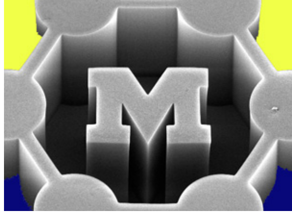
Nanomanufacturing
University of Michigan
ME599-002 | Winter 2010



07: **Intermolecular and surface forces**

February 3, 2010

John Hart
ajohnh@umich.edu
http://www.umich.edu/~ajohnh

Announcements

- …

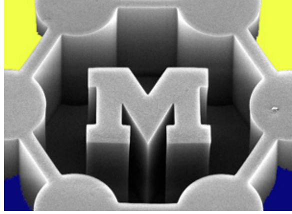
Recap: thermal properties

- Thermal energy in solids is carried by electrons and phonons

- Fourier's law (diffusive thermal transport) breaks down at small length scales and short times
  - Like electrical conductance, there is a quantum unit of thermal conductance
  - Quantized thermal conductance has been measured at VERY low temperatures in nanoscale structures, where the number of phonon modes is restricted
  - Ballistic phonon transport occurs in sub-micron length CNTs

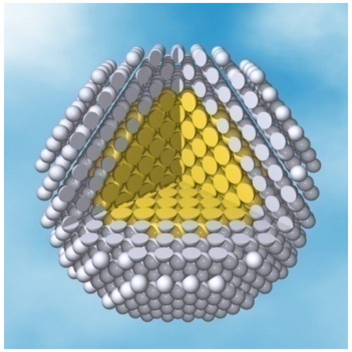
- Boundary scattering of phonons reduces thermal conductivity and governs interface conductance –this can be bad for contacts and good for thermoelectrics

Course outline



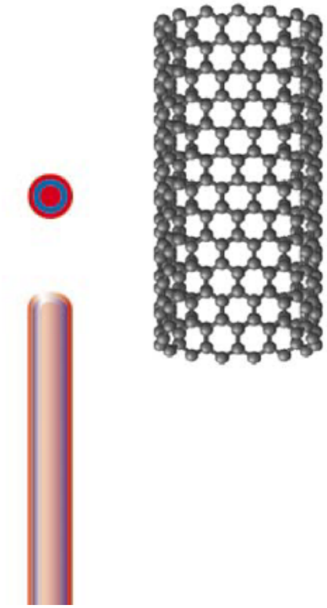
0: Introduction to nanotechnology

1: Properties of nanostructures (“building blocks”)



2: Interactions among nanostructures

3: Synthesis of nanostructures

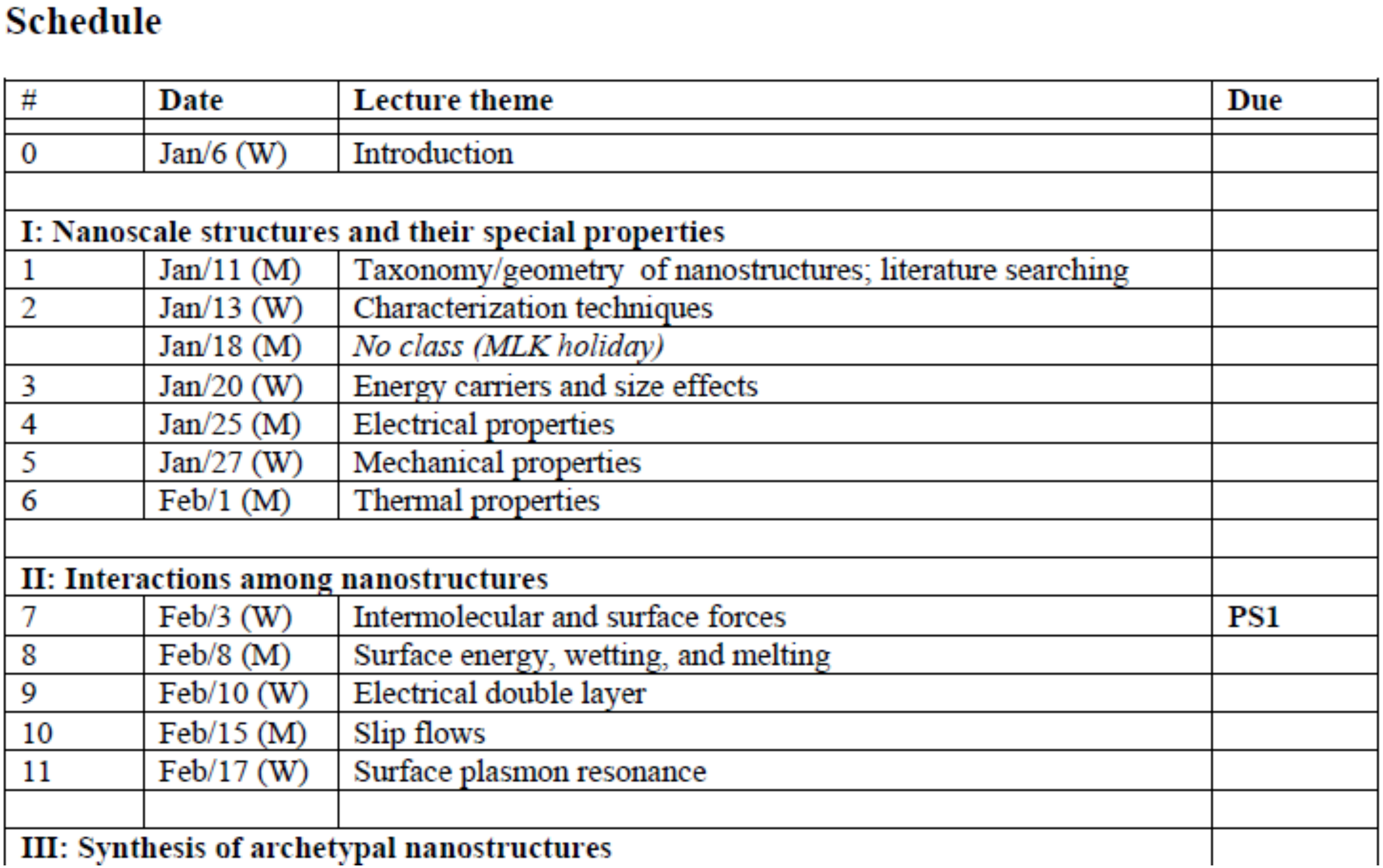


4: Assembly of nanostructures and property scaling

5: Case studies and project presentations

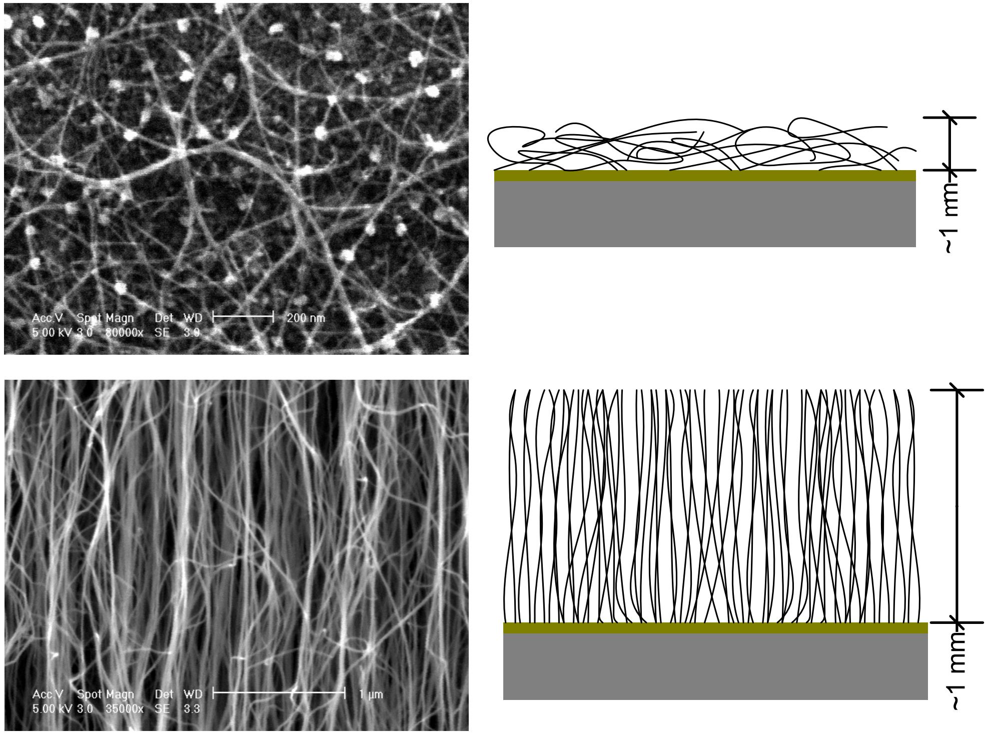
Assignments:

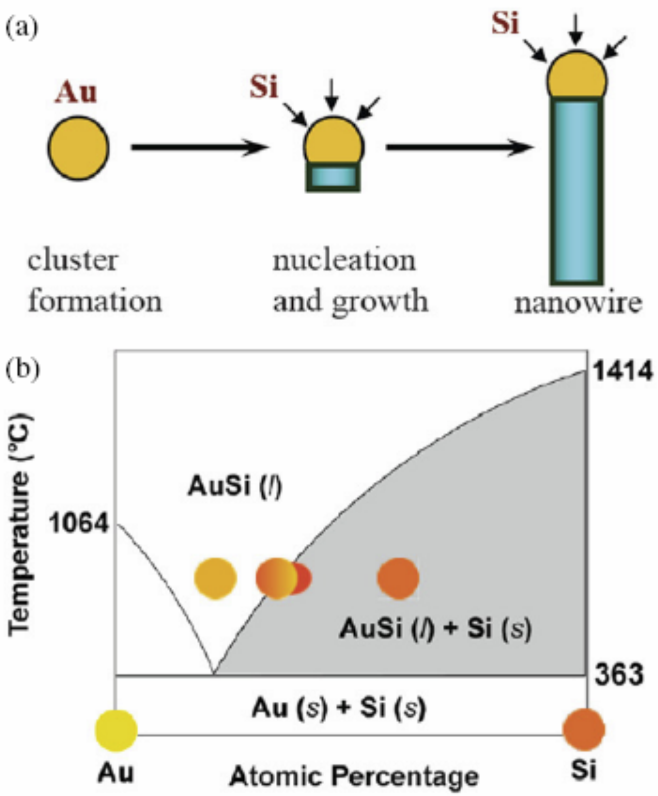
problem sets (4)
exam (1),
video assignment (1)
project (1)

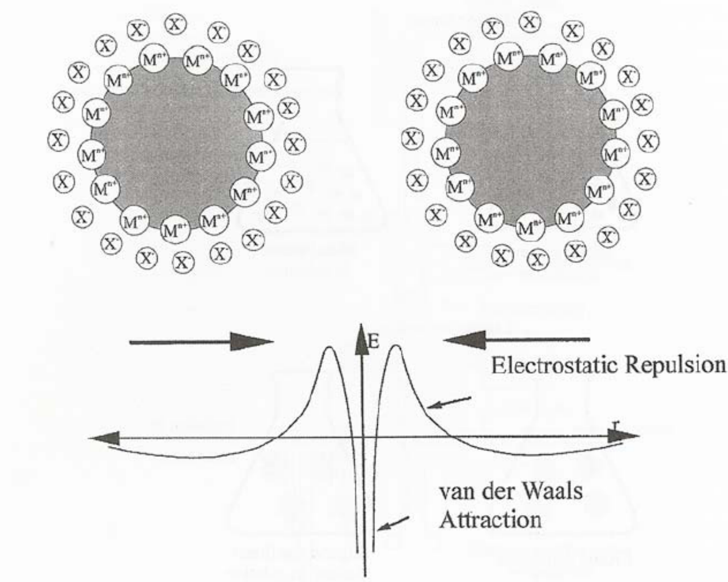


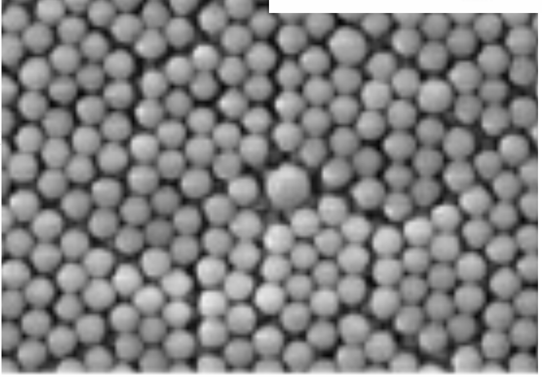
Schedule

#	Date	Lecture theme	Due
0	Jan/6 (W)	Introduction	
I: Nanoscale structures and their special properties			
1	Jan/11 (M)	Taxonomy/geometry of nanostructures; literature searching	
2	Jan/13 (W)	Characterization techniques	
	Jan/18 (M)	*No class (MLK holiday)*	
3	Jan/20 (W)	Energy carriers and size effects	
4	Jan/25 (M)	Electrical properties	
5	Jan/27 (W)	Mechanical properties	
6	Feb/1 (M)	Thermal properties	
II: Interactions among nanostructures			
7	Feb/3 (W)	Intermolecular and surface forces	**PS1**
8	Feb/8 (M)	Surface energy, wetting, and melting	
9	Feb/10 (W)	Electrical double layer	
10	Feb/15 (M)	Slip flows	
11	Feb/17 (W)	Surface plasmon resonance	
III: Synthesis of archetypal nanostructures			


