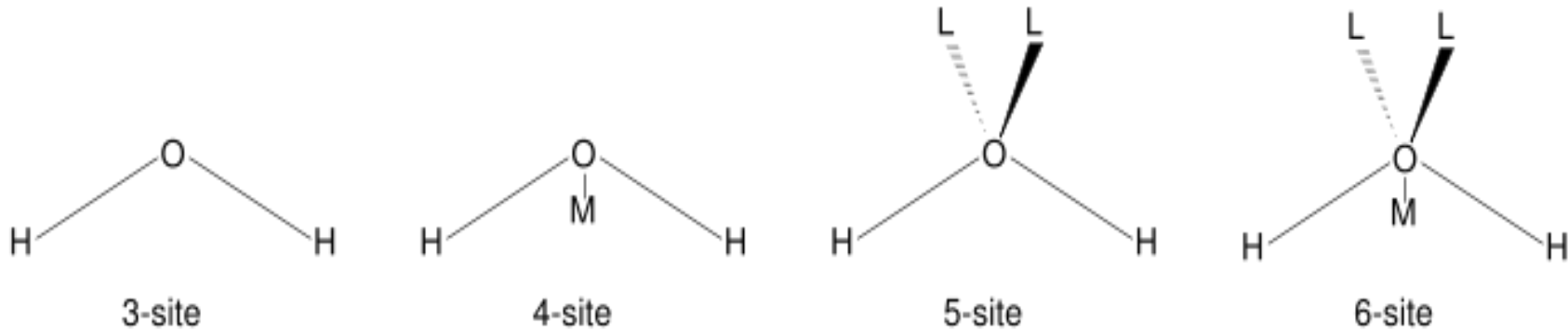
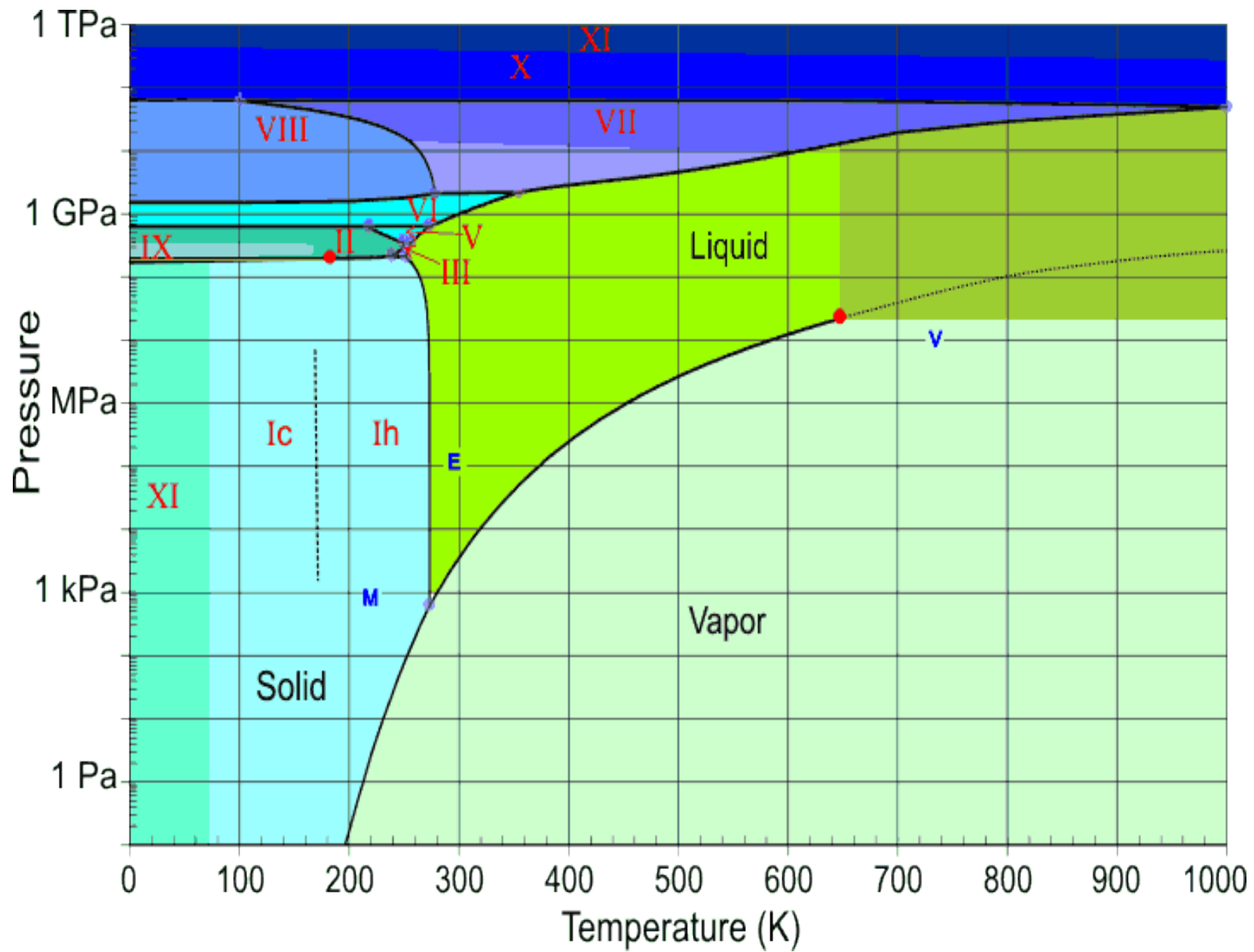


