van der Waals forces between macroscopic bodies

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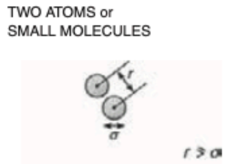
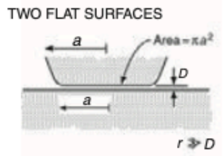
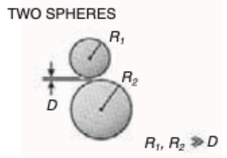
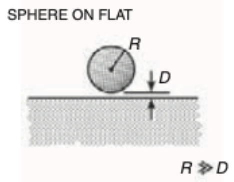
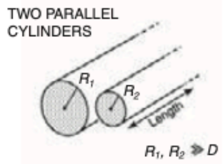
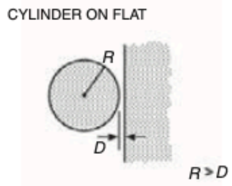
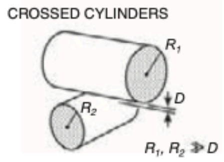
Geometry of bodies with surfaces D apart ($D \ll R$)		**Van der Waals Interaction***	
		Energy, W	**Force, $F = -dW/dD$**
Two atoms or small molecules		$-C/r^6$	$-6C/r^7$
Two flat surfaces (per unit area)		$W_{flat} = -A/12\pi D^2$	$-A/6\pi D^3$
Two spheres or macromolecules of radii R_1 and R_2		$\dfrac{-A}{6D}\left(\dfrac{R_1R_2}{R_1+R_2}\right)$	$\dfrac{-A}{6D^2}\left(\dfrac{R_1R_2}{R_1+R_2}\right)$ Also $F = 2\pi\left(\frac{R_1R_2}{R_1+R_2}\right)W_{flat}$
Sphere or macromolecule of radius R near a flat surface		$-AR/6D$	$-AR/6D^2$ Also $F = 2\pi RW_{flat}$
Two parallel cylinders or rods of radii R_1 and R_2 (per unit length)		$\dfrac{-A}{12\sqrt{2}D^{3/2}}\left(\dfrac{R_1R_2}{R_1+R_2}\right)^{1/2}$	$\dfrac{-A}{8\sqrt{2}D^{5/2}}\left(\dfrac{R_1R_2}{R_1+R_2}\right)^{1/2}$
Cylinder of radius R near a flat surface (per unit length)		$\dfrac{-A\sqrt{R}}{12\sqrt{2}D^{3/2}}$	$\dfrac{-A\sqrt{R}}{8\sqrt{2}D^{5/2}}$
Two cylinders or filaments of radii R_1 and R_2 crossed at 90°		$\dfrac{-A\sqrt{R_1R_2}}{6D}$	$\dfrac{-A\sqrt{R_1R_2}}{6D^2}$ Also $F = 2\pi\sqrt{R_1R_2}W_{flat}$

Hamaker constant

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

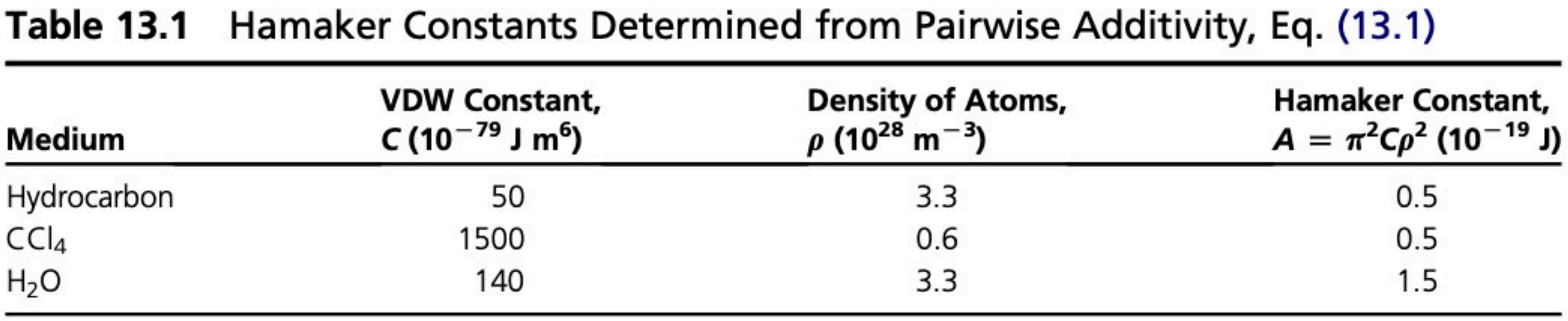


Table 13.1 Hamaker Constants Determined from Pairwise Additivity, Eq. (13.1)

Medium	VDW Constant, C (10^{-79} J m^6)	Density of Atoms, ρ (10^{28} m^{-3})	Hamaker Constant, $A = \pi^2 C\rho^2$ (10^{-19} J)
Hydrocarbon	50	3.3	0.5
CCl_4	1500	0.6	0.5
H_2O	140	3.3	1.5

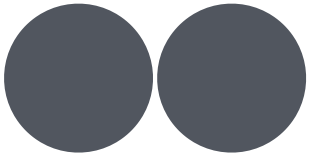
$$\alpha \sim v \qquad A \sim C\rho^2 \sim \alpha^2 \rho^2$$

$$\rho \sim 1/v \qquad A \sim \text{constant}$$

$$A \sim (0.4 - 4) \times 10^{-19} J$$

Only approximate – assumes pairwise additivity!