Acc.V Spot Magn Det WD 200 nm
5.00 kV 3.0 80000x SE 3.9
~1 mm
Acc.V Spot Magn Det WD 1 μm
5.00 kV 3.0 35000x SE 3.3
~1 mm


(a)
Au
Si
Si
cluster formation
nucleation and growth
nanowire
(b)
Temperature (°C)
1414
1064
AuSi (l)
AuSi (l) + Si (s)
363
Au (s) + Si (s)
Au
Atomic Percentage
Si


X
M
E
r
Electrostatic Repulsion
van der Waals Attraction



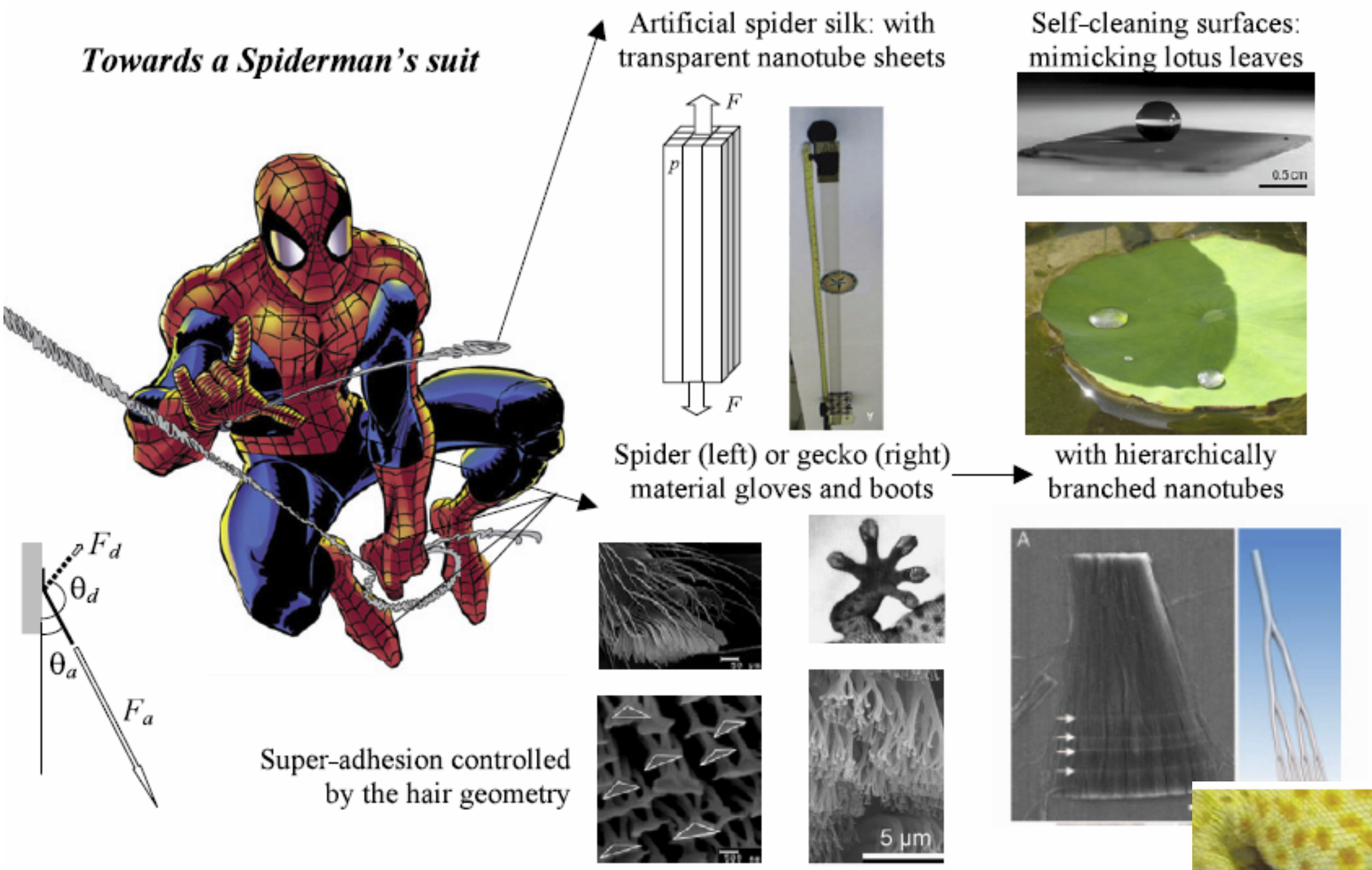


Figure 1. Spiderman (TM & © 2007 MARVEL.) must have large cobwebs and self-cleaning, superadhesive and releasable gloves and boots. Invisible large cables (Pugno 2006b) could be realized with nanotube bundles (related inset from (Zhang *et al* 2005)), whereas gloves and boots, mimicking spider (related inset from (Kesel *et al* 2004)) or gecko (related inset from (Gao *et al* 2005)) materials, with hierarchically branched nanotubes (related inset from (Meng *et al* 2005)) as suggested by our analysis. Note that the nanotube forest is superhydrophobic (water repellent) and thus self-cleaning (related inset from (Lau *et al* 2003)).

Pugno, J. Phys. Cond. Matt 19:395001, 2007.

Today's agenda

- Origin of intermolecular and surface forces
- Summation of forces between solid bodies, based on pairwise interaction potentials
- Calculation of van der Waals forces and adhesion forces for regular geometries
- Methods of measuring surface forces
- Adhesion in nature

Today's readings (ctools)

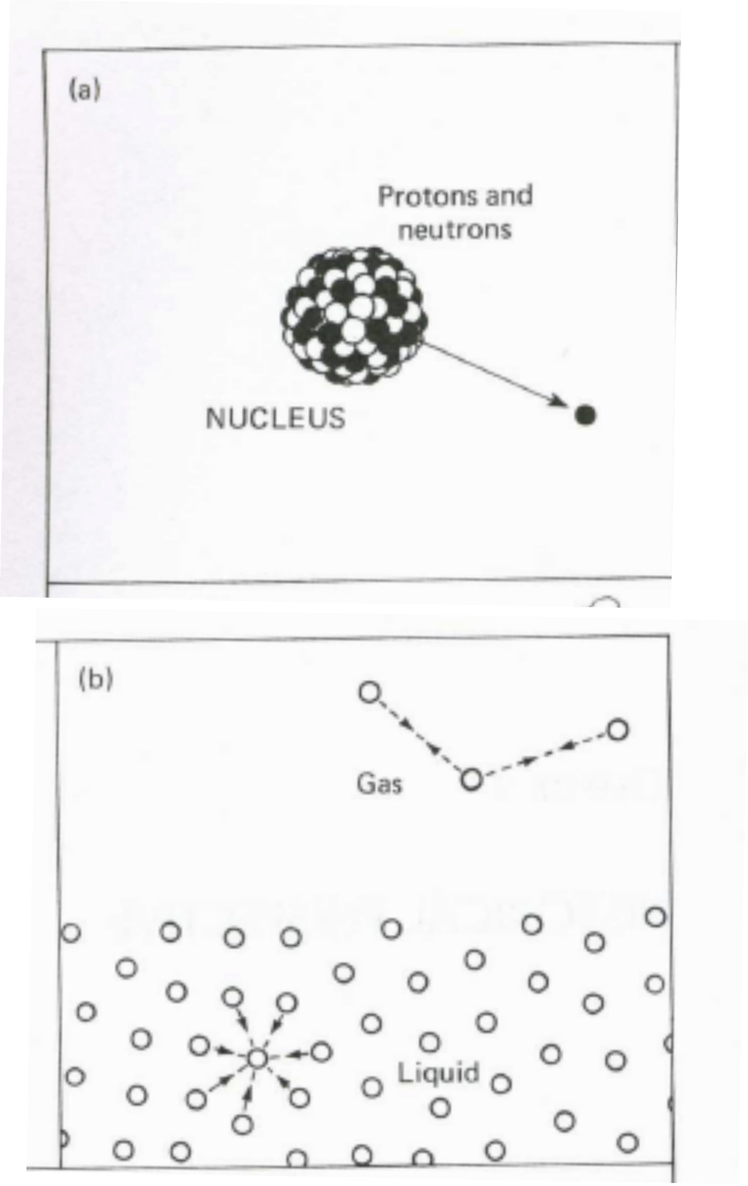
Nominal: (on ctools)

- Israelachvili, excerpts from Intermolecular and Surface Forces
- Arzt et al., "From micro to nano contacts in biological attachment devices"

Extras: (on ctools)

- Bishop et al., "Nanoscale forces and their uses in self-assembly"

Forces hold the universe together



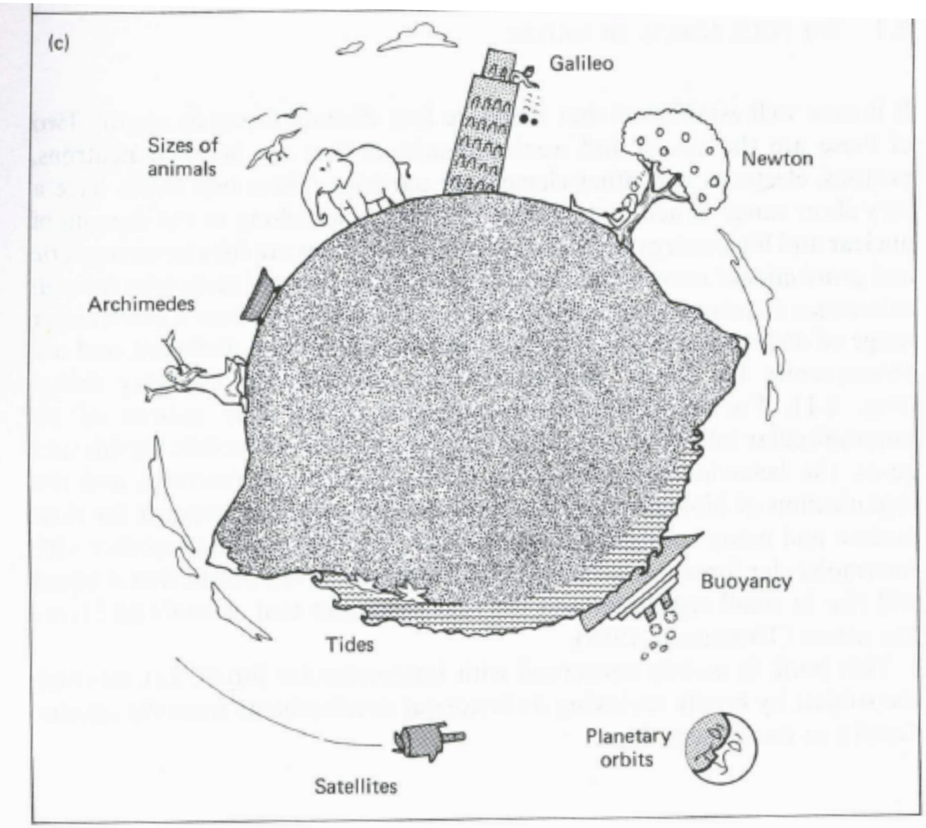


Fig. 1.1. The forces of nature. (a) Strong nuclear interactions hold protons and neutrons together in atomic nuclei. Weak interactions are involved in electron emission (β decay). (b) Electrostatic (intermolecular) forces determine the cohesive forces that hold atoms and molecules together in solids and liquids. (c) Gravitational forces affect tides, falling bodies and satellites. Gravitational and intermolecular forces acting together determine the maximum possible sizes of mountains, trees and animals.

