Non-Newtonian
Fluid Dynamics
Research Group

MASSACHUSETTS
INSTITUTE OF
TECHNOLOGY

Surface Tension of Polymers

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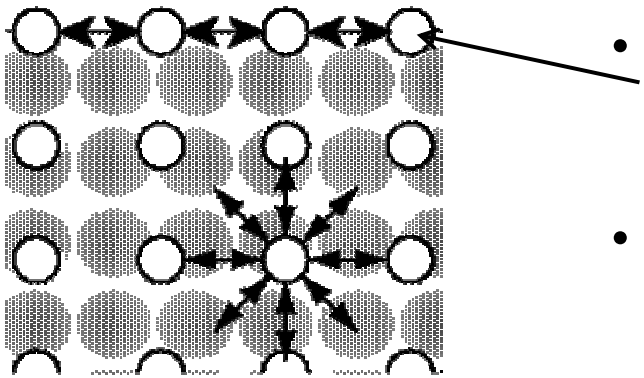
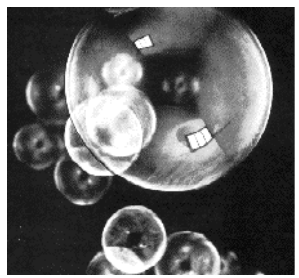
Physical origin of surface tension/surface energy



- "Unhappy" molecules at the surface: they are missing half their attractive interactions
- Unbalanced forces for the molecules at the surface lead to additional energy
- The additional free energy at the surface is known as *surface energy*
- This is the fundamental reason behind liquids adjusting their shapes to expose the smallest possible area

Examples of "minimal surfaces"

full dry hair vs. sticky wet hair



www.fairfied.edu

spherical shape of bubbles

Jose Bico, *Nature*, 2004

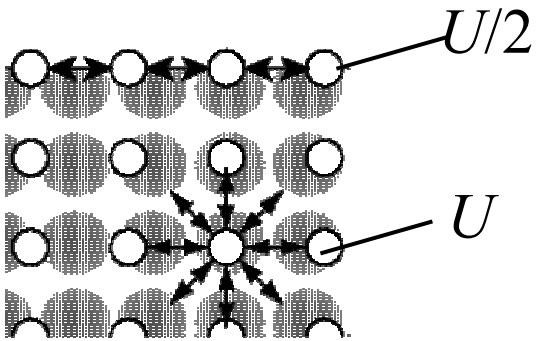
Mechanical definition: as a surface energy

Supply of energy is necessary to create surfaces

γ = specific free energy or surface tension (mJ/m^2)

Specific surface energy of a material is the excess energy per unit area due to the existence of the free surface

Estimation of surface tension based on intermolecular forces



U is the cohesion energy per molecule inside the liquid

Energy shortfall for a molecule sitting at the surface ~ $U/2$

a is the size of a molecule; a^2 is the exposed area of a molecule

Surface tension is then of order $\gamma \cong \frac{U}{2a^2}$ For van der Waals type interactions, $U \cong kT$

At a temperature of 25 °C, kT is equal to 1/40 eV, which gives γ = 20 mJ /m^2

(close to actual value for oils and alcohols)

Surface tension of a few common liquids in mJ/m^2

Helium (4 K)	Ethanol	Acetone	Glycerol	Water	Water (100°C)	Molten glass	Mercury
0.1	23	24	63	73	58	~300	485

hydrogen bonding

$U \approx 1$eV
strongly cohesive liquid

Mechanical definition: as a capillary force

Surface tension (γ) can also be viewed as a force per unit length (mN/m or N/m)

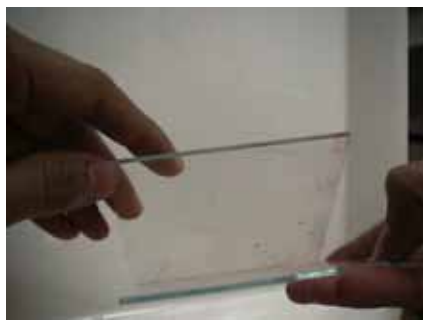
The term "surface tension" is tied to the concept that the surface stays under a tension

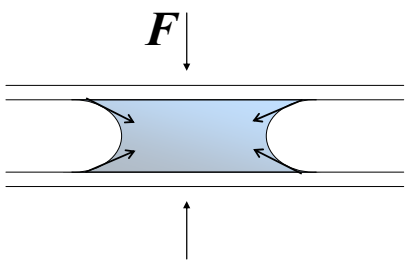
Examples where surface tension manifests itself as force