van der Waals forces and energies



Two 1cm spheres in contact
(in vacuum or air)

$$F(D) = -\frac{AR}{12D^2}$$

$$D \approx 0.2\mathrm{nm}$$

$$F \approx -2 \times 10^{-3} N$$

Two 20nm spheres, 10nm separation

$$W(D) = -\frac{AR}{12D}$$

$$W \approx 5kT$$

Pressure between two planar surfaces interacting

$$P = -A/6\pi D^3 \approx -7 \times 10^8 \ \mathrm{N\,m^{-2}} \approx 7000 \ \mathrm{atm}$$

Adhesion and surface energies

$$W = -\frac{A}{12\pi D^2} \quad \approx -66\,\mathrm{mJ/m^2}$$

$$\gamma = -\frac{1}{2}W \approx 33\,\mathrm{mJ/m^2}$$

Non-retarded van der Waals interactions at all separations

$$W(D) = -\frac{A}{6}\left\{\frac{2R_1R_2}{(2R_1+2R_2+D)D} + \frac{2R_1R_2}{(2R_1+D)(2R_2+D)} + \ln\frac{(2R_1+2R_2+D)D}{(2R_1+D)(2R_2+D)}\right\}$$

Hamaker (1937)

Lifshitz theory

The problem: calculate multi-body van der Waals interactions for macroscopic bodies

The solution: ignore atomic structure, treat as continuous media using bulk properties.
(dielectric constants, refractive indices)

$$A = \pi^2 C \rho_1 \rho_2 = \frac{6\pi^2 kT \rho_1 \rho_2}{(4\pi\varepsilon_0)^2} \sum_{n=0,1,2,\ldots}^{\infty}{}' \frac{\alpha_1(i\nu_n)\alpha_2(i\nu_n)}{\varepsilon_3^2(i\nu_n)}$$

McLachlan's equation

$$= \frac{3}{2} kT \sum_{n=0,1,2,\ldots}^{\infty}{}' \left[\frac{\varepsilon_1(i\nu_n) - \varepsilon_3(i\nu_n)}{\varepsilon_1(i\nu_n) + \varepsilon_3(i\nu_n)}\right] \left[\frac{\varepsilon_2(i\nu_n) - \varepsilon_3(i\nu_n)}{\varepsilon_2(i\nu_n) + \varepsilon_3(i\nu_n)}\right]$$

$$\nu_n = \frac{2\pi n kT}{h}$$

$$A \approx \frac{3}{4} kT \left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}\right) \left(\frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3}\right) + \frac{3h}{4\pi} \int_{\nu_1}^{\infty} \left(\frac{\varepsilon_1(i\nu) - \varepsilon_3(i\nu)}{\varepsilon_1(i\nu) + \varepsilon_3(i\nu)}\right) \left(\frac{\varepsilon_2(i\nu) - \varepsilon_3(i\nu)}{\varepsilon_2(i\nu) + \varepsilon_3(i\nu)}\right) d\nu,$$

Keesom and Debye contributions

London contributions

Lifshitz, 1956; Dzyaloshinskii et al., 1961
Israelachvili and Tabor, 1973; Israelachvili, 1974;
Mahanty and Ninham, 1976; Hough and White, 1980;
Bergström, 1997; Parsegian, 2006

$$A \approx \frac{3}{4}kT\left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}\right)\left(\frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3}\right) + \frac{3h}{4\pi}\int_{\nu_1}^{\infty}\left(\frac{\varepsilon_1(i\nu) - \varepsilon_3(i\nu)}{\varepsilon_1(i\nu) + \varepsilon_3(i\nu)}\right)\left(\frac{\varepsilon_2(i\nu) - \varepsilon_3(i\nu)}{\varepsilon_2(i\nu) + \varepsilon_3(i\nu)}\right)d\nu$$

Similar to frequency
dependence of polarizability

$$\varepsilon(\nu) = 1 + \frac{\text{constant}}{(1 - i\nu/\nu_{\text{rot}})} + \frac{\text{constant}}{(1 - \nu^2/\nu_{\text{e}}^2)},$$

$$\varepsilon(i\nu) = 1 + \frac{(\varepsilon - n^2)}{(1 + \nu/\nu_{\text{rot}})} + \underline{\frac{(n^2 - 1)}{(1 + \nu^2/\nu_{\text{e}}^2)},}$$

Absorption dominates

$$\varepsilon(0) = 1 + (\varepsilon - n^2) + (n^2 - 1) = \varepsilon, \quad \varepsilon(\infty) = 1,$$

$$n^2 = \varepsilon_{\text{vis}}$$

For identical absorption frequencies in all three media,

$$\begin{aligned} A_{\text{total}} &= A_{\nu=0} + A_{\nu>0} \approx \frac{3}{4}kT\left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}\right)\left(\frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3}\right) \\ &+ \frac{3h\nu_{\text{e}}}{8\sqrt{2}}\frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{(n_1^2 + n_3^2)^{1/2}(n_2^2 + n_3^2)^{1/2}\{(n_1^2 + n_3^2)^{1/2} + (n_2^2 + n_3^2)^{1/2}\}} \end{aligned}$$