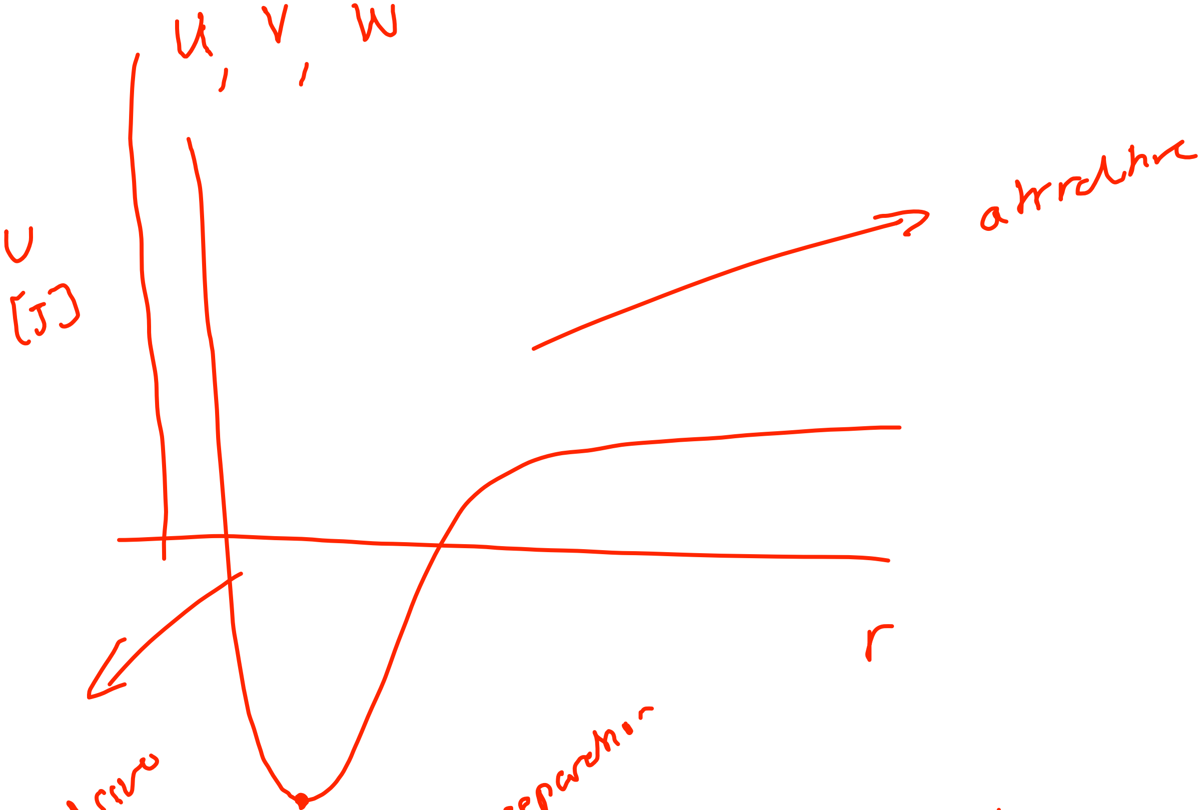
Israelachvili.

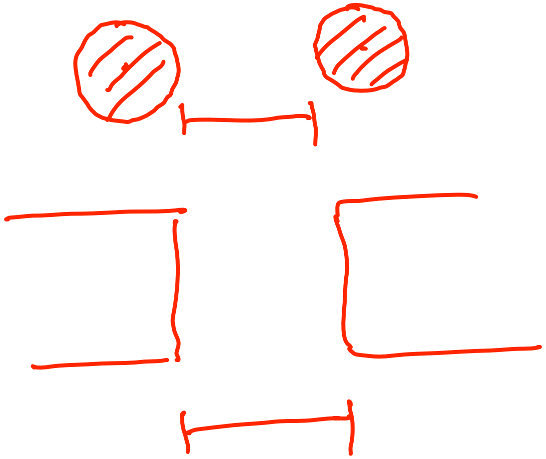
Classification of intermolecular forces

- **Electrostatic:** Coulomb force between charges, and permanent dipole-dipole interactions
- **Polarization:** Dipole moments induced in atoms by electric fields of nearby charges, and by permanent dipoles
- **Quantum mechanical:** give rise to chemical bonding

- **Short-range:** <1 nm (close to contact)
- **Long-range:** <100 nm

- **Exponent on the force law is always > 3 (i.e., $1/r^{>3}$)**, else interaction energy would increase for long distances and large bodies





$$U\,[J] : \frac{dU}{dr}\,[N]$$

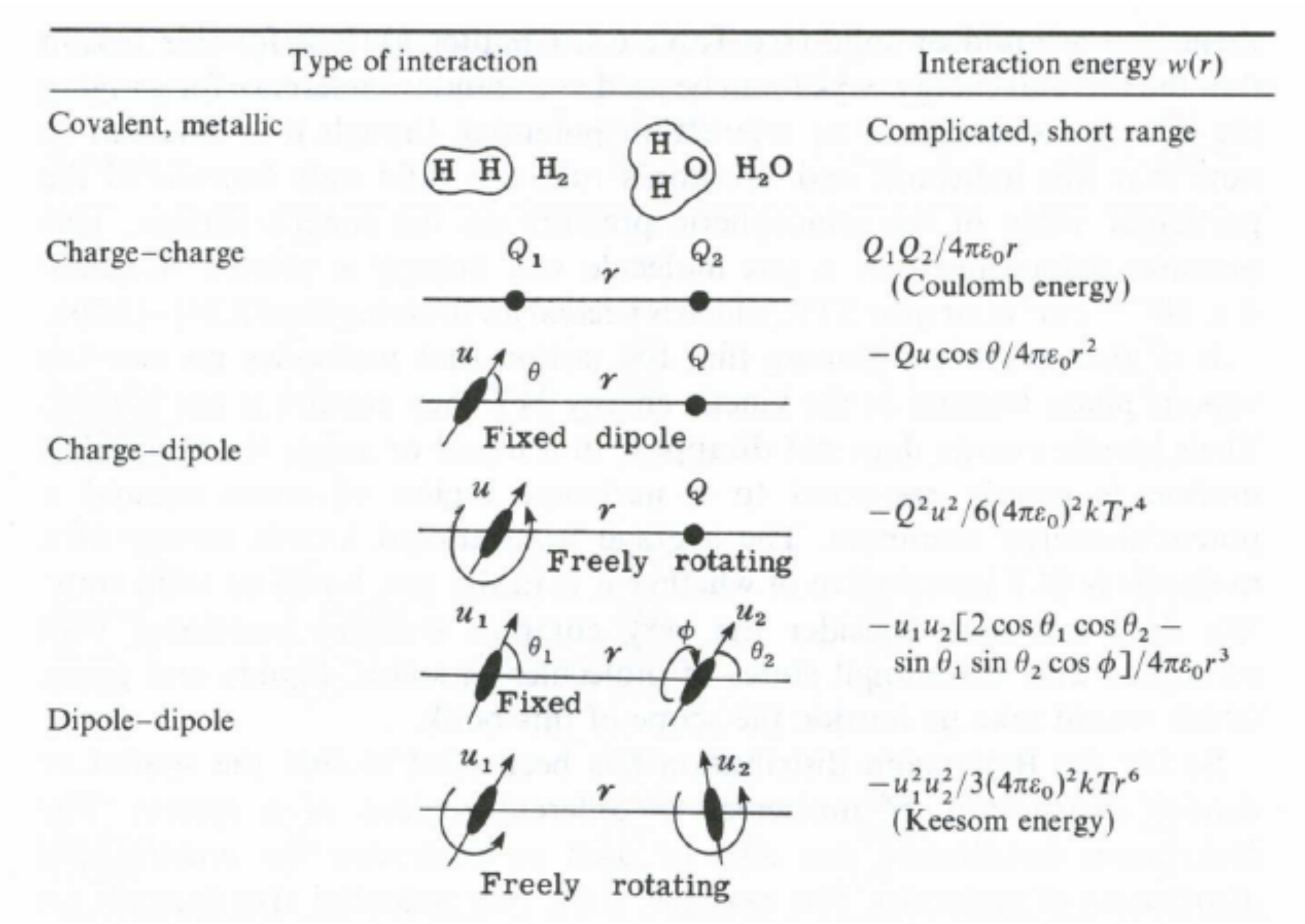
$$\frac{dU}{dz}$$

$$U = \frac{C}{r^n}, \quad n > 3$$

Mie

$$W(r) = \overbrace{-\frac{A}{r^n}}^{\text{attr}} + \overbrace{\frac{B}{r^m}}^{\text{repulsion}}$$

Atomic, ionic, and molecular interactions



Type of interaction	Interaction energy $w(r)$
Covalent, metallic	Complicated, short range
Charge–charge	$Q_1Q_2/4\pi\varepsilon_0 r$ (Coulomb energy)
Charge–dipole Fixed dipole	$-Qu\cos\theta/4\pi\varepsilon_0 r^2$
Charge–dipole Freely rotating	$-Q^2u^2/6(4\pi\varepsilon_0)^2kTr^4$
Dipole–dipole Fixed	$-u_1u_2[2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi]/4\pi\varepsilon_0 r^3$
Dipole–dipole Freely rotating	$-u_1^2u_2^2/3(4\pi\varepsilon_0)^2kTr^6$ (Keesom energy)

Quantum mechanical (bonding)

Electrostatic (charge-charge)

Polarization (charge-dipole, dipole-dipole)

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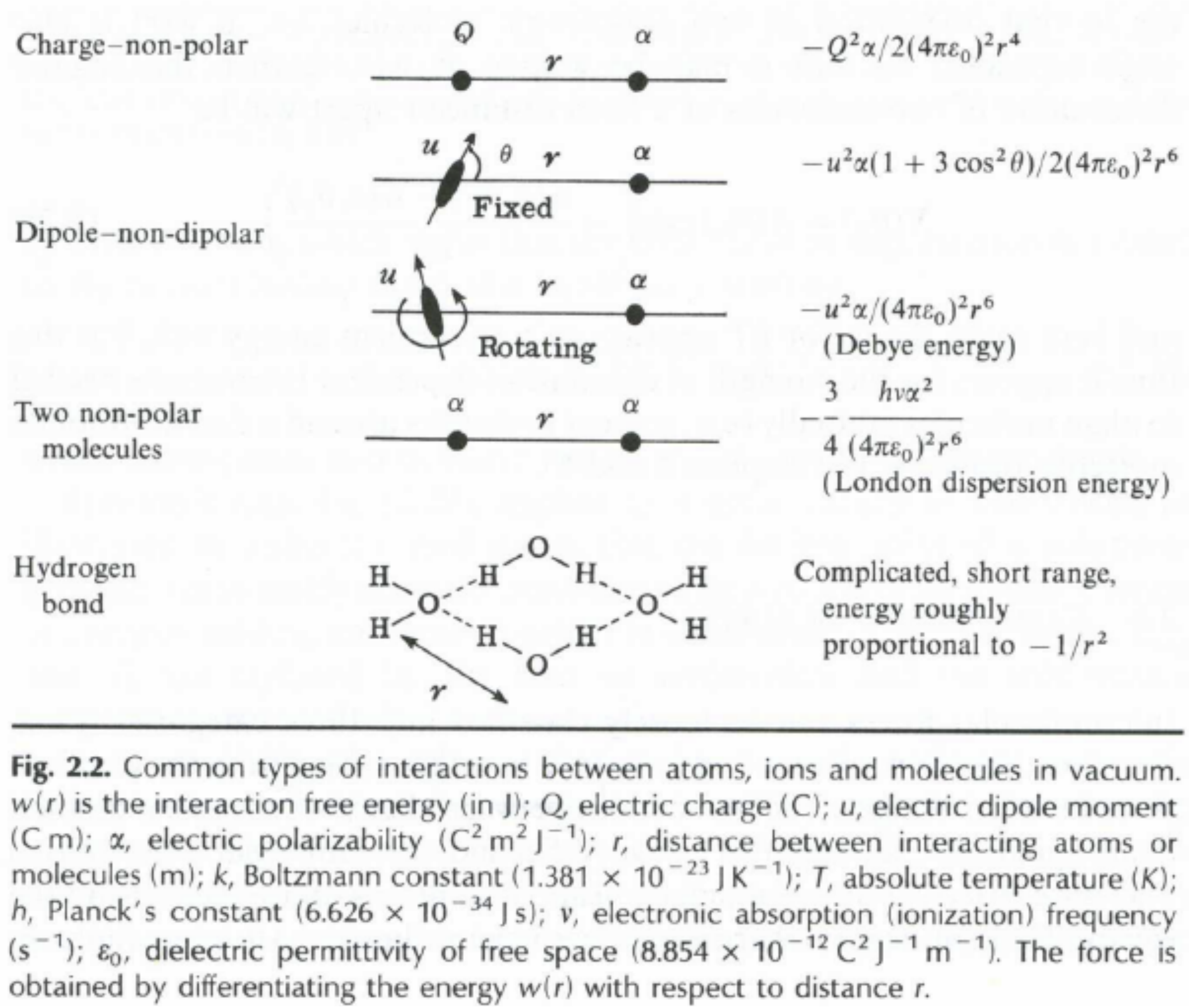