1) Slider

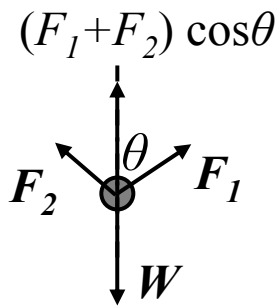
$$F\,dx = 2\gamma\,l\,dx$$

2) Capillary adhesion





3) Objects on water



end view of the leg

$F_1=F_2=\gamma l$

Contents

Relationship of surface tension with other material properties

Derivation of surface tension theoretically from knowledge of intermolecular forces

1) Surface energy of polymer liquids and melts

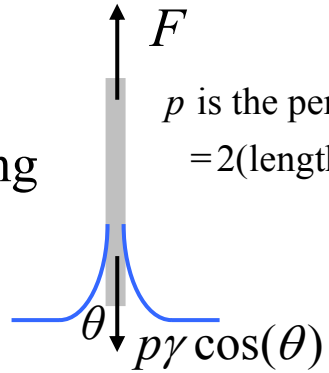
2) Surface energy of solid polymers

3) Interfacial tension between a solid and a liquid

1. Surface energy of liquids and melts

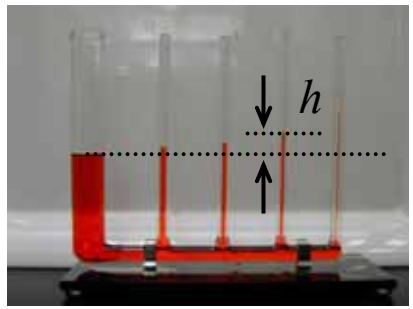
Existing methods for determining the surface tension of liquids

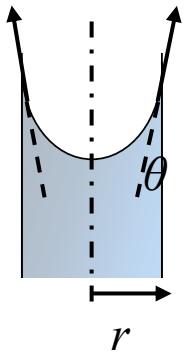
1) Wilhelmy's method, in which one dips a thin plate or ring in the liquid and measures the capillary force acting on the plate



p is the perimeter of the plate
= 2(length + width)

2) The rise of a liquid in a small capillary tube

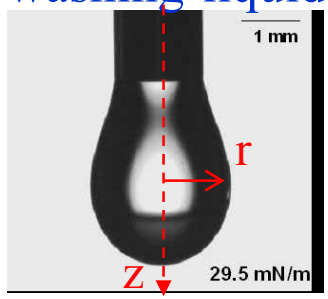


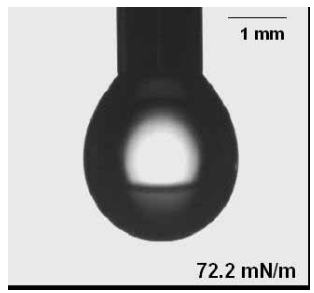


3) The method of drops, in which one characterizes the shape of drops

$$\gamma C = \rho g z$$

$$C = -\frac{r_{zz}}{\left(1+r_z^2\right)^{3/2}} + \frac{1}{r\left(1+r_z^2\right)^{1/2}}$$





Estimation of surface tension from related properties

Since the surface tension is a manifestation of intermolecular forces, it may be expected to be related to other properties derived from intermolecular forces, such as work of cohesion internal pressure, and compressibility.

1) Relationship between work of cohesion and surface tension (Grunberg 1949)

V = molar vol.; V/N_A = molecular vol.; $\left(\frac{N_A}{V}\right)^{2/3}$ = molecules/unit surf. area;

$$W_{coh} = 2\gamma N_A^{1/3} V^{2/3}$$

γ = surf. energy per unit area; $\gamma V^{2/3} / N_A^{2/3}$ = surface energy per molecule;

$\gamma N_A^{1/3} V^{2/3}$ = molar surf. energy; $2\gamma N_A^{1/3} V^{2/3}$ = work of cohesion;

2) Relationship between surface tension and solubility parameter (Hildebrand 1950)

$$\delta = 4.1\left(\frac{\gamma}{V^{1/3}}\right)^{0.43} \text{(cgs units)}$$

$\gamma / V^{1/3} \sim$ molar surf. energy$/V = \Delta E_v / V = \delta^2$;

ΔE_v is the energy of vaporization; δ is the solubility parameter;

3) Relationship between compressibility and surface tension (McGowan 1967)

$$\kappa\gamma^{3/2} = 1.33 \times 10^{-8} \text{(cgs units)}$$

$\kappa \uparrow \rightarrow \gamma \downarrow$

Introduction to parachor

Macleod *et* al. (*Trans. Faraday So.*, **1923**, *19*, 38)

$$\gamma = C(D-d)^4$$

valid for different compounds and at different temperatures

γ is the surface tension, D and d are the density of liquid and vapor at same temperature. C is a a characteristic constant for a given liquid.