Symmetric case

$$A = \frac{3}{4}kT\left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}\right)^2 + \frac{3h\nu_e}{16\sqrt{2}}\frac{(n_1^2 - n_3^2)^2}{(n_1^2 + n_3^2)^{3/2}}.$$

- vdw force between identical bodies in a medium is always attractive (A>0)
- vdw force between different bodes in a medium can be attractive or repulsive (A<0)
- vdw force between any two condensed bodies in air or vacuum is attractive
- Dispersion energy contribution can be high if one medium has a high refractive index
- Zero-frequency contribution can never exceed 3/4kT
- Interactions between nonconducting (dielectric) media across a vacuum, the zero-frequency contribution is usually small (less than 5%)
- For some interactions in a medium the zero-frequency contribution can dominate over the dispersion contribution
- Hamaker constants of metals up to an order of magnitude higher than nonconducting media

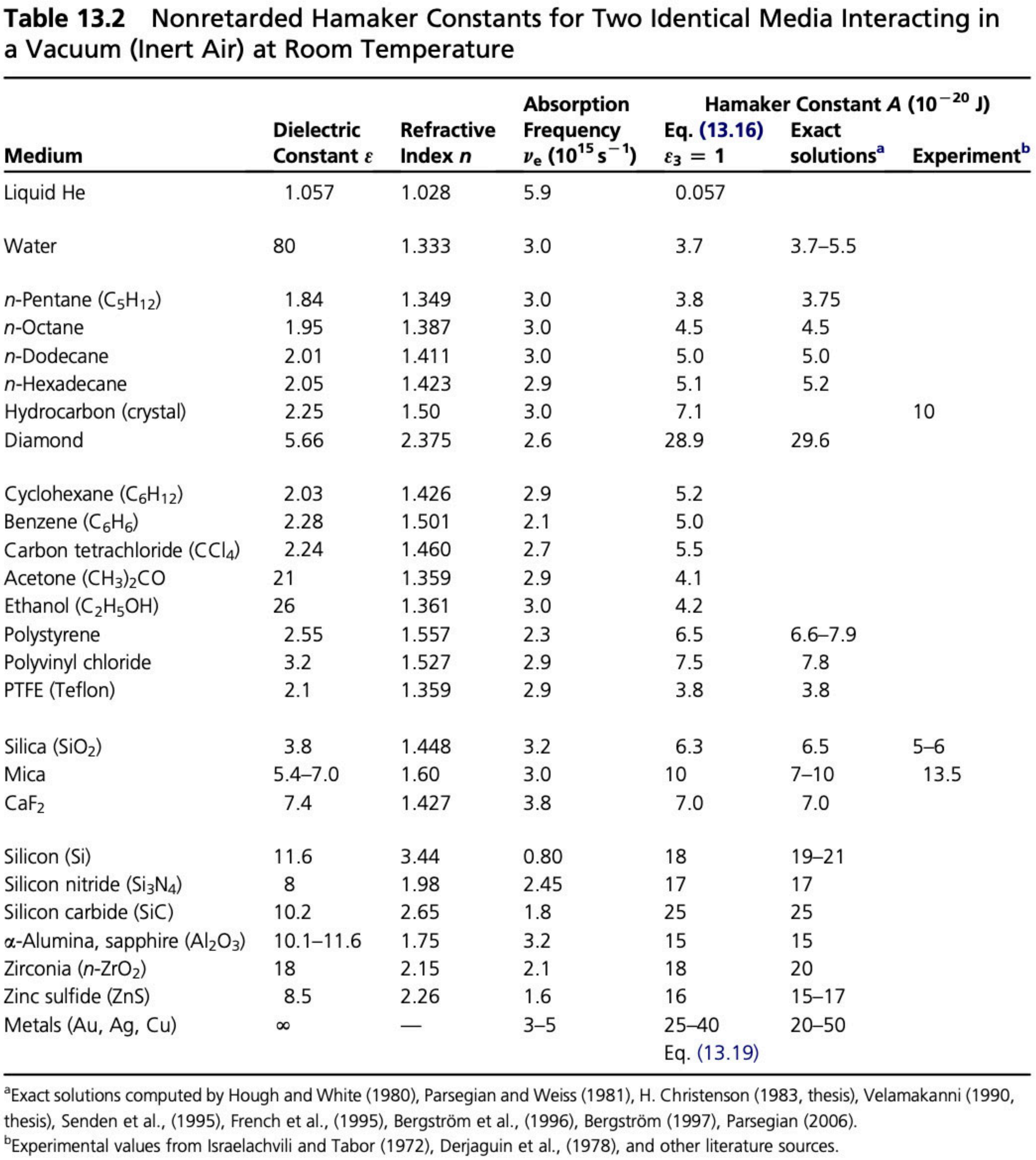


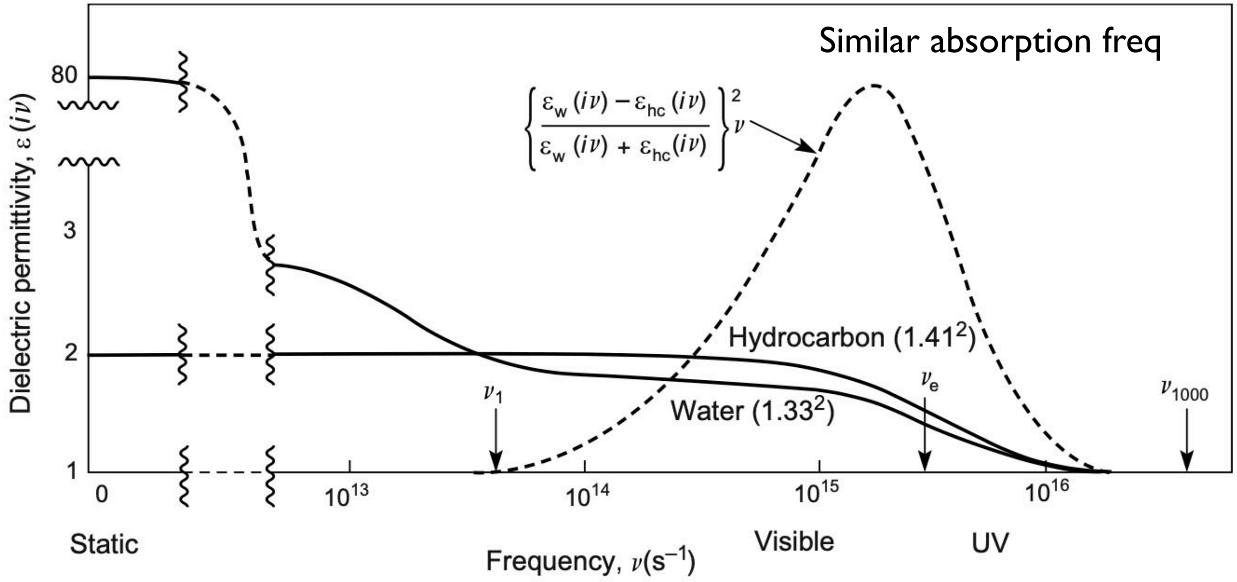
Table 13.2 Nonretarded Hamaker Constants for Two Identical Media Interacting in a Vacuum (Inert Air) at Room Temperature

Medium	Dielectric Constant ε	Refractive Index n	Absorption Frequency ν_e ($10^{15}\,s^{-1}$)	Hamaker Constant A (10^{-20} J)		
				Eq. (13.16) $\varepsilon_3 = 1$	Exact solutions[a]	Experiment[b]
Liquid He	1.057	1.028	5.9	0.057		
Water	80	1.333	3.0	3.7	3.7–5.5	
