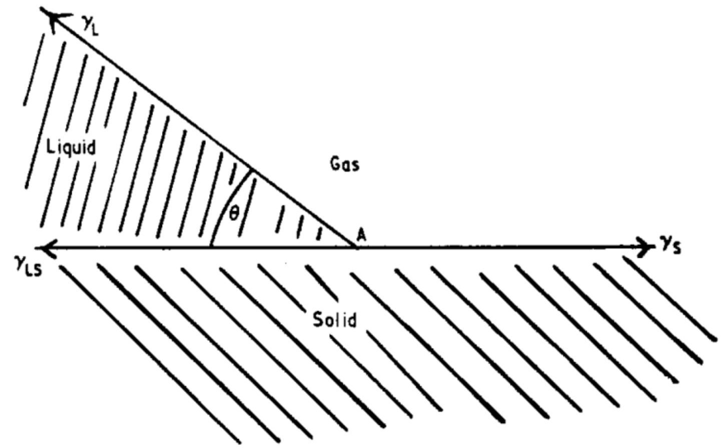
The contact angle and surface energies (gas, liquid, solid)

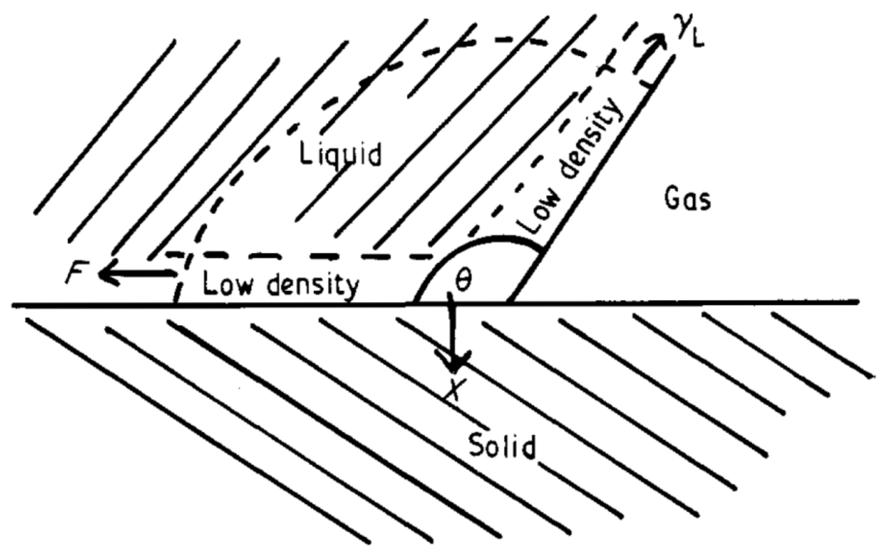


Forces on fluid near line of contact in 'wetting' case.

$$F = \gamma_S - \gamma_{LS} \qquad X = \gamma_L \sin\theta$$

$$\gamma_L \cos\theta = F = \gamma_S - \gamma_{LS}$$





Forces on fluid near line of contact in 'non-wetting' case.

Young's law: Thomas Young (1773-1829)

The molecular mechanism of surface tension. M. V. Berry 1971 Phys. Educ. 6, 79

Summary

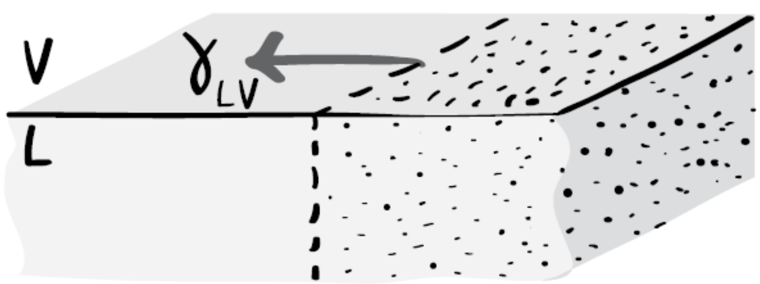
$$P_{\alpha\beta}V = \sum_i m v_\alpha^i v_\beta^i + \sum_i \sum_{j>i} r_\alpha^{ij} F_\beta(r^{ij})$$

$\alpha = \text{x, y, or z}$ and $\beta = \text{x, y, z}$

$$\begin{pmatrix} P_{xx} & P_{xy} & P_{xz} \\ P_{yx} & P_{yy} & P_{yz} \\ P_{zx} & P_{zy} & P_{zz} \end{pmatrix}$$

At equilibrium, only diagonal elements are non zero.

($P_{\alpha\beta}$ = Microscopic Pressure-Stress Tensor)



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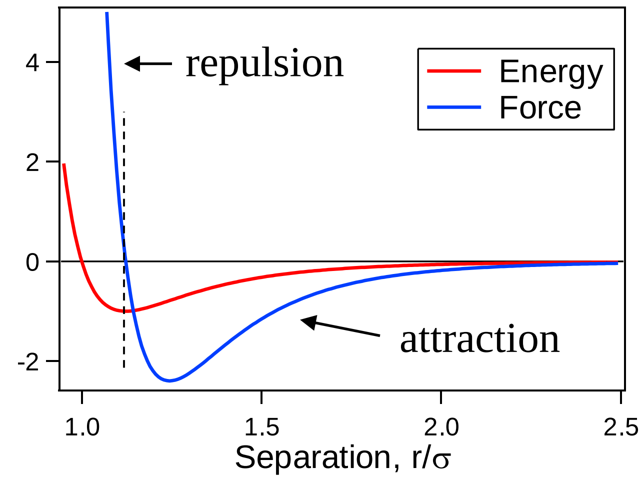

Surface tension a force per unit length parallel to the liquid-vapor interface.

Surface tension:

$$\gamma = \int [P_N(z) - P_T(z)]dz$$

$$\gamma = \int_{-10\sigma}^{10\sigma} [P_{zz}(z) - \frac{1}{2}(P_{xx}(z) + P_{yy}(z))]dz$$