Sugden S. *J.* (*Chem. Soc.*, **1924**, *125,* 1177)

Unit of P_s $(cm^3/mol)\times(erg/cm^2)^{1/4}$ or $(m^3/mol)\times(mJ/m^2)^{1/4}$

$$P_s = C^{1/4}M = \frac{M}{D-d}\gamma^{1/4}$$

at low temperature, d becomes small

molecular volume V

P_s for different substances is a comparison of molecular volumes at temperatures at which liquids have the same surface tension

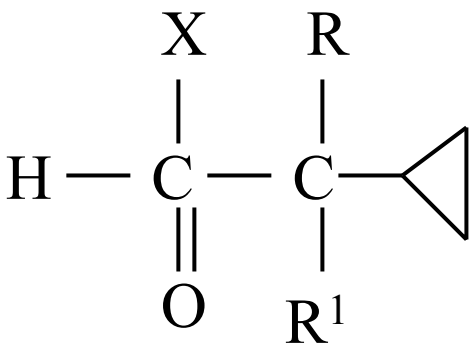
$$P_s = 0.78V_c$$

P_s bears an constant ratio to the critical volume, which suggests that it is a true measure of the molecular volume

P_s is called parachor (from $\pi\alpha\rho\alpha$ = by the side of, and $\chi o\rho o\varsigma$ = space to signify comparative volumes)

Useful properties of parachor

P_s is only a function of chemical composition and it is an **additive function**



From experimental data for P_s, it is found that

- P_s can be reproduced by adding together two sets of constants, one for the atoms in the molecule, the other for the unsaturation or ring closure.
- The values for a particular atom is independent of the manner in which it is situated
- The values for individual element are same from compound to compound.

The molecular parachor is a useful means of estimating surface tensions

$$\gamma = \left(\frac{P_s}{V} \right)^4$$

M is the molecular weight, V is the molar volume, ρ is the density. If the group contributions of P_s and V are known, γ results from the above expression

Atomic and structural contributions to the parachor

Deduction of atomic constants:
Difference for CH_2 in paraffins, esters, ethers, and ketones has a mean value of 40.0

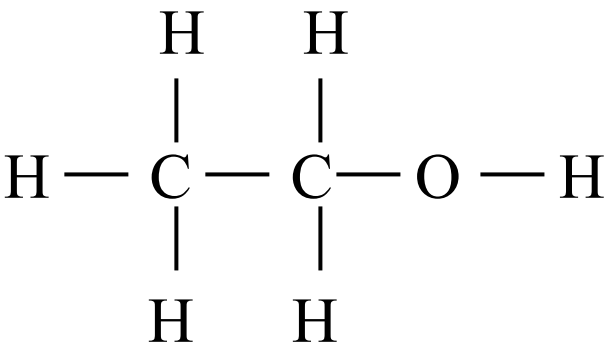
Subtracting $n$$CH_2$ from a series of values for the paraffins C_nH_{2n+2}, values for 2H can be calculated

Unit	Value
CH_2	40.0
C	9.0
H	15.5
O	19.8
O_2 (in esters)	54.8
N	17.5
S	49.1
F	26.1
Cl	55.2

Unit	Value
Br	68.0
I	90.3
Double bond	16.3–19.1
Triple bond	40.6
Three-membered ring	12.5
Four-membered ring	6.0
Five-membered ring	3.0
Six-membered ring	0.8
Seven-membered ring	4.0

Quayle O.R. Chem. Revs. 53 (1953) 439

Example: ethanol



Unit	Contribution to parachor
O	19.8
C	9.0
H	15.5

$$P_s = 1\times 19.8 + 6\times 15.5 + 2\times 9 = 130.8\,(\mathrm{cm^3/mol})\times(\mathrm{erg/cm^2})^{1/4}$$

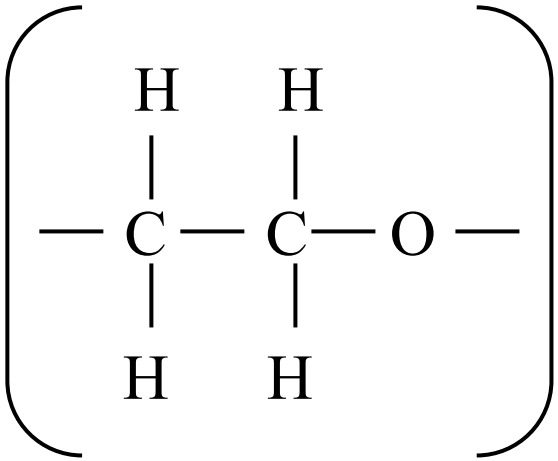
$$\rho = 0.789\,\mathrm{g/cm^3};\; M = 46\,\mathrm{g/mol}$$

$$V = \frac{M}{\rho} = 58.3\ \mathrm{cm^3/mol}$$

$$\gamma = \left(\frac{P_s}{V}\right)^4 = \left(\frac{130.8}{58.3}\right)^4 = (2.24)^4 = 25.3\ \mathrm{erg/cm^2}\ \text{or}\ 25.3\,\mathrm{mJ/m^2}$$

close to the actual value of 24 mJ/m^2

Example: poly (ethylene oxide)