n-Pentane (C_5H_{12})	1.84	1.349	3.0	3.8	3.75	
n-Octane	1.95	1.387	3.0	4.5	4.5	
n-Dodecane	2.01	1.411	3.0	5.0	5.0	
n-Hexadecane	2.05	1.423	2.9	5.1	5.2	
Hydrocarbon (crystal)	2.25	1.50	3.0	7.1		10
Diamond	5.66	2.375	2.6	28.9	29.6	
Cyclohexane (C_6H_{12})	2.03	1.426	2.9	5.2		
Benzene (C_6H_6)	2.28	1.501	2.1	5.0		
Carbon tetrachloride (CCl_4)	2.24	1.460	2.7	5.5		
Acetone $(CH_3)_2CO$	21	1.359	2.9	4.1		
Ethanol (C_2H_5OH)	26	1.361	3.0	4.2		
Polystyrene	2.55	1.557	2.3	6.5	6.6–7.9	
Polyvinyl chloride	3.2	1.527	2.9	7.5	7.8	
PTFE (Teflon)	2.1	1.359	2.9	3.8	3.8	
Silica (SiO_2)	3.8	1.448	3.2	6.3	6.5	5–6
Mica	5.4–7.0	1.60	3.0	10	7–10	13.5
CaF_2	7.4	1.427	3.8	7.0	7.0	
Silicon (Si)	11.6	3.44	0.80	18	19–21	
Silicon nitride (Si_3N_4)	8	1.98	2.45	17	17	
Silicon carbide (SiC)	10.2	2.65	1.8	25	25	
α-Alumina, sapphire (Al_2O_3)	10.1–11.6	1.75	3.2	15	15	
Zirconia (n-ZrO_2)	18	2.15	2.1	18	20	
Zinc sulfide (ZnS)	8.5	2.26	1.6	16	15–17	
Metals (Au, Ag, Cu)	∞	—	3–5	25–40 Eq. (13.19)	20–50	

[a] Exact solutions computed by Hough and White (1980), Parsegian and Weiss (1981), H. Christenson (1983, thesis), Velamakanni (1990, thesis), Senden et al., (1995), French et al., (1995), Bergström et al., (1996), Bergström (1997), Parsegian (2006).

[b] Experimental values from Israelachvili and Tabor (1972), Derjaguin et al., (1978), and other literature sources.