Charge–non-polar		$-Q^2\alpha/2(4\pi\varepsilon_0)^2r^4$
Dipole–non-dipolar	Fixed	$-u^2\alpha(1+3\cos^2\theta)/2(4\pi\varepsilon_0)^2r^6$
	Rotating	$-u^2\alpha/(4\pi\varepsilon_0)^2r^6$ (Debye energy)
Two non-polar molecules		$-\frac{3}{4}\frac{h\nu\alpha^2}{(4\pi\varepsilon_0)^2r^6}$ (London dispersion energy)
Hydrogen bond		Complicated, short range, energy roughly proportional to $-1/r^2$

Fig. 2.2. Common types of interactions between atoms, ions and molecules in vacuum. $w(r)$ is the interaction free energy (in J); Q, electric charge (C); u, electric dipole moment (C m); α, electric polarizability ($C^2 m^2 J^{-1}$); r, distance between interacting atoms or molecules (m); k, Boltzmann constant (1.381×10^{-23} J K^{-1}); T, absolute temperature (K); h, Planck's constant (6.626×10^{-34} J s); ν, electronic absorption (ionization) frequency (s^{-1}); ε_0, dielectric permittivity of free space (8.854×10^{-12} $C^2 J^{-1} m^{-1}$). The force is obtained by differentiating the energy $w(r)$ with respect to distance r.

Quantum mechanical (exclusion)

Israelachvili.

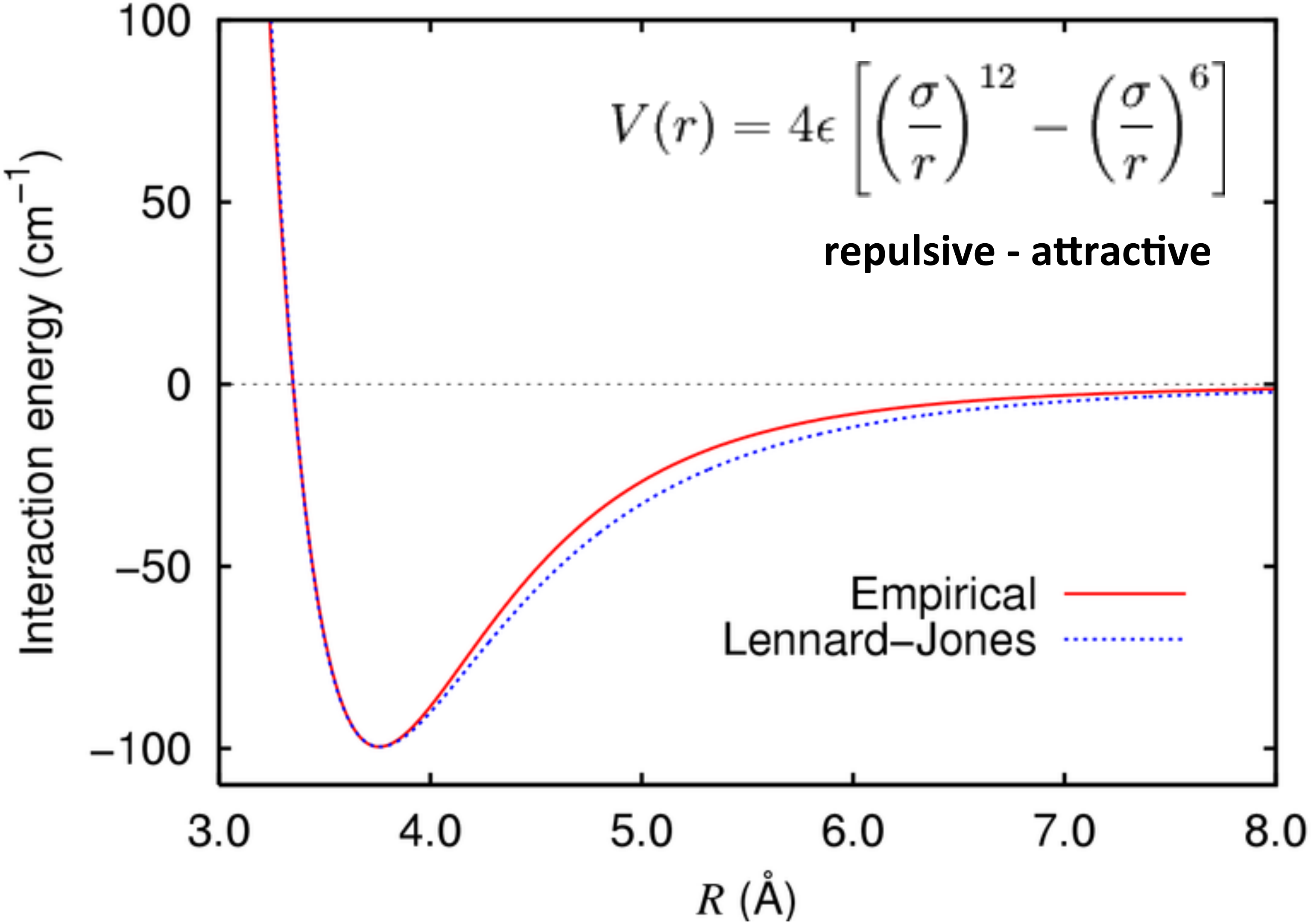
Definition of van der Waals (VDW) forces

The attractive or repulsive forces between molecular entities (or between groups within the same molecular entity) other than those due to bond formation or to the electrostatic interaction of ions (or ionic groups) with one another or with neutral molecules.

The term includes: **dipole–dipole**, **dipole–induced dipole** and **London** (instantaneous induced dipole–induced dipole) **forces**. The term is sometimes used loosely for the **totality of nonspecific attractive or repulsive intermolecular forces**.

Israelachvili; http://goldbook.iupac.org/V06597.html.

Lennard-Jones potential: neutral atoms or molecules



$$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

repulsive - attractive

Repulsive-attractive balance = colloid stability

http://en.wikipedia.org/wiki/Lennard-Jones_potential

Summing pairwise interactions

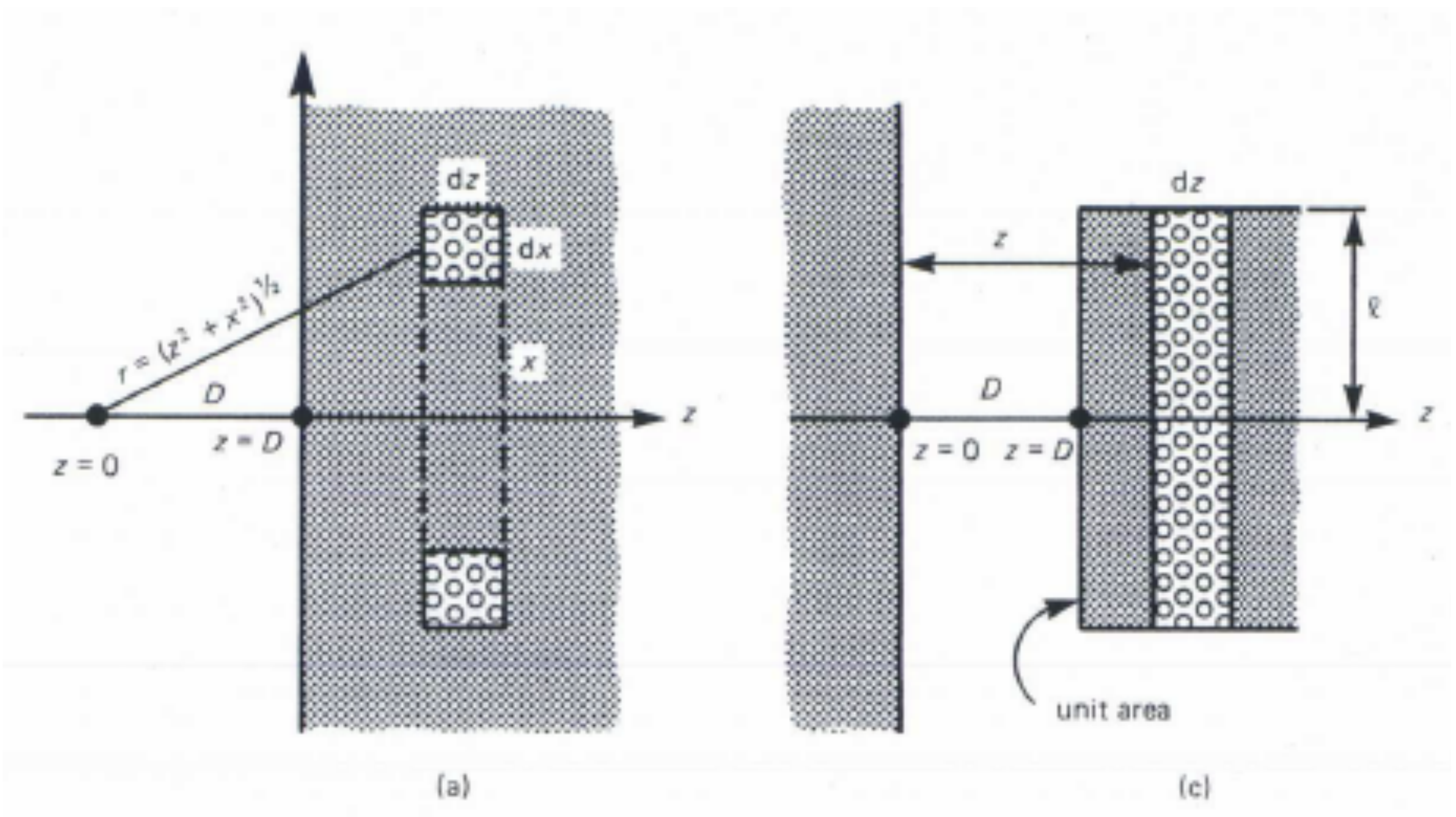


Fig. 10.2. Methods of summing (integrating) the interaction energies between molecules in condensed phases to obtain the interaction energies between macroscopic bodies. (a) Molecule near a flat surface or 'wall'. (b) Spherical particle near a wall ($R \gg D$). (c) Two planar surfaces ($l \gg D$).