Unit	Contribution to parachor
O	19.8
C	9.0
H	15.5

$$P_s = 1\times 19.8 + 4\times 15.5 + 2\times 9 = 99.8\,(\mathrm{cm^3/mol})\times(\mathrm{erg/cm^2})^{1/4}$$

$$\rho = 1.12\,\mathrm{g/cm^3};\; M = 44\,\mathrm{g/mol}$$

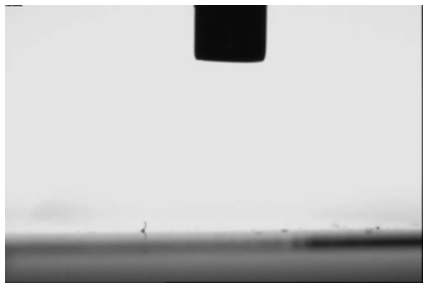
$$V = \frac{M}{\rho} = \mathrm{cm^3/mol}$$

$$\gamma = \left(\frac{P_s}{V}\right)^4 = \left(\frac{99.8}{39.28}\right)^4 = (2.54)^4 = 41.6\ \mathrm{erg/cm^2}\ \text{or}\ 41.6\,\mathrm{mJ/m^2}$$

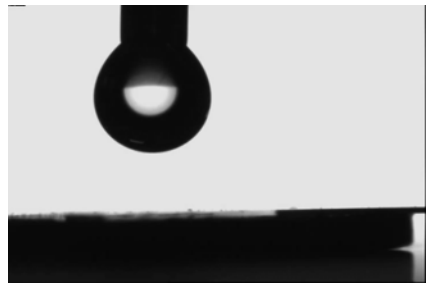
close to the actual value of 43 $\mathrm{mJ/m^2}$

Contact between solids and liquids

Solid/liquid pair

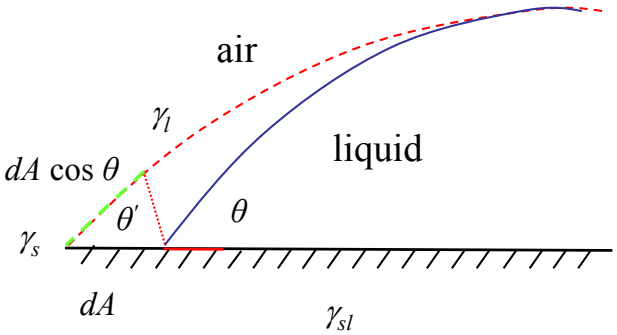


wetting



partially wetting

non-wetting



Change in Gibbs free energy dG when the drop spreads an infinitesimal amount

$$dG = \gamma_{sl}dA - \gamma_s dA + \gamma_l dA\cos\theta$$

At equilibrium $dG/dA = 0 \rightarrow \gamma_{sl} - \gamma_s + \gamma_l\cos\theta = 0$

$$\cos\theta = \frac{\gamma_s - \gamma_{sl}}{\gamma_l}$$

γ_l and θ are directly measurable;
γ_s and γ_{sl} are not

wetting behavior dependent on interfacial and solid surface energy as well

2. Surface tension of solid surfaces (γ_s)

Methods for determining the surface tension of solids

a) By measuring the contact angle between the solid and liquid

b) By determining critical surface tension (γ_{cr}) according to Zisman (1964), with the assumption that $\gamma_{cr} \approx \gamma_s$

c) By extrapolating surface tension data of polymer melts to room temperature (Roe, 1965; Wu, 1969–71)

No direct method available for measurement of surface tension of solid polymers

2a. Estimation of solid surface energy from contact angle

$$\gamma_{sl} - \gamma_s + \gamma_l \cos\theta = 0$$

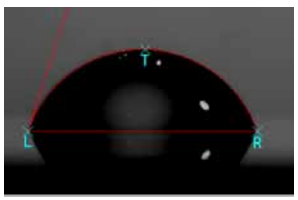
$$\gamma_{sl} = \gamma_s + \gamma_l - 2\Phi(\gamma_s\gamma_l)^{1/2}$$

$$\Phi = \frac{4(V_s V_l)^{1/3}}{\left(V_s^{1/3} + V_l^{1/3}\right)^2}$$

$$\gamma_s \approx \gamma_l \left(\frac{(1+\cos\theta)^2}{4\Phi^2} \right)$$

Girifalco and Good (1956)