Water force fields

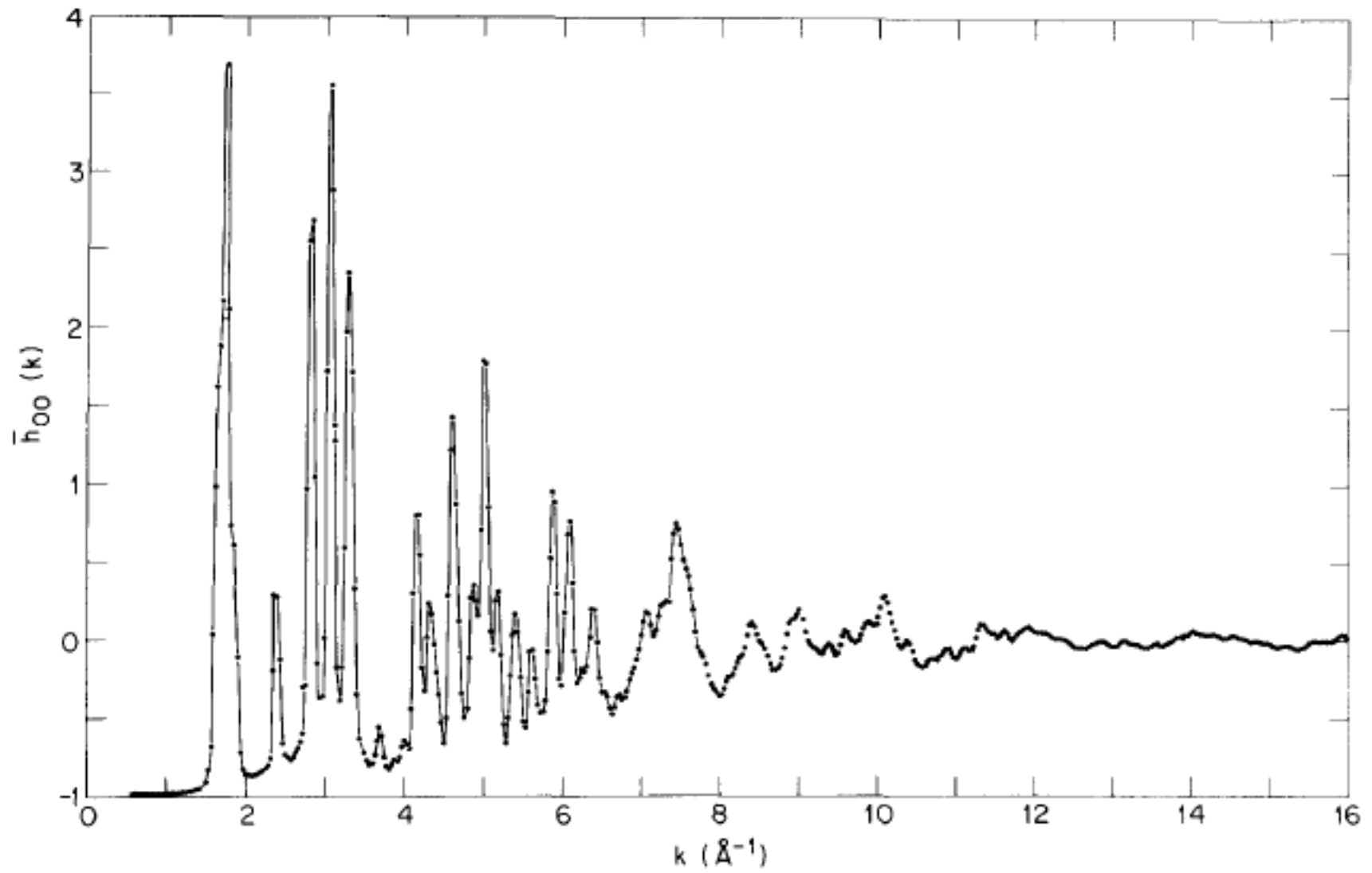


$$E_{12} = \sum_{1, j} \sum_{2, m} \left(\frac{q_j q_m}{r_{jm}} + 4\epsilon_{jm} \left[\frac{\sigma}{r_{jm}^{12}} - \frac{\sigma}{r_{jm}^6} \right] \right)$$

Acronym (date)	Reference	Status	Type	Sites	$\mu_g(D)$	$\mu_l(D)$
BF (1933)	7	empirical	R	4	2.0	2.0
R (1951)	21	empirical	R	5	1.84	1.84
BNS (1971)	22	empirical	R	5	2.17	2.17
ST2 (1973,1993)	23	empirical	R	5	2.35	2.35
CF (1975,1978,1995)	24	empirical	F	3	1.86	1.98
MCY (1976)	25	ab initio	R	4	2.19	2.19
DCF (1978,1980,1993)	26	empirical	F,D,P	3	1.855	-
PE (1979)	27	empirical	P	1	1.855	2.50
SPC (1981)	14	empirical	R	3	2.27	2.27
TIP3P (1981,1983)	15	empirical	R	3	2.35	2.35
RWK (1982)	28	empirical	F	4	1.85	1.89
TIP4P (1983)	15	empirical	R	4	2.18	2.18
BJH (1983)	29	empirical	F	3	1.87	1.99
SPC/F (1985)	30	empirical	F	3	2.27	2.42
MCYL (1986)	31	ab initio	F	4	2.19	2.26
SPC/E (1987)	32	empirical	R	3	2.35	2.35
WK (1989)	33	empirical	R	4	2.60	2.60
SPCP (1989)	34	empirical	P	3	1.85	2.90
CKL (1990)	35	empirical	F,P	4	1.88	2.20
MCHO (1990)	36	ab initio	P	6	2.12	≈ 3.0