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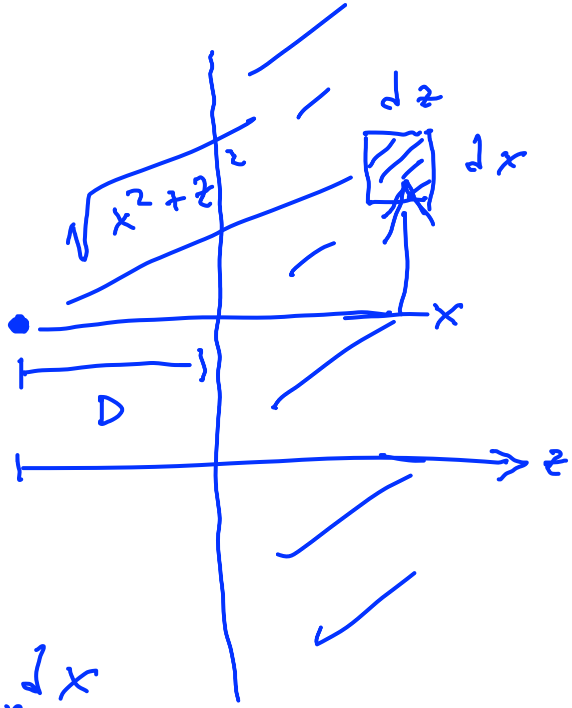
$$W = \int_{\forall} w \rho \, d\forall$$

\# particles / volume

$$w = -C/r^n \, , \quad r = \sqrt{x^2 + z^2}$$

$$d\forall = 2\pi \underline{x} \, dx \, dz$$



$$W = \int_{\forall} w \rho \, d\forall = \underline{-2\pi \rho C} \int_{D}^{\infty} dz \int_{0}^{\infty} \frac{x}{\left(\sqrt{x^2 + z^2}\right)^n} dx$$

$$= (x^2 + z^2)^{n/2}$$

$$\int \frac{x}{(x^2 + z^2)^{n/2}} dx = \frac{1}{(n-2)(x^2+z^2)^{n/2 - 1}}$$

$$W = -2\pi\rho C \int_0^\infty dz \left(\frac{1}{(n-2)(x^2+z^2)^{n/2-1}} \right)_0^\infty$$

$$\Downarrow$$

$$\frac{-1}{(n-2)(z^2)^{n/2-1}}$$

$$= z^{n-2}$$

$$W = \frac{2\pi\rho C}{n-2} \int_0^\infty \frac{1}{z^{n-2}} = \frac{2\pi\rho C}{n-2} \left(\frac{1}{n-3}\right) \left(\frac{1}{z^{n-3}}\right)_0^\infty$$

$$W(D) = \frac{-2\pi\rho C}{(n-2)(n-3)}\left(\frac{1}{D^{(n-3)}}\right)$$

D^{n-3}

VDW attraction

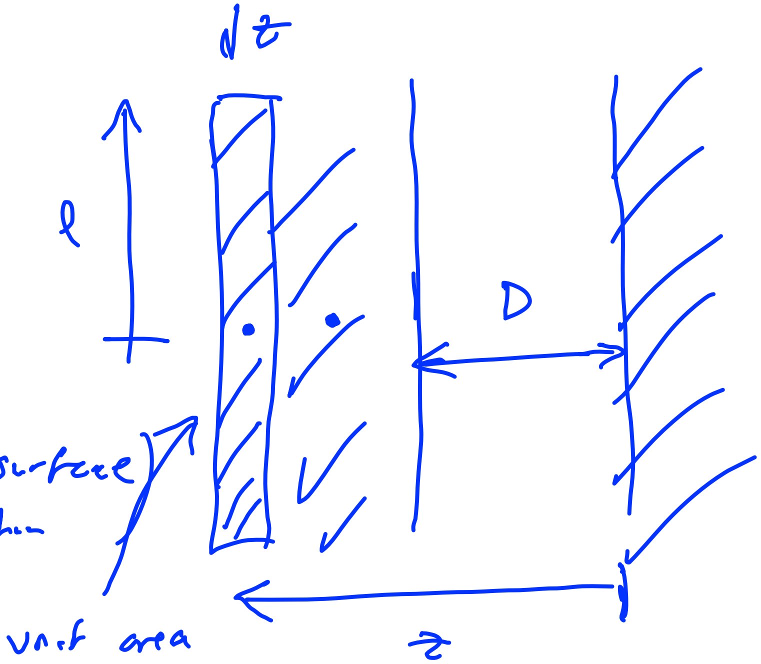
always $n > 3$

$$\underline{w_{VDW}} = C/\text{separatn}^6 = \underline{C/r^{\boxed{6}}} \rightarrow n = 6$$

$$\underline{W(D) = \frac{-\pi\rho C}{6D^3}}$$

VDW energy

$dV =$ "unit-area" dz



total energy

$$\int_V (\text{unit area})\,\rho\,dz \cdot (\text{particle-surface interaction})$$

previous slide

$$\frac{W}{\text{area}} = -\frac{2\pi C\rho^2}{(n-2)(n-3)}\int_D^\infty \frac{dz}{z^{n-3}} = \frac{-2\pi C\rho^2}{(n-2)(n-3)(n-4)}\left(\frac{1}{D^{n-4}}\right)$$

$$W(D)_{pl-pl,\ vdW} = \frac{-\pi C \rho^2}{12 D^2}$$

recall F : $\frac{dW}{dz} = \frac{dW}{dD}$

plane-plane $$F = \frac{d}{dD}\left(-\frac{\pi C \rho^2}{12 D^2}\right) = \underline{\frac{+\pi C \rho^2}{6 D^3}}$$

Sphere-plate (Langbein approximation)

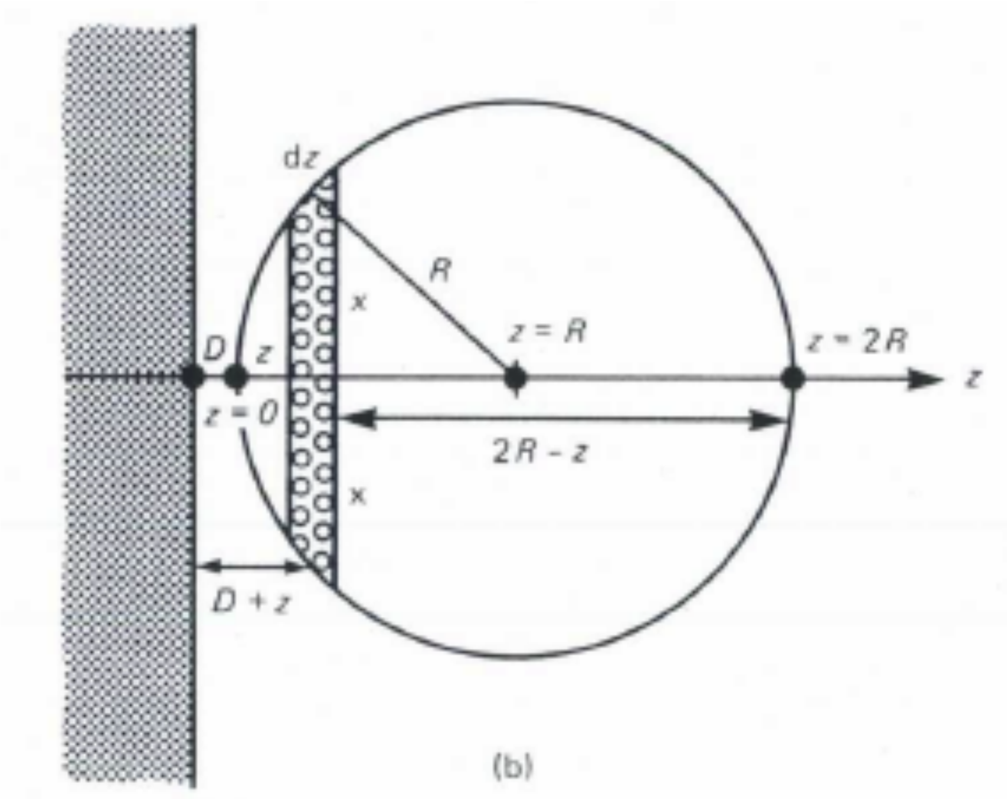


Fig. 10.2. Methods of summing (integrating) the interaction energies between molecules in condensed phases to obtain the interaction energies between macroscopic bodies. (a) Molecule near a flat surface or 'wall'. (b) Spherical particle near a wall ($R \gg D$). (c) Two planar surfaces ($l \gg D$).

$$W(D) = -\frac{4\pi C\rho^2 R}{(n-2)(n-3)(n-4)(n-5)D^{n-5}}$$

$$n = 6, W(D) = -\frac{\pi^2 C\rho^2 R}{6D}$$

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Derjaguin approximation

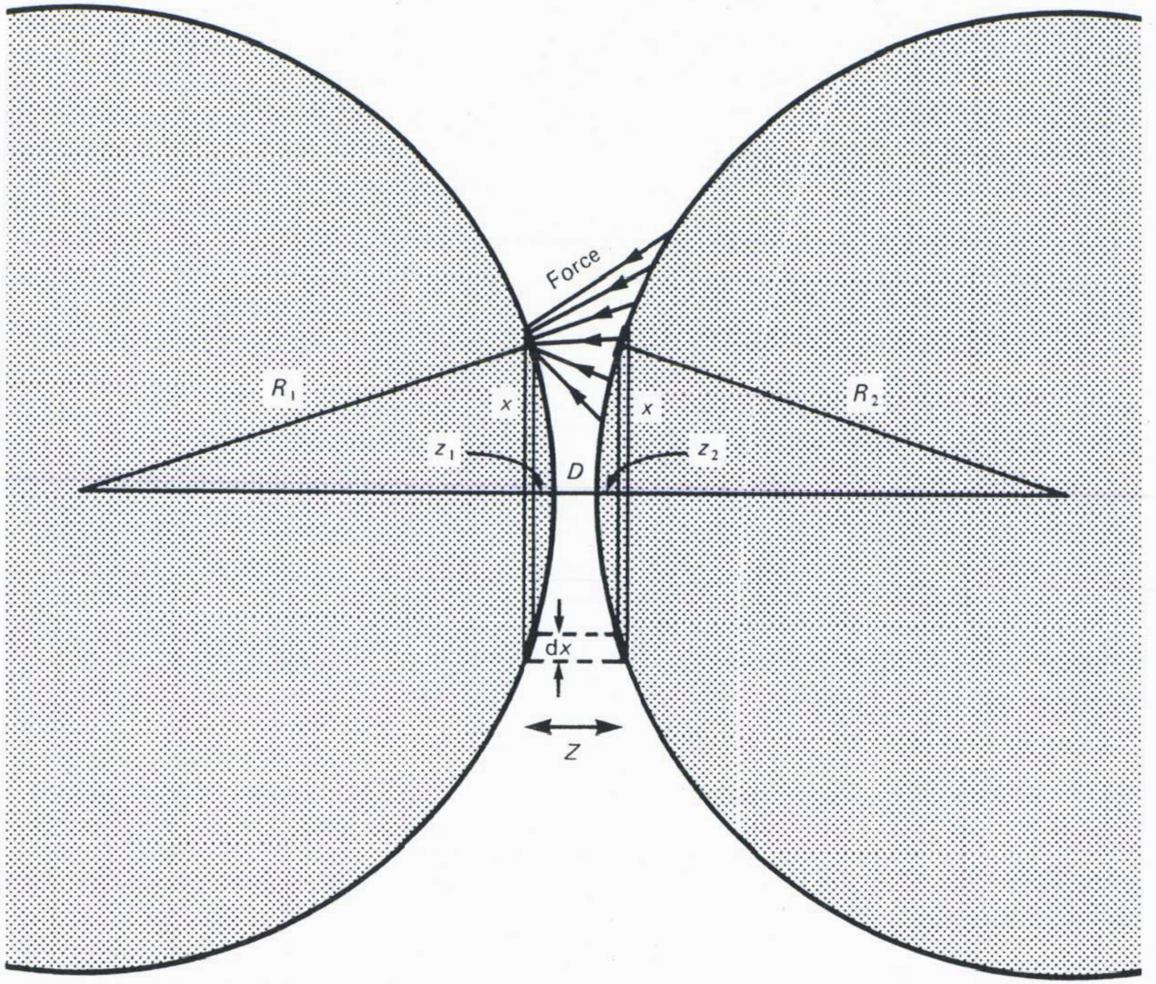

Fig. 10.3. The Derjaguin approximation (Derjaguin, 1934), which relates the force law $F(D)$ between two spheres to the energy per unit area $W(D)$ of two flat surfaces by $F(D) = 2\pi[R_1R_2/(R_1 + R_2)]W(D)$.