Example: PMMA



68–72°

$$\rho_{PMMA} = 1.17\ \text{g/cm}^3;\ M_{PMMA} = 100.1\ \text{g/mol} \qquad V_{PMMA} = \frac{M_{PMMA}}{\rho_{PMMA}} = 86.5\ \text{cm}^3/\text{mol}$$

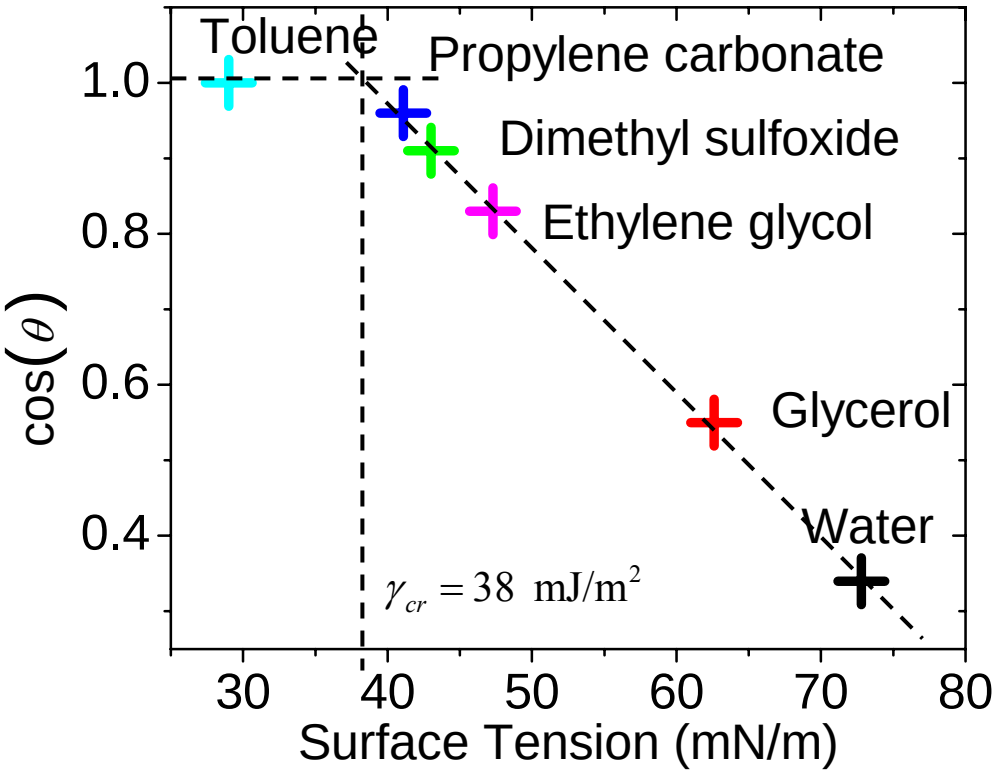
$$\rho_{H_2O} = 1\ \text{g/cm}^3;\ M_{H_2O} = 18\ \text{g/mol} \qquad V_{H_2O} = \frac{M}{\rho} = 18\ \text{cm}^3/\text{mol};\ \gamma_{H_2O} = 72\ \text{mJ/m}^2$$

$$\Phi = \frac{4(18\times 86.5)^{1/3}}{\left(18^{1/3} + 86.5^{1/3}\right)^2} = 0.93$$

$$\gamma_s \approx 72.8 \left(\frac{\left(1+\cos(69^\circ)\right)^2}{4\times 0.93^2} \right) \approx 38\ \text{mJ/m}^2$$

By means of the boxed equation, surface tension of solid surface can be calculated from measurements of contact angle and surface tension of liquid

2b. Determining solid surface tension using Zisman plot



Zisman plot for PMMA using various testing liquids

Zisman found that $\cos\theta$ is usually a monotonic function of γ_l

$$\cos\theta = a - b\gamma_l = 1 - \beta\left(\gamma_l - \gamma_{cr}\right)$$

γ_{cr} is called the "critical surface tension" of a solid and is a characteristic property of any given solid

Any liquid with $\gamma_l < \gamma_{cr}$ will wet the surface

It is found that critical surface tension is close to the solid surface tension of polymer