NCC (1990)	37	ab initio	P	6	1.85	2.80
NEMO (1990,1995)	38	ab initio	P	5	2.04	2.89
PTIP4P (1991)	39	empirical	P	4	1.85	2.80
SPC/FP (1991)	40	empirical	F,P	3	1.85	2.44
PSRWK (1991)	41	empirical	P	4	1.88	2.63
KJ (1992)	42	empirical	P	4	1.85	-
NCCvib (1992)	37b	ab initio	F,P	6	1.85	3.11
ASP-W (1992,1998)	43	ab initio	P	3	1.85	2.90
RPOL (1992)	44	empirical	P	3	2.02	2.62
CPMD (1993,1999)	45	DFT+CP	F,D,P	nucl.+cl.	1.87	2.95
PPC (1994)	46	ab initio	P	4	2.14	2.51
SPC/FQ (1994)	47	empirical	P	3	1.85	2.83
TIP4P/FQ (1994)	47	empirical	P	4	1.85	2.62
KKY (1994)	48	empirical	F,D	3	2.38	2.21
SQPM (1995)	49	valence bond	P	4	1.85	2.62
SCPD (1996)	50	empirical	P	4	1.85	2.87
TAB/10D (1998)	51	SCF+MD	P	5	1.85	2.65
NSPCE (1998)	52	empirical	R	3	2.18	2.18
NCF (1998)	53	empirical	F	3	1.85	1.90
MCDHO (2000)	54	ab initio	F, P	4	1.85	3.01
TIP5P (2000)	55	empirical	R	5	2.29	2.29
SPC/HW (2001)	56	empirical	R	3	2.41	2.41
DEC (2001)	57	empirical	R	3	1.85	1.85
SWFLEX (2001)	58	empirical	P	4	1.85	2.59
POLARFLEX (2001)	59	valence bond	F,P	3	1.85	2.55
POL5 (2001)	60	ab initio	P	5	1.85	2.71