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Derjaguin approximation

- *F(Z), W(D) as derived for two planes*
- *D << (R$_1$,R$_2$)*
- Applies to any force law

force curved surfaces (R$_1$, R$_2$)

$$F(D) = \int_{Z=D}^{Z=\infty} 2\pi x dx f(Z)$$

force law for planes

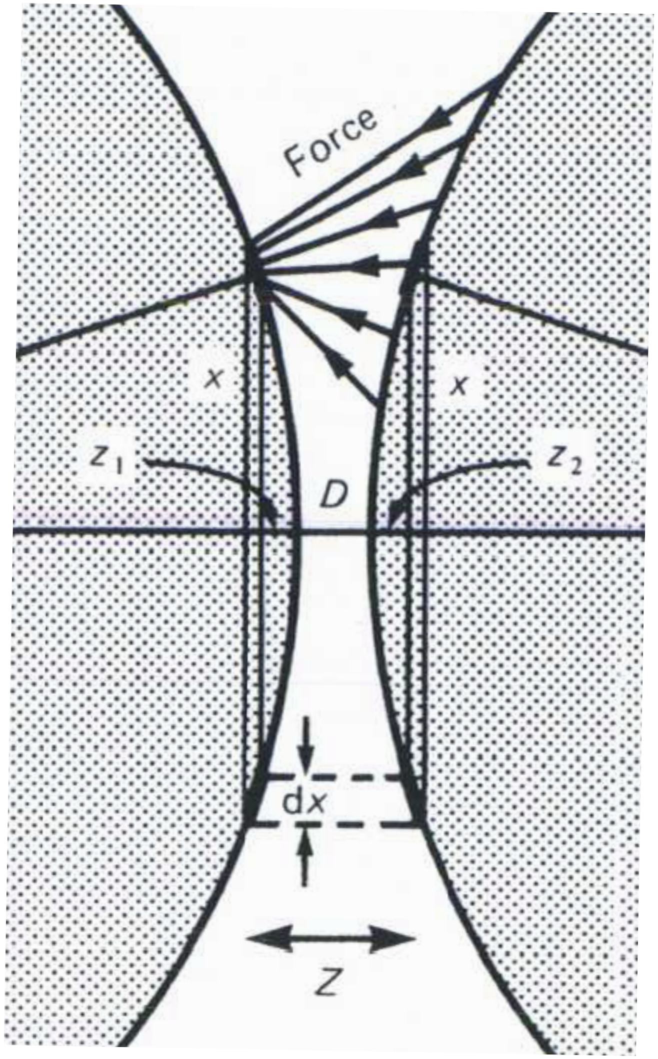
$$Z = D + z_1 + z_2 = D + \frac{x^2}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

$$dZ = \left(\frac{1}{R_1} + \frac{1}{R_2}\right) x dx$$

$$F(D) \approx \int_D^\infty 2\pi \left(\frac{R_1 R_2}{R_1 + R_2}\right) f(Z) dZ$$

$$= 2\pi \left(\frac{R_1 R_2}{R_1 + R_2}\right) W(D)$$

for 2 planes



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Plane-plane versus sphere-sphere

- Equilibrium at points where force is zero (local minima of interaction energy)

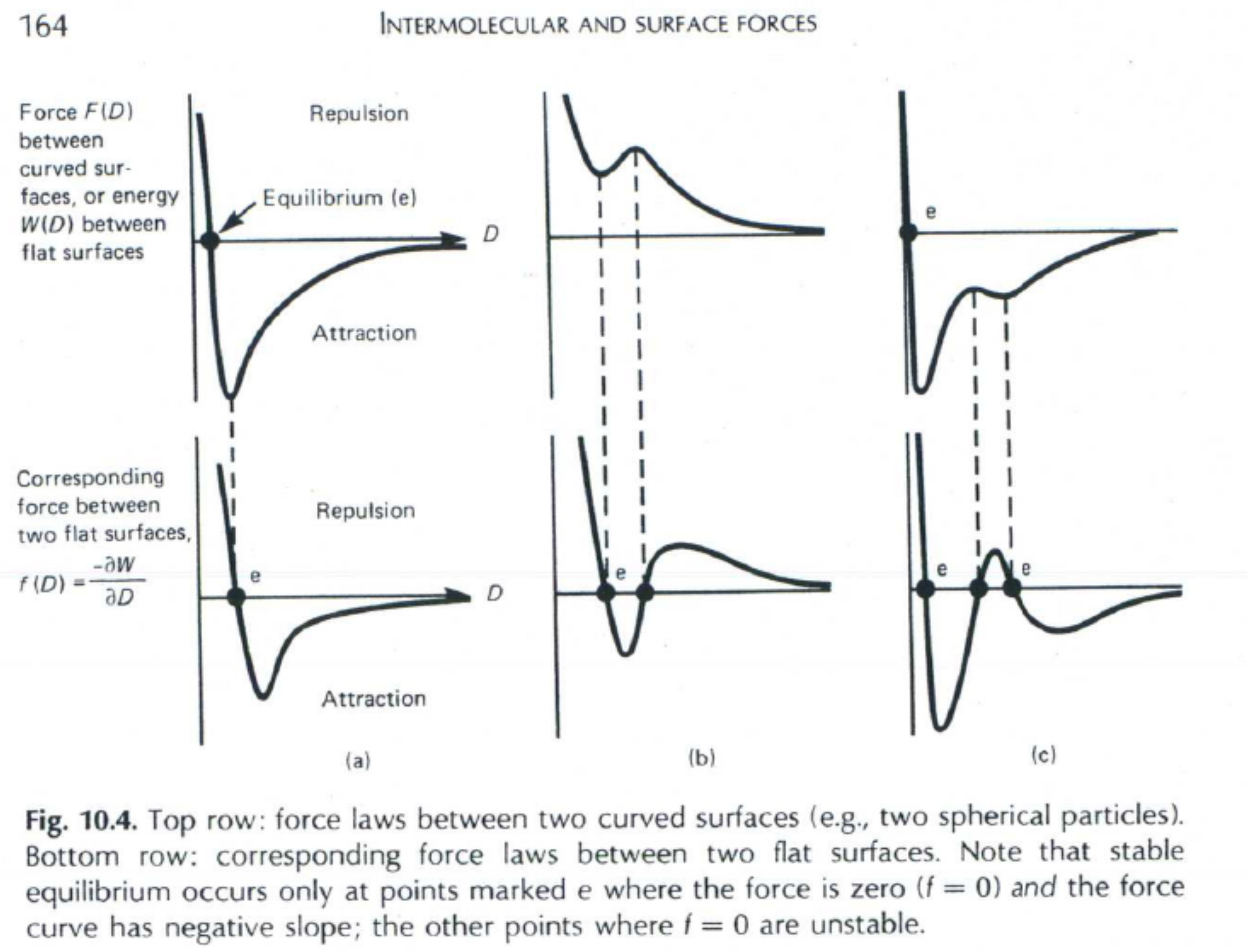

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Fig. 10.4. Top row: force laws between two curved surfaces (e.g., two spherical particles). Bottom row: corresponding force laws between two flat surfaces. Note that stable equilibrium occurs only at points marked e where the force is zero ($f = 0$) *and* the force curve has negative slope; the other points where $f = 0$ are unstable.

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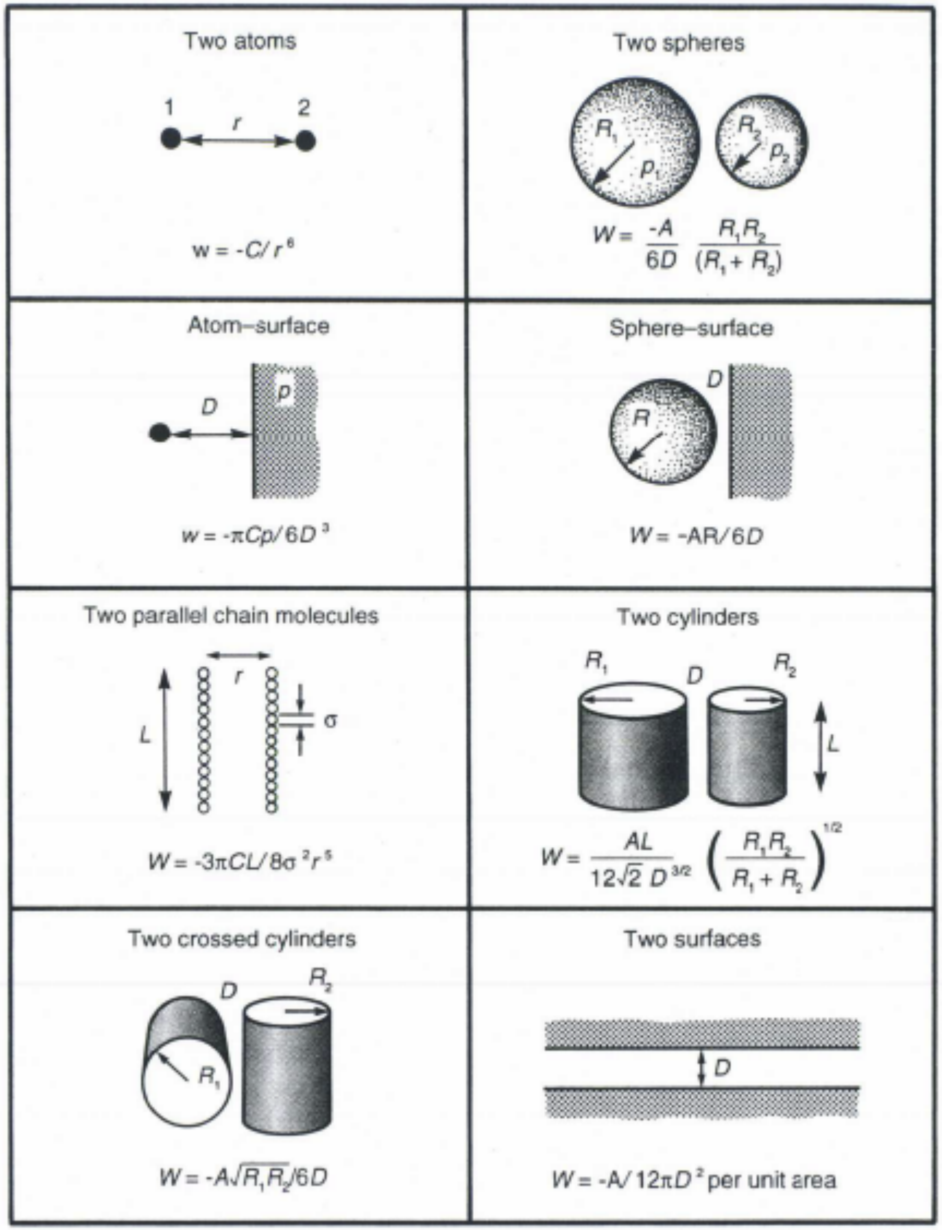
VDW energies for regular geometries



Two atoms $w = -C/r^6$	Two spheres $W = \frac{-A}{6D}\frac{R_1R_2}{(R_1+R_2)}$
Atom–surface $w = -\pi C\rho/6D^3$	Sphere–surface $W = -AR/6D$
Two parallel chain molecules $W = -3\pi CL/8\sigma^2 r^5$	Two cylinders $W = \frac{AL}{12\sqrt{2}\,D^{3/2}}\left(\frac{R_1R_2}{R_1+R_2}\right)^{1/2}$
Two crossed cylinders $W = -A\sqrt{R_1R_2}/6D$	Two surfaces $W = -A/12\pi D^2$ per unit area

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Hamaker constant

- How do we determine the pair potential constant (*C*) for calculations of total interaction energy?

$$A = \pi^2 C \rho_1 \rho_2$$

previously $\rho_1 = \rho_2$

$$C = \frac{A}{\pi^2 \rho_1 \rho_2}, \qquad \underline{A \simeq 10^{-19}\ J} \text{ in vacuum}$$

ex: 2 planes in "contact", $D \approx 2\ nm$

10^{-19}

$$F = \frac{\pi C \rho^2}{6D^3} = \frac{A}{\pi^{\cancel{2}} \cancel{\rho^2}}\left(\frac{\cancel{\pi} \cancel{\rho^2}}{6D^3}\right) = \frac{A}{6\pi D^3} = 7E8\ N/m^2$$

$= 7000$ atm!