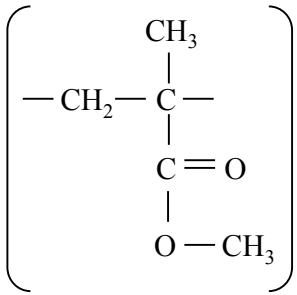
$$\gamma_s \approx \gamma_{cr}$$

2c. Estimation of γ from extrapolating data of polymer melt

Extrapolation of surface tensions of melts to room temperature leads to reliable values for solid polymers

Hence, surface tension of solid polymers may be calculated using $\gamma = \left(\frac{P_s}{V}\right)^4$

Example: PMMA



$$P_s = 8\times\mathrm{H} + 5\times\mathrm{C} + 2\times\mathrm{O} + 1\times\text{double bond}$$

$$P_s = 8\times 17.1 + 5\times 4.8 + 2\times 20 + 1\times 23.2$$

$$= 220.8\,(\mathrm{cm^3/mol})\times(\mathrm{erg/cm^2})^{1/4}$$

Unit	Contribution to parachor
O	20
C	9
H	17.1
Double bond	23.2

$$\rho = 1.17\,\mathrm{g/cm^3};\ M = 100.1\,\mathrm{g/mol}$$

$$V = \frac{M}{\rho} = 86.5\ \mathrm{cm^3/mol} \qquad \gamma = \left(\frac{P_s}{V}\right)^4 = \left(\frac{220.8}{86.5}\right)^4 = (2.55)^4$$

$$= 42.5\ \mathrm{erg/cm^2}\ \text{or}\ 42.5\,\mathrm{mJ/m^2}$$

Example: contact angle of water on PMMA

$$\cos\theta \approx 2\Phi\left(\frac{\gamma_s}{\gamma_l}\right)^{1/2} - 1 \qquad \Phi = \frac{4(V_s V_l)^{1/3}}{\left(V_s^{1/3} + V_l^{1/3}\right)^2}$$

$$\rho_{H_2O} = 1\,\text{g/cm}^3; M_{H_2O} = 18\,\text{g/mol}$$

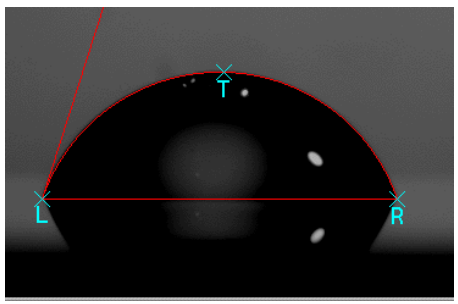
$$V_{H_2O} = \frac{M}{\rho} = 18\ \text{cm}^3/\text{mol};\ \gamma_{H_2O} = 72\,\text{mJ/m}^2$$

$$V_{PMMA} = 86.5\ \text{cm}^3/\text{mol};\ \gamma_{PMMA} = 42.5\ \text{mJ/m}^2$$

$$\Phi = \frac{4(18\times 86.5)^{1/3}}{\left(18^{1/3} + 86.5^{1/3}\right)^2} = 0.93$$

$$\cos\theta \approx 2\times 0.93\left(\frac{42.5}{72}\right)^{1/2} - 1 = 0.43$$

$$\theta = 65^{\circ}$$



contact angle of water on PMMA = 68–72 °

Temperature dependence of surface tension

1) Since the parachor P_s is independent of the temperature

$$\gamma = \left(\frac{P_s}{V} \right)^4$$

$$\gamma = \gamma(298) \left(\frac{\rho(T)}{\rho(298)} \right)^4$$

2) Guggenheim (1945) relationship

--surface tension of a liquid decreases with temperature

--surface tension vanishes at the critical point

$$\gamma = \gamma(0) \left(1 - \frac{T}{T_{cr}} \right)^{1+r}$$

r=2/9

T_{cr} is the imaginary critical temperature of the polymer

$$-\frac{d\gamma}{dT} = \frac{11}{9} \frac{\gamma(0)}{T_{cr}} \left(1 - \frac{T}{T_{cr}} \right)^{2/9}$$

for low values of T/T_{cr} , $d\gamma/dT$ will be constant

Molecular mass dependence of surface tension

The surface tension of homologous series tends to increase with increasing molecular weight

The bulk properties (e.g. heat capacity, tensile strength, specific volume etc.) vary linearly with the reciprocal of molecular weight

The surface tension, instead, varies linearly with $M_n^{-2/3}$

At infinite molecular weight, surface tension is finite, γ_∞

$$\gamma = \gamma_\infty - \frac{k_e}{\bar{M}_n^{2/3}}$$

k_e is a constant

Polymer	γ_∞	k_e
polyethylene	36	386
polystyrene	30	373
Polydimethylsiloxane	21	166
polyethylene oxide	43	343