X-ray structure of ice Ih



Pair distribution function of water

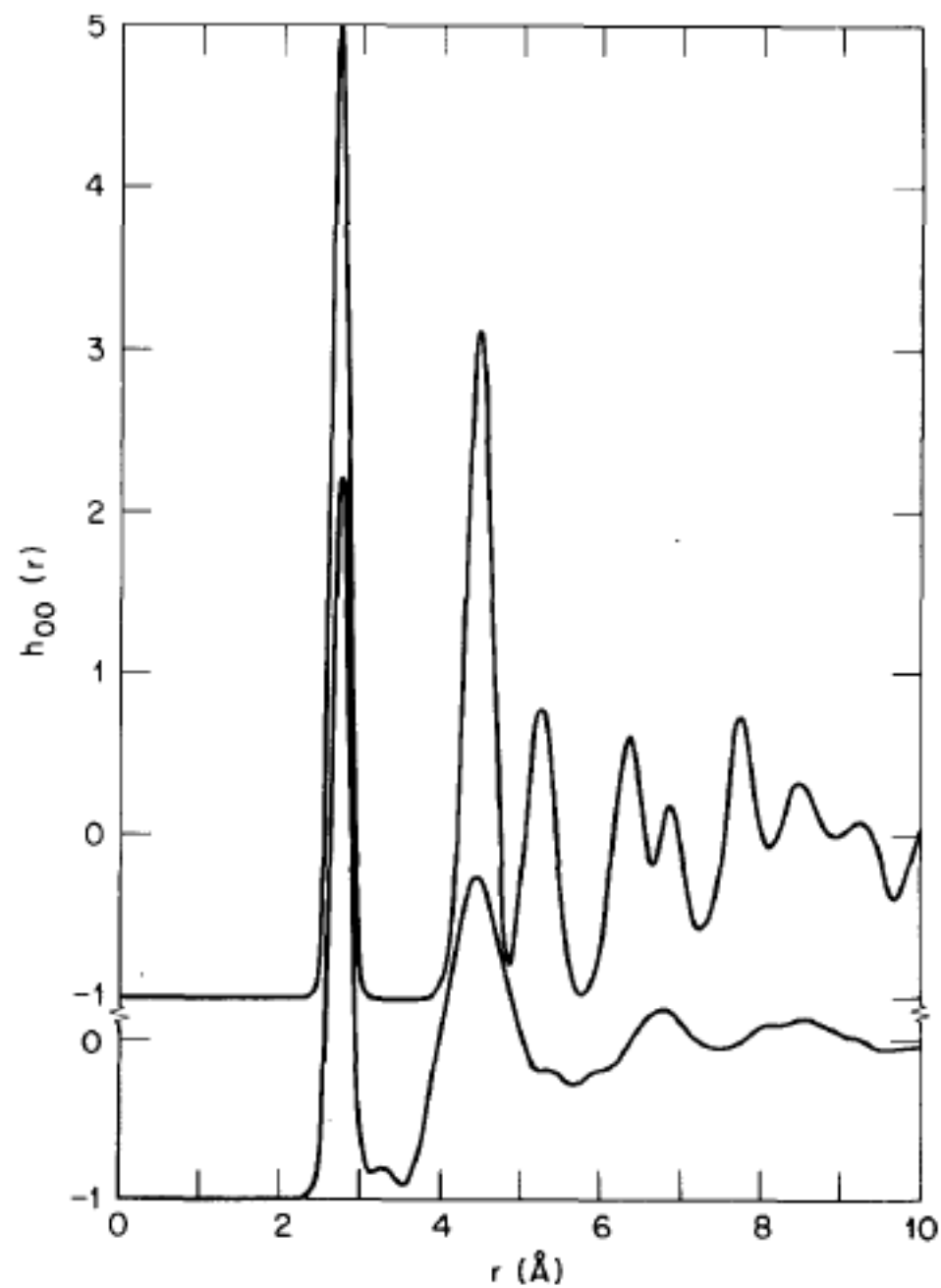
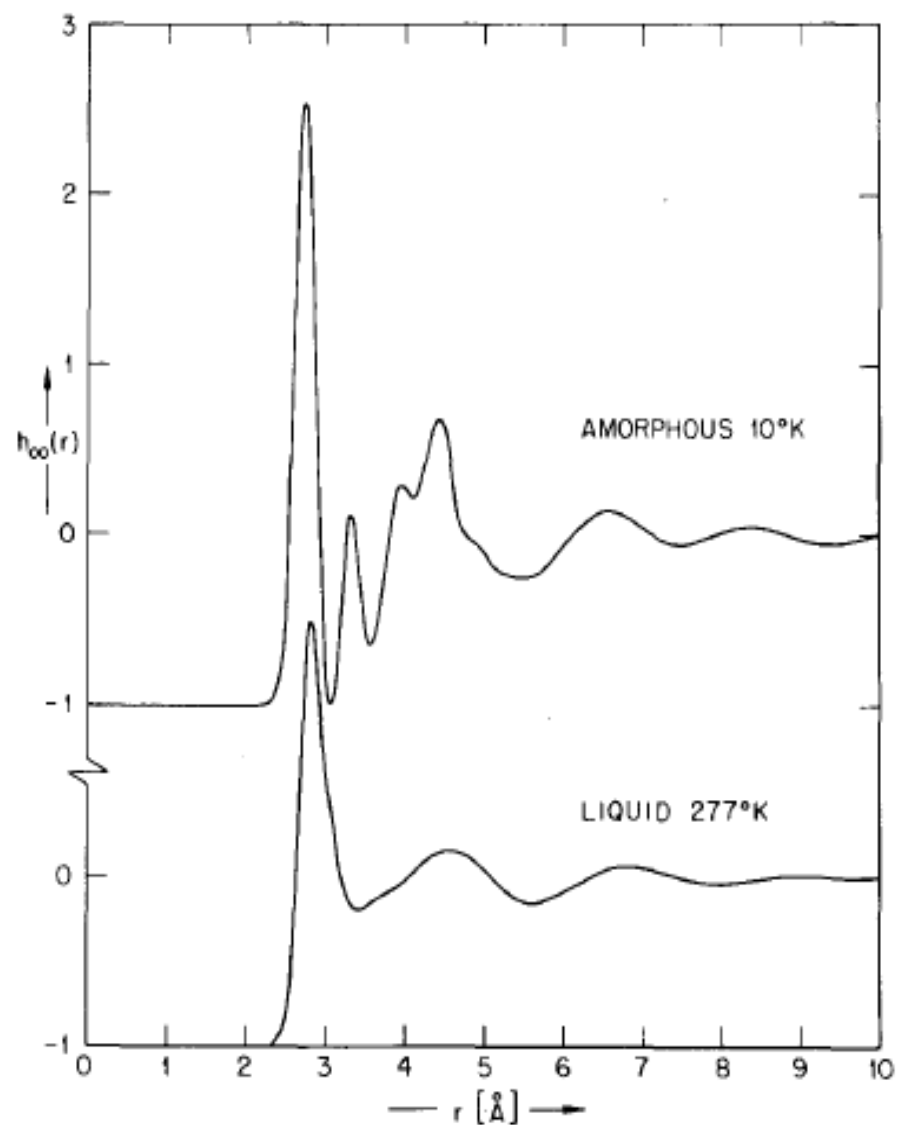