Lifshitz theory for interactions through a medium



Similar absorption freq

FIGURE 13.4 Dielectric permittivity $\varepsilon(i\nu)$ as a function of frequency ν for water and hydrocarbon (water interacting across hydrocarbon, and vice versa). In the visible and UV range these are given by

$$\varepsilon_w(i\nu) = 1 + \left(n_w^2 - 1\right)/\left(1 + \nu^2/\nu_e^2\right),\ n_w = 1.33$$

$$\varepsilon_{hc}(i\nu) = 1 + \left(n_{hc}^2 - 1\right)/\left(1 + \nu^2/\nu_e^2\right),\ n_{hc} = 1.41$$

where $\nu_e = 3.0 \times 10^{15}\ \mathrm{s}^{-1}$ for both. The total Hamaker constant for this system at 300 K is about 0.45×10^{-20} J.

$$A_{\nu>0} = \frac{3(6.63\times10^{-34})(3\times10^{15})}{16\sqrt{2}} \frac{(1.41^2-1.33^2)^2}{(1.41^2+1.33^2)^{3/2}} \approx 0.17\times10^{-20}\ \mathrm{J}.$$

$$A_{\nu=0} = \frac{3}{4}kT\left(\frac{80-2}{80+2}\right)^2 \approx 0.28\times10^{-20}\ \mathrm{J}\ \text{at 300 K.}$$

The vow interaction between hydrocarbons across water is dominated by zero-frequency contribution

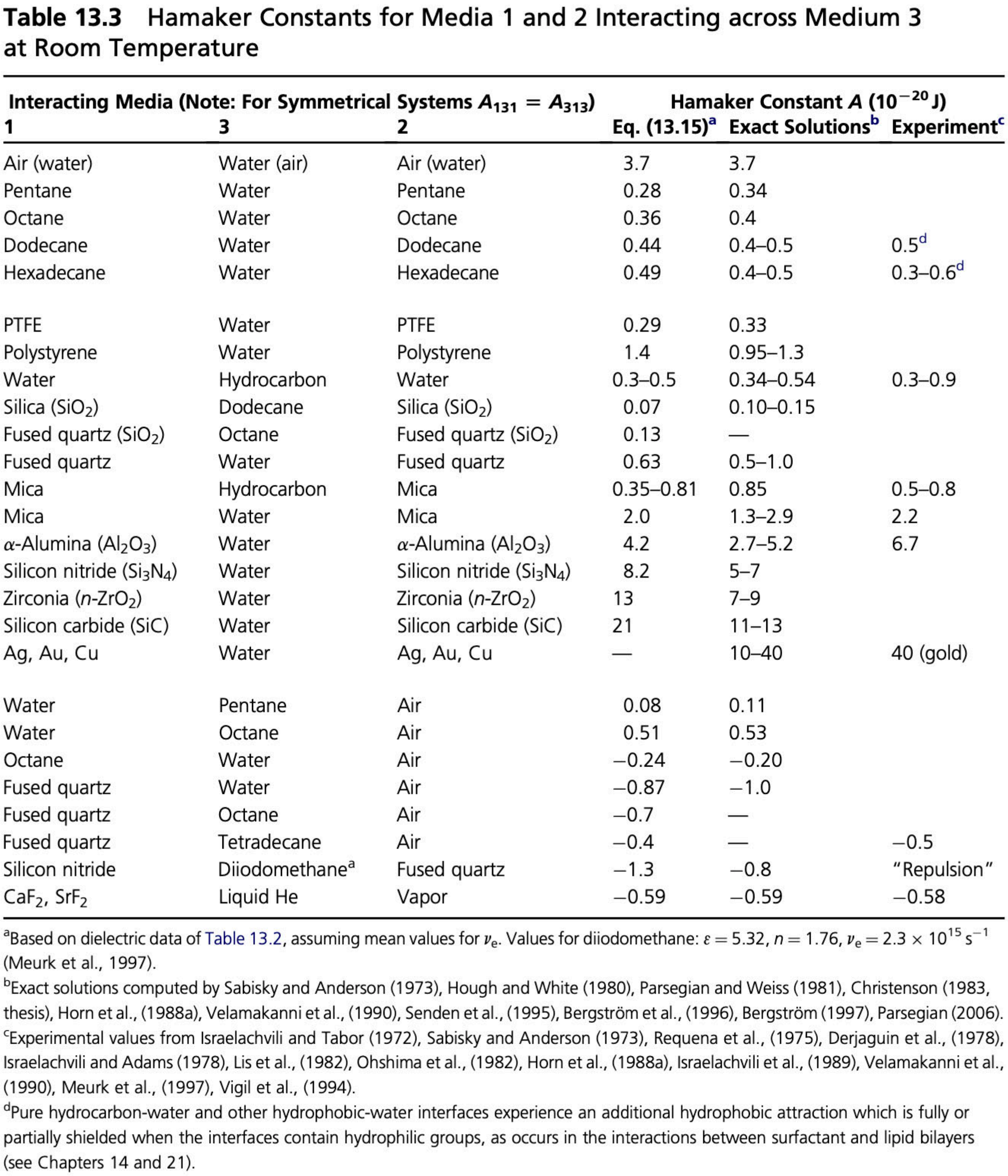


Table 13.3 Hamaker Constants for Media 1 and 2 Interacting across Medium 3 at Room Temperature