$8E-27$

Hamaker constants

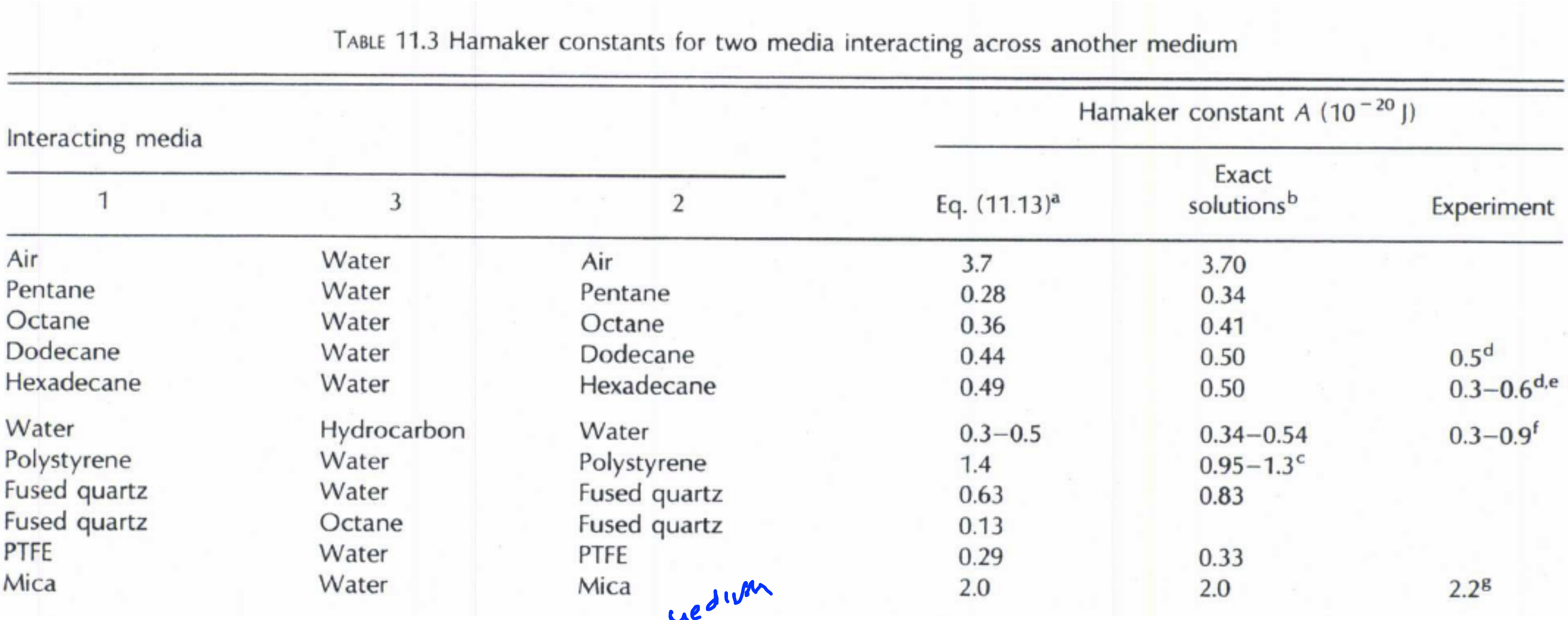

TABLE 11.3 Hamaker constants for two media interacting across another medium

Interacting media			Hamaker constant A (10^{-20} J)		
1	3	2	Eq. (11.13)[a]	Exact solutions[b]	Experiment
Air	Water	Air	3.7	3.70	
Pentane	Water	Pentane	0.28	0.34	
Octane	Water	Octane	0.36	0.41	
Dodecane	Water	Dodecane	0.44	0.50	0.5[d]
Hexadecane	Water	Hexadecane	0.49	0.50	0.3–0.6[d,e]
Water	Hydrocarbon	Water	0.3–0.5	0.34–0.54	0.3–0.9[f]
Polystyrene	Water	Polystyrene	1.4	0.95–1.3[c]	
Fused quartz	Water	Fused quartz	0.63	0.83	
Fused quartz	Octane	Fused quartz	0.13		
PTFE	Water	PTFE	0.29	0.33	
Mica	Water	Mica	2.0	2.0	2.2[g]

$$A_{12} \approx \sqrt{A_{11}A_{22}} \quad , \quad A_{1\overset{\text{medium}}{3}1} \cong \underline{\left(\sqrt{A_{11}} - \sqrt{A_{33}}\right)^2}$$

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VDW-induced CNT deformation

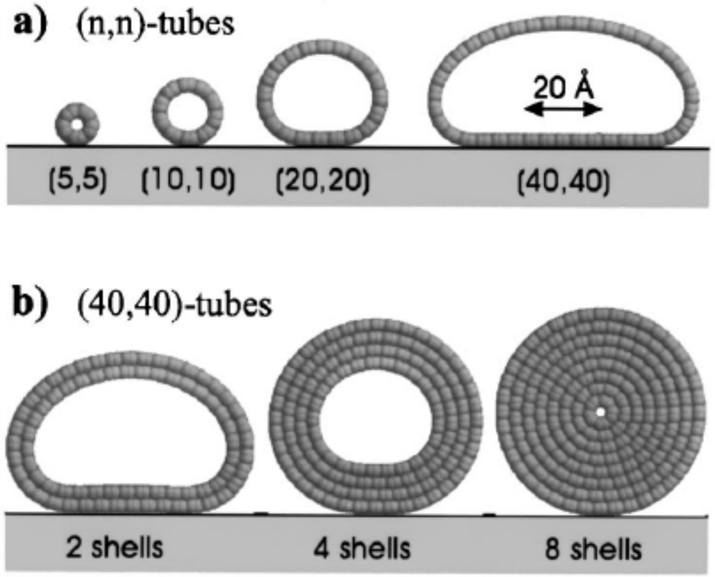
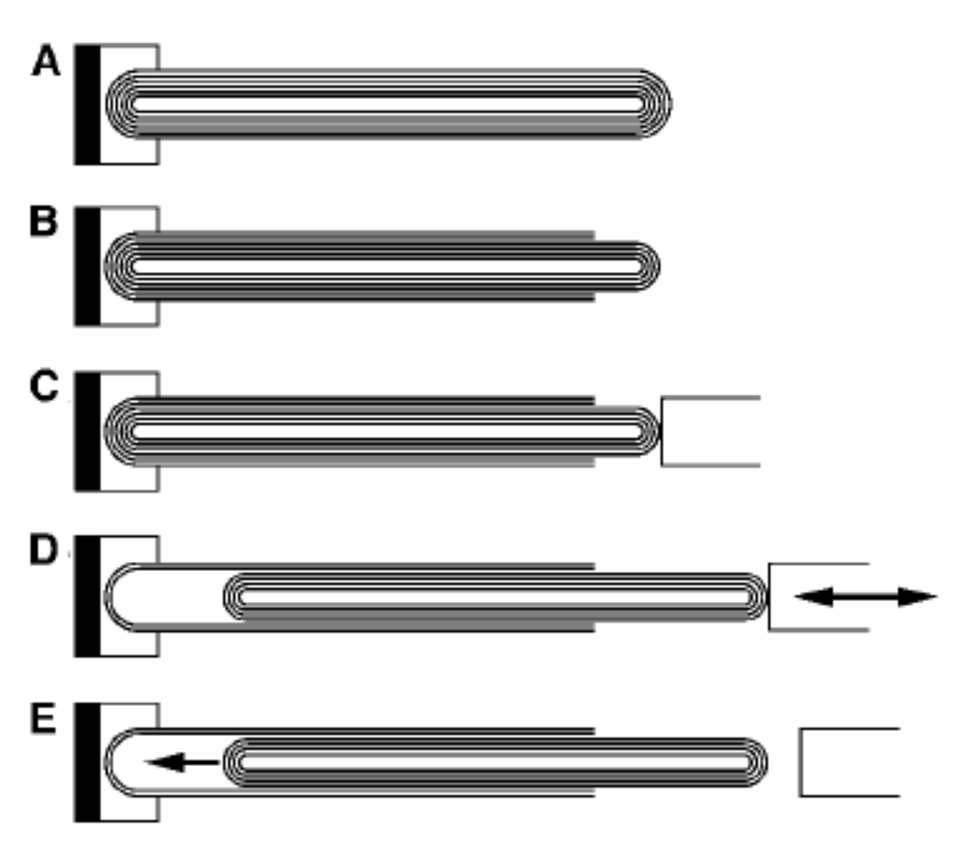


FIG. 2. Radial deformations of adsorbed carbon nanotubes calculated using molecular mechanics. The deformations shown are true representations of the results. (a) The radial compressions of adsorbed single-walled nanotubes with respect to the undistorted free tubes are: 0%, 2%, 13%, and 42%, for 6.7-, 13.5-, 27.1-Å, and 54.2-Å tubes, respectively. (b) When the number of inner shells is increased the compressions are reduced from 42% to 25%, 5% and to less than 1% for (40,40) tubes with 1, 2, 4, and 8 shells, respectively.

Hertel et al., Physical Review B 58(20):13870, 1998.

MWNT telescoping "bearings"



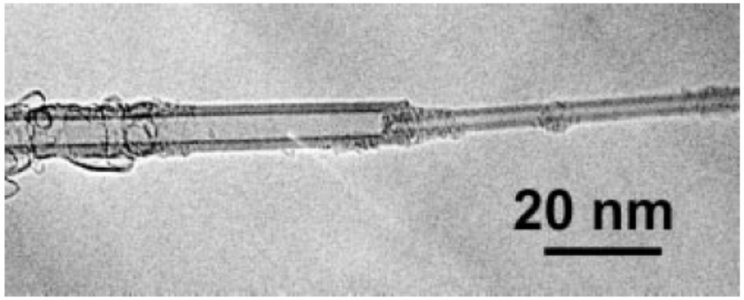
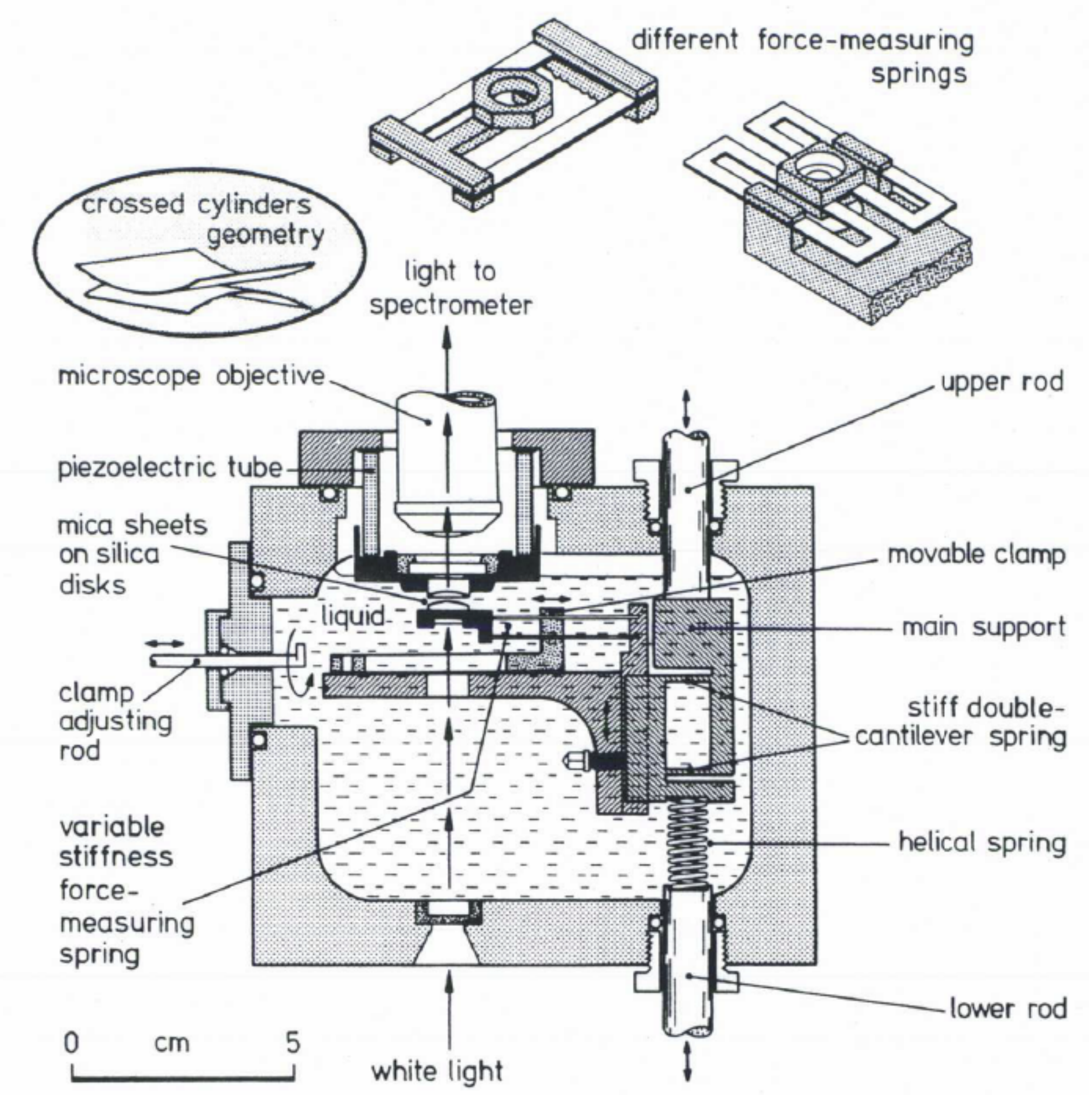


Fig. 2. A TEM image of a telescoped nanotube. This particular nanotube originally had nine shells, but upon telescoping a four-shell core has been nearly completely extracted.