FIG. 6. Oxygen atom pair correlation functions for polycrystalline ice Ih (top) and for $H_2O(as)$ (bottom), both prepared and studied at 77°K, derived from x-ray diffraction.

Excluded volume

With fixed diameter σ there is an upper limit to the number of molecules that can be contained in a fixed volume V . In 3D the densest possible packing is

$$\frac{V}{N} = v_c = \sigma^3 / \sqrt{2}$$

Packing fraction:
$$\frac{V_{liq}}{V} = \frac{\pi/6 \sigma^3 N}{V} = (\pi/6) \sigma^3 \rho$$

Maximum possible packing fraction:

$$\eta = \frac{V_{liq}}{V} = \pi\sqrt{2}/6 \simeq 0.7405$$

For liquids, $\eta = 0.64$

From ideal gas to liquid

Ideal gas:

$$\frac{PV_m}{kT} = \frac{P\pi\sigma^3/6}{kT} = \eta$$

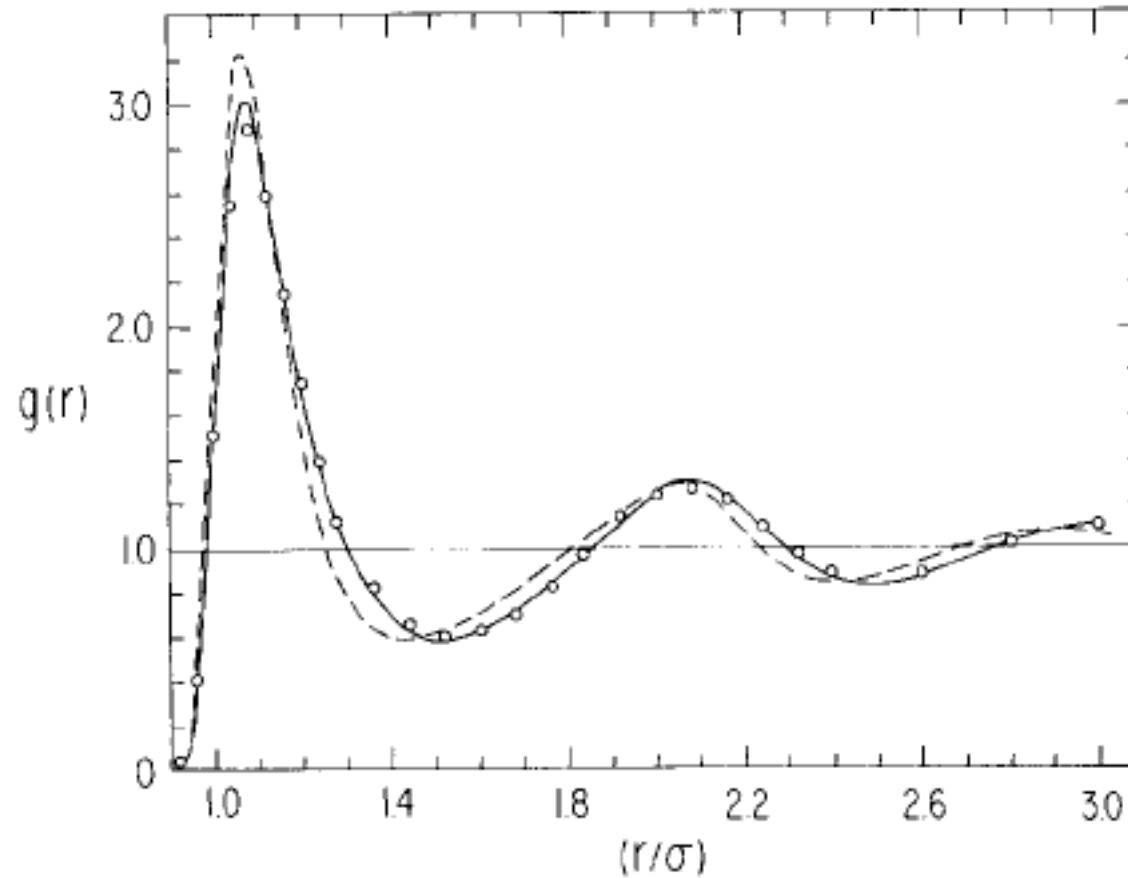
One-dimensional gas (rods in the tube):

$$\frac{PV_m}{kT} = \frac{\eta}{1 - \eta}$$

Three-dimensional liquid of hard spheres:

$$\frac{PV_m}{kT} = \frac{\eta(1 + \eta + \eta^2 - \eta^3)}{(1 - \eta)^3}$$

Radial pair distribution function obtained from the liquid of hard spheres (line) compared to molecular dynamics simulations (points)
J. Chem. Phys., 1971.



Van Der Waals liquid

$$\frac{PV}{kT} = Z_{rep} - Z_{att}$$

$$Z_{rep} = \frac{1}{1 - b\eta} \quad Z_{att} = -a\eta^2$$

Generalized van der Waals equation:

$$\frac{PV}{kT} = \frac{(1 + \eta + \eta^2 - \eta^3)}{(1 - \eta)^3} - a\eta^2$$

Putting stuff in: Solvation

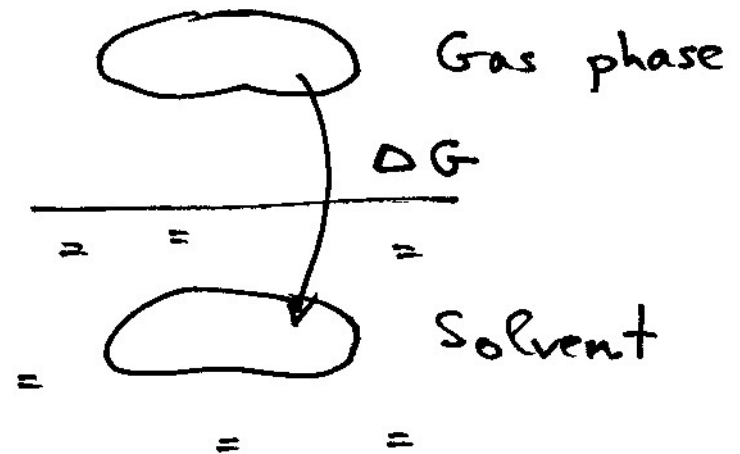
What makes molecules like to be there?