Interacting Media (Note: For Symmetrical Systems $A_{131} = A_{313}$) 1	3	2	Hamaker Constant A (10^{-20} J) Eq. (13.15)[a]	Exact Solutions[b]	Experiment[c]
Air (water)	Water (air)	Air (water)	3.7	3.7	
Pentane	Water	Pentane	0.28	0.34	
Octane	Water	Octane	0.36	0.4	
Dodecane	Water	Dodecane	0.44	0.4–0.5	0.5[d]
Hexadecane	Water	Hexadecane	0.49	0.4–0.5	0.3–0.6[d]
PTFE	Water	PTFE	0.29	0.33	
Polystyrene	Water	Polystyrene	1.4	0.95–1.3	
Water	Hydrocarbon	Water	0.3–0.5	0.34–0.54	0.3–0.9
Silica (SiO_2)	Dodecane	Silica (SiO_2)	0.07	0.10–0.15	
Fused quartz (SiO_2)	Octane	Fused quartz (SiO_2)	0.13	—	
Fused quartz	Water	Fused quartz	0.63	0.5–1.0	
Mica	Hydrocarbon	Mica	0.35–0.81	0.85	0.5–0.8
Mica	Water	Mica	2.0	1.3–2.9	2.2
α-Alumina (Al_2O_3)	Water	α-Alumina (Al_2O_3)	4.2	2.7–5.2	6.7
Silicon nitride (Si_3N_4)	Water	Silicon nitride (Si_3N_4)	8.2	5–7	
Zirconia (n-ZrO_2)	Water	Zirconia (n-ZrO_2)	13	7–9	
Silicon carbide (SiC)	Water	Silicon carbide (SiC)	21	11–13	
Ag, Au, Cu	Water	Ag, Au, Cu	—	10–40	40 (gold)
Water	Pentane	Air	0.08	0.11	
Water	Octane	Air	0.51	0.53	
Octane	Water	Air	−0.24	−0.20	
Fused quartz	Water	Air	−0.87	−1.0	
Fused quartz	Octane	Air	−0.7	—	
Fused quartz	Tetradecane	Air	−0.4	—	−0.5
Silicon nitride	Diiodomethane[a]	Fused quartz	−1.3	−0.8	"Repulsion"
CaF_2, SrF_2	Liquid He	Vapor	−0.59	−0.59	−0.58

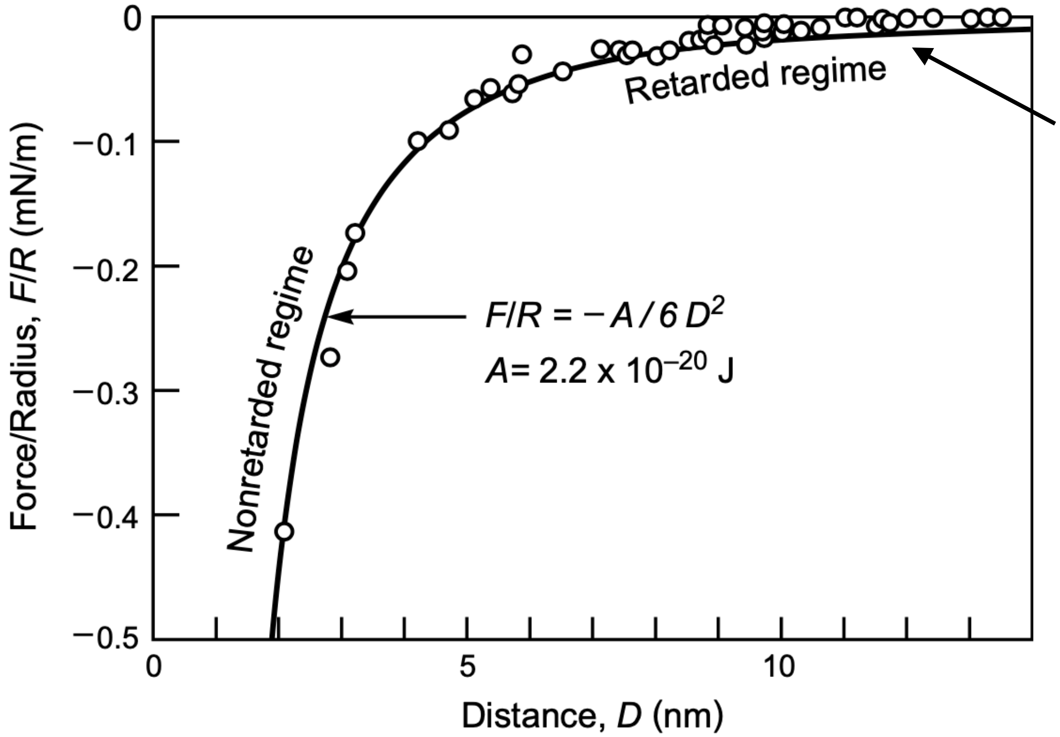
[a] Based on dielectric data of Table 13.2, assuming mean values for ν_e. Values for diiodomethane: $\varepsilon = 5.32$, $n = 1.76$, $\nu_e = 2.3 \times 10^{15}\ s^{-1}$ (Meurk et al., 1997).

[b] Exact solutions computed by Sabisky and Anderson (1973), Hough and White (1980), Parsegian and Weiss (1981), Christenson (1983, thesis), Horn et al., (1988a), Velamakanni et al., (1990), Senden et al., (1995), Bergström et al., (1996), Bergström (1997), Parsegian (2006).

[c] Experimental values from Israelachvili and Tabor (1972), Sabisky and Anderson (1973), Requena et al., (1975), Derjaguin et al., (1978), Israelachvili and Adams (1978), Lis et al., (1982), Ohshima et al., (1982), Horn et al., (1988a), Israelachvili et al., (1989), Velamakanni et al., (1990), Meurk et al., (1997), Vigil et al., (1994).