3. Estimation of interfacial surface energy

The additional free energy at the interface between two condensed phases is known as interfacial energy

$$\gamma_{sl} - \gamma_s + \gamma_l \cos\theta = 0 \qquad \gamma_{sl} = \gamma_s + \gamma_l - 2\Phi(\gamma_s \gamma_l)^{1/2}$$

$$\Phi = \frac{4(V_s V_l)^{1/3}}{\left(V_s^{1/3} + V_l^{1/3}\right)^2}$$

eliminating γ_s

$$\gamma_{sl} = \gamma_l \left(\frac{(1+\cos\theta)^2}{4\Phi^2} - \cos\theta \right)$$

By means of this equation, interfacial tension can be calculated from measurements of contact angle and surface tension of liquid

Estimation of interfacial tension

Lorentz-Berthelot Mixing Rules

$$\frac{A_{ab}}{\left(A_{aa}A_{bb}\right)^{1/2}} = 1$$

A_{ab} = interaction energy between unlike molecules

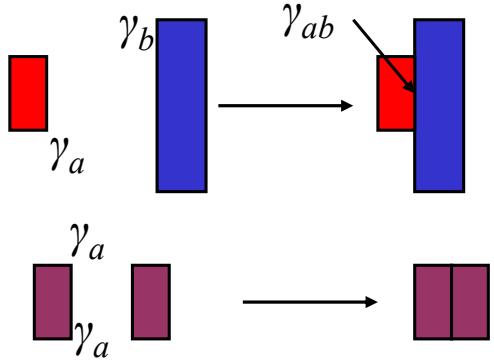
A_{aa}, A_{bb} = interaction energy between like molecules

Girifalco and Good (1956)

$$-\frac{\Delta F_{ab}}{\left(\Delta F_{aa}\Delta F_{bb}\right)^{1/2}} = \Phi$$

ΔF_{ab} = free energy of adhesion ΔF_{aa} = free energy of cohesion

Φ = interaction parameter



adhesion

$$\Delta F_{ab} = \gamma_{ab} - \gamma_b - \gamma_a$$

cohesion

$$\Delta F_{aa} = -2\gamma_a$$

$$\gamma_{ab} = \gamma_a + \gamma_b - 2\Phi(\gamma_a\gamma_b)^{1/2}$$

$$\Phi = \frac{4(V_sV_l)^{1/3}}{\left(V_s^{1/3} + V_l^{1/3}\right)^2}$$

General expression for the interfacial tension

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\Phi(\gamma_s\gamma_l)^{1/2}$$

Equation is only valid for substances interacting with additive dispersive forces and without hydrogen bonds. (Fowkes, 1964)

$$\gamma_{sl} \approx \left(\gamma_l^{1/2} - \gamma_s^{1/2}\right)^2$$ since $\Phi \approx 1$ for most polymers

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Fowkes has suggested that total free energy at a surface is the sum of contributions from the different intermolecular forces at the surface.

$$\gamma = \gamma^d + \gamma^a$$

d and *a* refer to the dispersion forces and a-scalar forces (the combined polar interactions: dipole, induction, and hydrogen bonding

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\left(\gamma_l^d\gamma_s^d\right)^{1/2}$$

for apolar liquids/solids

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\left(\gamma_l^d\gamma_s^d\right)^{1/2} - 2\left(\gamma_l^a\gamma_s^a\right)^{1/2}$$

Owens and Wendt extended the formulation

General expression for the interfacial tension

$$\gamma_{12} = \left[\left(\gamma_1^d\right)^{1/2} - \left(\gamma_2^d\right)^{1/2}\right]^2 + \left[\left(\gamma_1^a\right)^{1/2} - \left(\gamma_2^a\right)^{1/2}\right]^2$$

Substances 1 and 2 may either be liquids, or solids, or they may be a combination of a solid and a liquid

Liquid	γ_1	γ_1^d	γ_1^a
n-hexane	18.4	18.4	0
cyclohexane	25.5	25.5	0
glycol	48	33.8	14.2
methylene iodide	50.8	49.5	1.3
glycerol	63.4	37.0±4	26
water	72.8	21.8±0.7	51

Calculation of force components of surface tension

Liquid 1 (e.g. water): γ_1^a, γ_1^d

- Measure the surface tension of this liquid $(\gamma_1 = 72.3\ \mathrm{mJ/m^2})$
- Take another liquid (e.g. cyclohexane) which is immiscible with Liquid 1 and is apolar $(\gamma_2^a = 0;\ \gamma_2 = 25\mathrm{mJ/m^2};\rightarrow \gamma_2^d = 25\mathrm{mJ/m^2})$
- Measure the interfacial tension by one of the available methods $(\gamma_{12} = 50.2\ \mathrm{mJ/m^2})$
- Solve the following the two equations simultaneously