Gibbs energy reaches its minimum for spontaneous processes at constant T and P

$$G = E - TS + PV$$

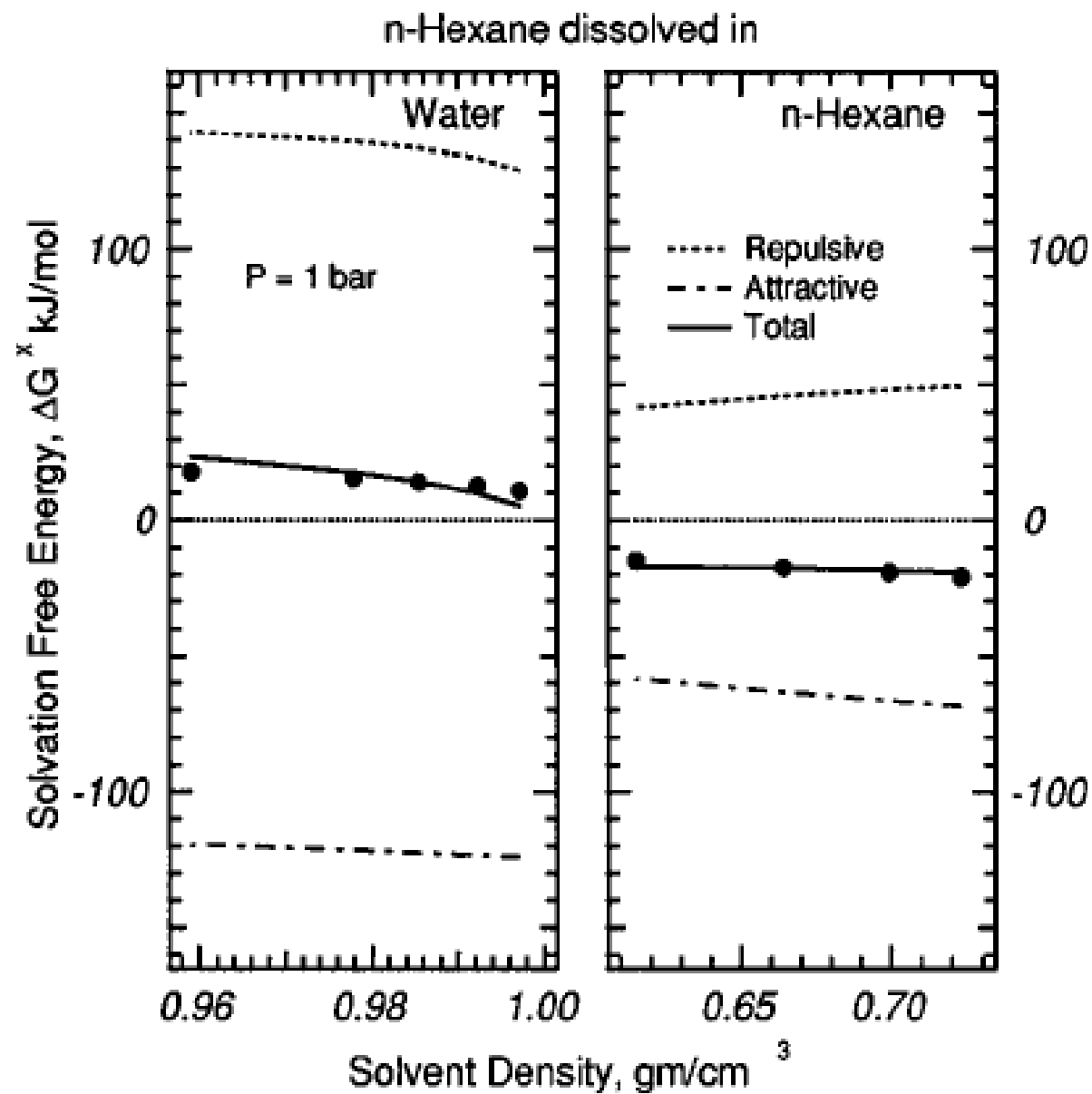
Reaching minimum: either by minimizing the energy or by maximizing the entropy (number of states). The second route gains in importance at increasing temperature

Solvation



Electrostatic part
of solvation Gibbs
energy

$$\Delta G = \Delta G_{rep} + \Delta G_{att}$$



Why does soda lose gas when heated?