[d] Pure hydrocarbon-water and other hydrophobic-water interfaces experience an additional hydrophobic attraction which is fully or partially shielded when the interfaces contain hydrophilic groups, as occurs in the interactions between surfactant and lipid bilayers (see Chapters 14 and 21).

Retardation effects



Measured force < calculated for D > 5nm

Pentane wets, dodecane does not

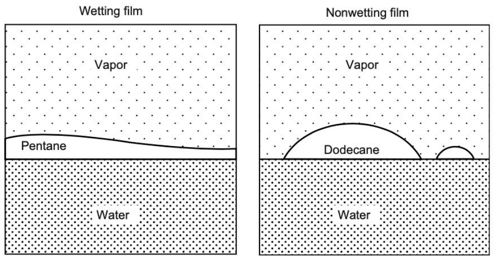


FIGURE 13.6 Attractive van der Waals force F between two curved mica surfaces of radius $R \approx 1$ cm measured in water and aqueous electrolyte solutions. The measured nonretarded Hamaker constant is $A = 2.2 \times 10^{-20}$ J. Retardation effects are apparent at distances above 5 nm where the measured forces are weaker than the extrapolated nonretarded force (solid line). *[Data from SFA experiments with surfaces in the crossed-cylinder geometry, equivalent to a sphere of radius R near a flat surface or two spheres of radius 2R, adapted from Israelachvili and Adams (1978) and Israelachvili and Pashley (unpublished).]*

Only affects the dispersion contribution
Hydrocarbons interacting in water – role of zero-frequency contribution

Screening by electrolytes

Affects the zero-frequency contribution

$$A \approx A_{\nu=0} e^{-\kappa D} + A_{\nu>0}$$

$$\kappa^{-1} = \left(\frac{kT\epsilon\epsilon_0}{2Ie^2} \right)^{\frac{1}{2}}$$

Debye length
for ionic strength, I

$$I = \frac{1}{2} \sum_{i=1}^{N} z_i^2 n_{s,i}$$

$$\kappa^{-1} = \left(\frac{\epsilon\epsilon_0 k_B T}{\sum_i n_i e^2 z_i^2} \right)^{1/2}$$

NaCl (mM)	κ^{-1} (nm)
0.1	31
1	9.7
10	3.1
100	0.97

Combining relations

interaction in
medium 3

$$A_{132} \approx \pm\sqrt{A_{131}A_{232}}$$

$$A_{12} \approx \sqrt{A_{11}A_{22}}$$

interaction in
vacuum or air

$$A_{131} = A_{313} \approx A_{11} + A_{33} - 2A_{13}$$

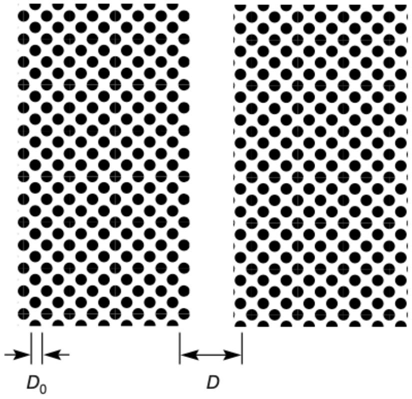
$$\approx \left(\sqrt{A_{11}} - \sqrt{A_{33}}\right)^2$$

$$A_{131} \approx \left(\sqrt{A_{11}} - \sqrt{A_{33}}\right)\left(\sqrt{A_{22}} - \sqrt{A_{33}}\right)$$

- Applicable only when dispersion forces dominate
- Break down for media with high dielectric constants (e.g. water) or dominant zero-frequency contribution
- Ultimately: fast numerical methods like those of Parsegian limit the need for combining relations

Surface energies

The surface energy is half the energy needed to separate two flat surfaces from contact to infinity (half the adhesion energy)



$$W = -\frac{A}{12\pi D_0^2} = -2\gamma$$

$$\gamma = \frac{A}{24\pi D_0^2}$$

Complications: Close contact, Lifshitz theory does not apply
Unclear what separation to use