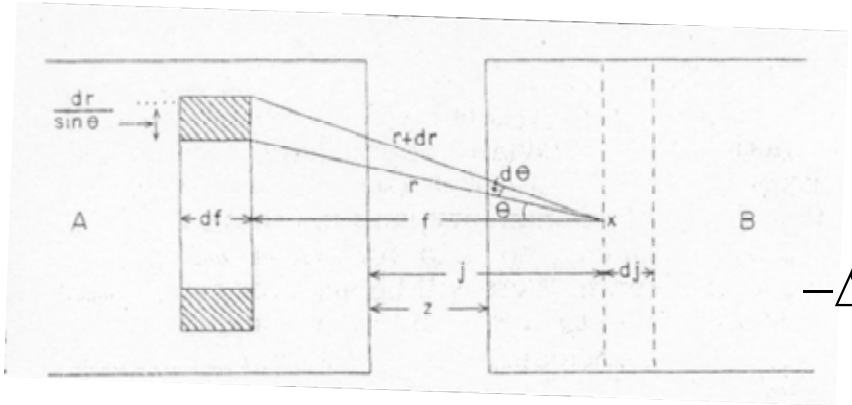
$$\gamma_{12} = \left[\left(\gamma_1^d\right)^{1/2} - \left(\gamma_2^d\right)^{1/2}\right]^2 + \left[\left(\gamma_1^a\right)^{1/2} - \left(\gamma_2^a\right)^{1/2}\right]^2 \qquad \gamma_1 = \gamma_1^d + \gamma_1^a$$

$$\gamma_{H_2O,ch} = 50.2 = 25 + 72 - 2\left(25\gamma_{H_2O}^d\right)^{1/2} \qquad \gamma_{H_2O}^d = 22.7, \gamma_{H_2O}^a = 72 - 22.7 = 49.3$$

Conclusions

- The specific energy of a polymer can be estimated by means of an additive quantity, the parachor
- It may be alternatively calculated from different related material properties e.g. cohesive energy, compressibility, solubility parameter
- Rules are given for the estimation of the interfacial tension and the contact angle of a liquid on a solid

Extra slides: estimation of Φ



$$F_{ab}(z) = 2\pi \int_z^\infty n_b d_j \int_j^\infty f\, df \int_f^\infty n_a \frac{\partial \varepsilon_{ab}}{\partial r} dr$$

$$-\Delta F_{ab}(z) = 2\pi \int_z^\infty dx \int_x^\infty n_b d_j \int_j^\infty f\, df \int_f^\infty n_a \frac{\partial \varepsilon_{ab}}{\partial r} dr$$

Carrying out the integrations and equating the net force to 0 when $z=d_{AB}$ (equilibrium distance)

$$\Delta F_{ab} = \frac{n_a n_b A_{ab}}{6 d_{ab}^2}\left(\frac{1}{2} - \frac{1}{m-4}\right)$$

$$\Delta F_{aa} = \frac{n_a^2 A_{aa}}{6 d_{aa}^2}\left(\frac{1}{2} - \frac{1}{m-4}\right)$$

$$-\frac{\Delta F_{ab}}{\left(\Delta F_{aa}\Delta F_{bb}\right)^{1/2}} = \Phi \longrightarrow \Phi = \frac{d_{aa} d_{bb}}{d_{ab}^2} \times \frac{A_{ab}}{\left(A_{aa} A_{bb}\right)^2}$$

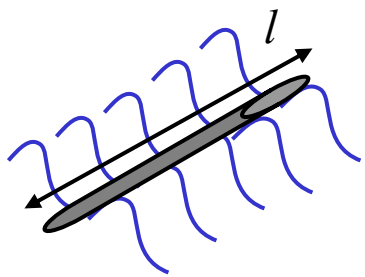
Lennnard-Jones potential $\varepsilon_{ab} = -\frac{A_{ab}}{r^6} + \frac{B_{ab}}{r^m}$

Interaction force $\frac{\partial \varepsilon_{ab}}{\partial r} = \frac{6A_{ab}}{r^7} - \frac{mB_{ab}}{r^{m+1}}$

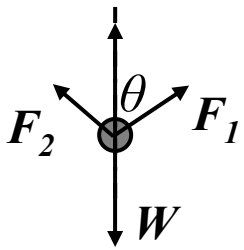
$$\Phi = \frac{4(V_s V_l)^{1/3}}{\left(V_s^{1/3} + V_l^{1/3}\right)^2}$$

Girifalco and Good (1956)

1) Floating needles



$(F_1+F_2)\cos\theta$



end view of needle

$F_1=F_2=\gamma l$