- Relaxation time = nanoseconds
- VDW forces make this a constant-force spring

Cumings, Science 289:602, 2000.

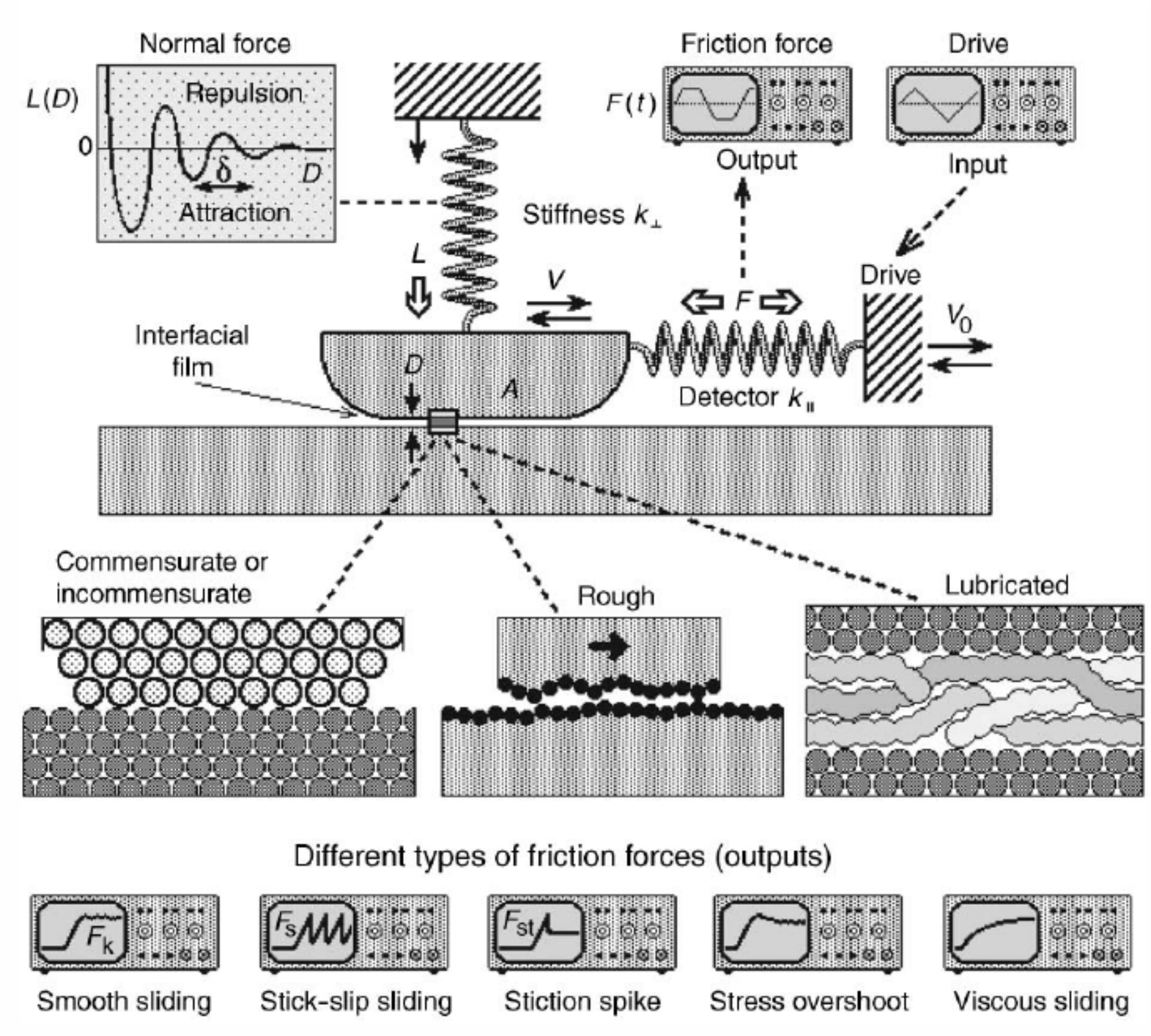
Surface force apparatus (Israelachvili)



- Adjustment using interchangeable and variable-stiffness springs
- Use optical fringes to detect contact and measure separation
- Calculate force knowing displacement and spring stiffness
- Separation controlled to 1 A

Israelachvili.

Surface force apparatus (Israelachvili)



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(captions for previous slides)

Fig. 10.7. Surface Forces Apparatus (SFA) for directly measuring the force laws between surfaces in liquids or vapours at the ångstrom resolution level. With the SFA technique two atomically smooth surfaces immersed in a liquid can be brought towards each other in a highly controlled way (the surface separation being controlled to 1 Å). As the surfaces approach each other they trap a very thin film of liquid between them and the forces between the two surfaces (across the liquid film) can be measured. In addition, the surfaces can be moved laterally past each other and the shear forces also measured during sliding. The results on many different liquids have revealed ultrathin film properties that are profoundly different from those of the bulk liquids, for example, that liquids can support both normal loads and shear stresses, and that molecular relaxations can take 10^{10} times longer in a 10 Å film that in the bulk liquid. Only molecular theories, rather than continuum theories, can explain such phenomena. However, most long-range interactions are adequately explained by continuum theories.

Fig. 10.6. Different types of measurements that provide information on the forces between particles and surfaces. (a) Adhesion measurements (practical applications: xerography, particle adhesion, powder technology, ceramic processing). (b) Peeling measurements (practical applications: adhesive tapes, material fracture and crack propagation). (c) Direct measurements of force as a function of surface separation (practical applications: testing theories of intermolecular forces). (d) Contact angle measurements (practical applications: testing wettability and stability of surface films, detergency). (e) Equilibrium thickness of thin free films (practical applications: soap films, foams). (f) Equilibrium thickness of thin adsorbed films (practical applications: wetting of hydrophilic surfaces by water, adsorption of molecules from vapour, protective surface coatings and lubricant layers, photographic films). (g) Interparticle spacing in liquids (practical applications: colloidal suspensions, paints, pharmaceutical dispersions). (h) Sheet-like particle spacings in liquids (practical applications: clay and soil swelling behaviour, microstructure of soaps and biological membranes). (i) Coagulation studies (practical application: basic experimental technique for testing the stability of colloidal preparations).

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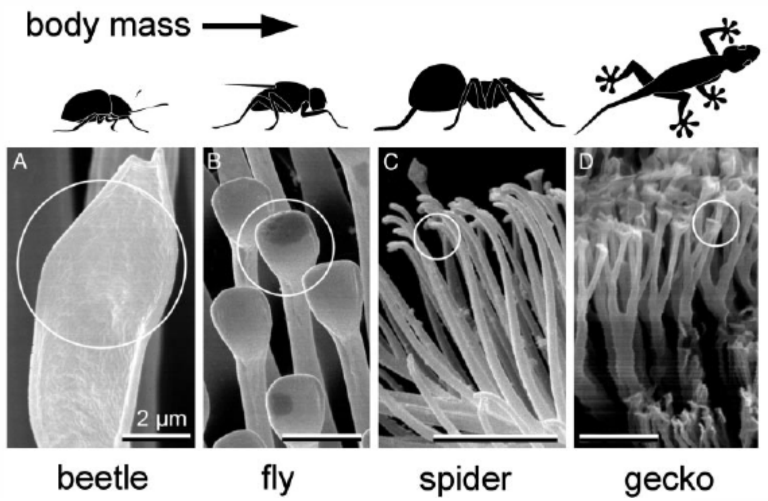
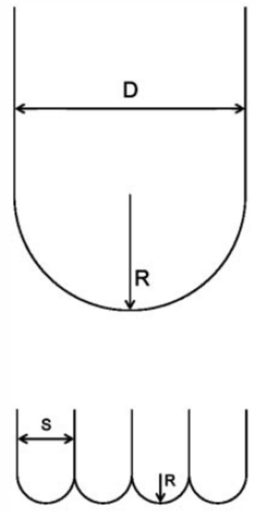
Adhesion scaling in nature





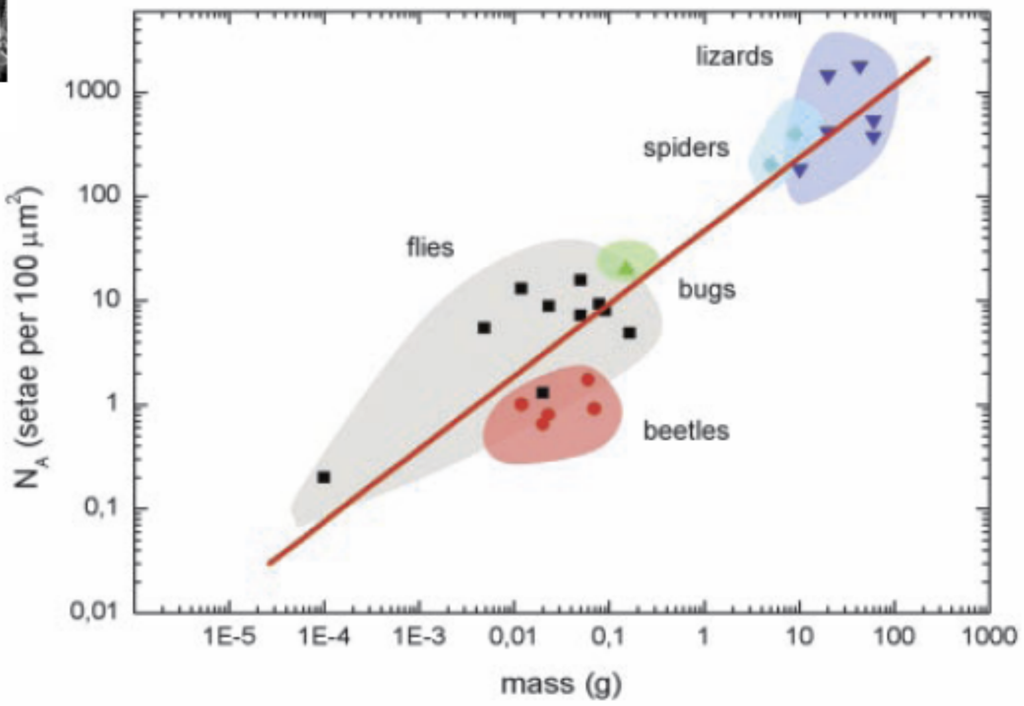


Fig. 2. Dependence of the terminal element density (N_A) of the attachment pads on the body mass (m) in hairy-pad systems of diverse animal groups ($\log \cdot N_A(m^{-2}) = 13.8 + 0.699 \cdot \log \cdot m(kg)$, $R = 0.919$).

Artl et al., PNAS 100(19):10603-10606, 2003.