$$\gamma \approx \frac{A}{24\pi (0.165\mathrm{nm})^2}$$

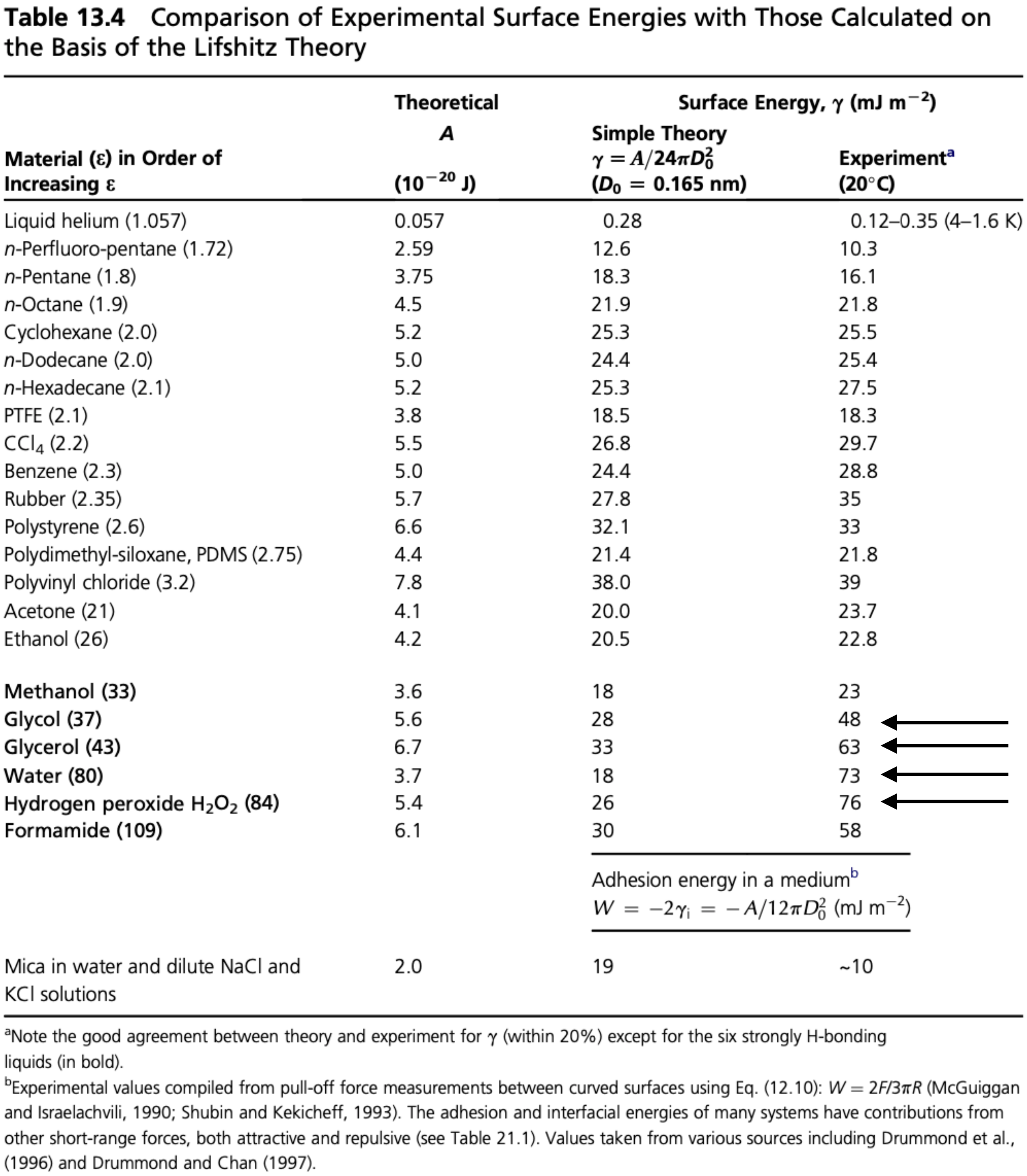


Table 13.4 Comparison of Experimental Surface Energies with Those Calculated on the Basis of the Lifshitz Theory

Material (ε) in Order of Increasing ε	Theoretical A (10^{-20} J)	Surface Energy, γ (mJ m^{-2}) Simple Theory $\gamma = A/24\pi D_0^2$ (D_0 = 0.165 nm)	Experiment[a] (20°C)
Liquid helium (1.057)	0.057	0.28	0.12–0.35 (4–1.6 K)
n-Perfluoro-pentane (1.72)	2.59	12.6	10.3
n-Pentane (1.8)	3.75	18.3	16.1
n-Octane (1.9)	4.5	21.9	21.8
Cyclohexane (2.0)	5.2	25.3	25.5
n-Dodecane (2.0)	5.0	24.4	25.4
n-Hexadecane (2.1)	5.2	25.3	27.5
PTFE (2.1)	3.8	18.5	18.3
CCl_4 (2.2)	5.5	26.8	29.7
Benzene (2.3)	5.0	24.4	28.8
Rubber (2.35)	5.7	27.8	35
Polystyrene (2.6)	6.6	32.1	33
Polydimethyl-siloxane, PDMS (2.75)	4.4	21.4	21.8
Polyvinyl chloride (3.2)	7.8	38.0	39
Acetone (21)	4.1	20.0	23.7
Ethanol (26)	4.2	20.5	22.8
Methanol (33)	3.6	18	23
Glycol (37)	5.6	28	48
Glycerol (43)	6.7	33	63
Water (80)	3.7	18	73
Hydrogen peroxide H_2O_2 (84)	5.4	26	76
Formamide (109)	6.1	30	58
		Adhesion energy in a medium[b] $W = -2\gamma_i = -A/12\pi D_0^2$ (mJ m^{-2})	
Mica in water and dilute NaCl and KCl solutions	2.0	19	~10

[a] Note the good agreement between theory and experiment for γ (within 20%) except for the six strongly H-bonding liquids (in bold).

[b] Experimental values compiled from pull-off force measurements between curved surfaces using Eq. (12.10): $W = 2F/3\pi R$ (McGuiggan and Israelachvili, 1990; Shubin and Kekicheff, 1993). The adhesion and interfacial energies of many systems have contributions from other short-range forces, both attractive and repulsive (see Table 21.1). Values taken from various sources including Drummond et al., (1996) and Drummond and Chan (1997).

poor agreement for H-bonding molecules