Cavity Gibbs energy / kT (BMCSL):

d =ratio of solute/solvent diameters

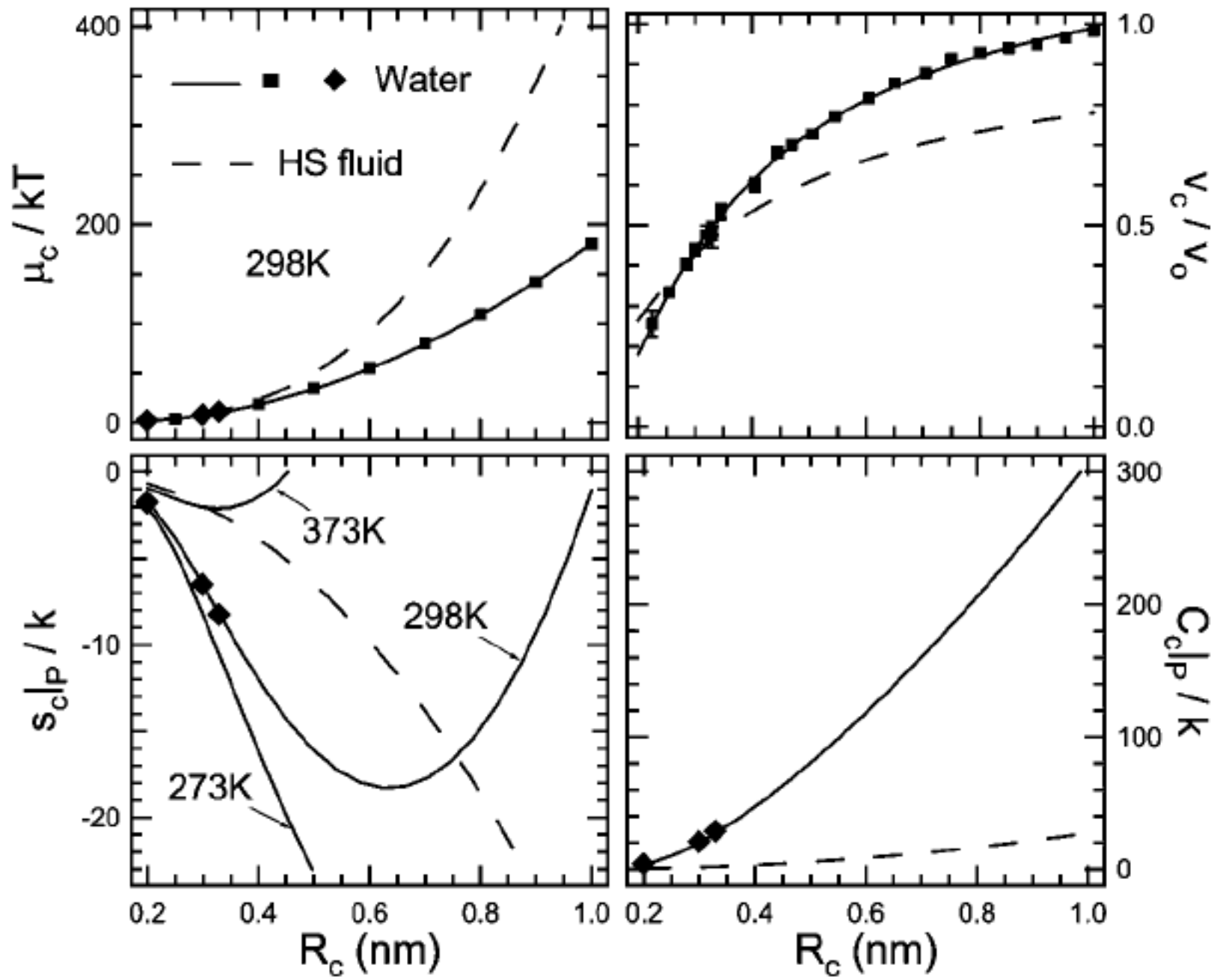
$$\beta_{\mu}^x(d, \eta) = \frac{2\eta d^3}{(1-\eta)^3} + \frac{3\eta d^2}{(1-\eta)^2} + \frac{3\eta d(1+d-d^2)}{(1-\eta)} - (1-3d^2+2d^3)\ln(1-\eta).$$

DM'97:

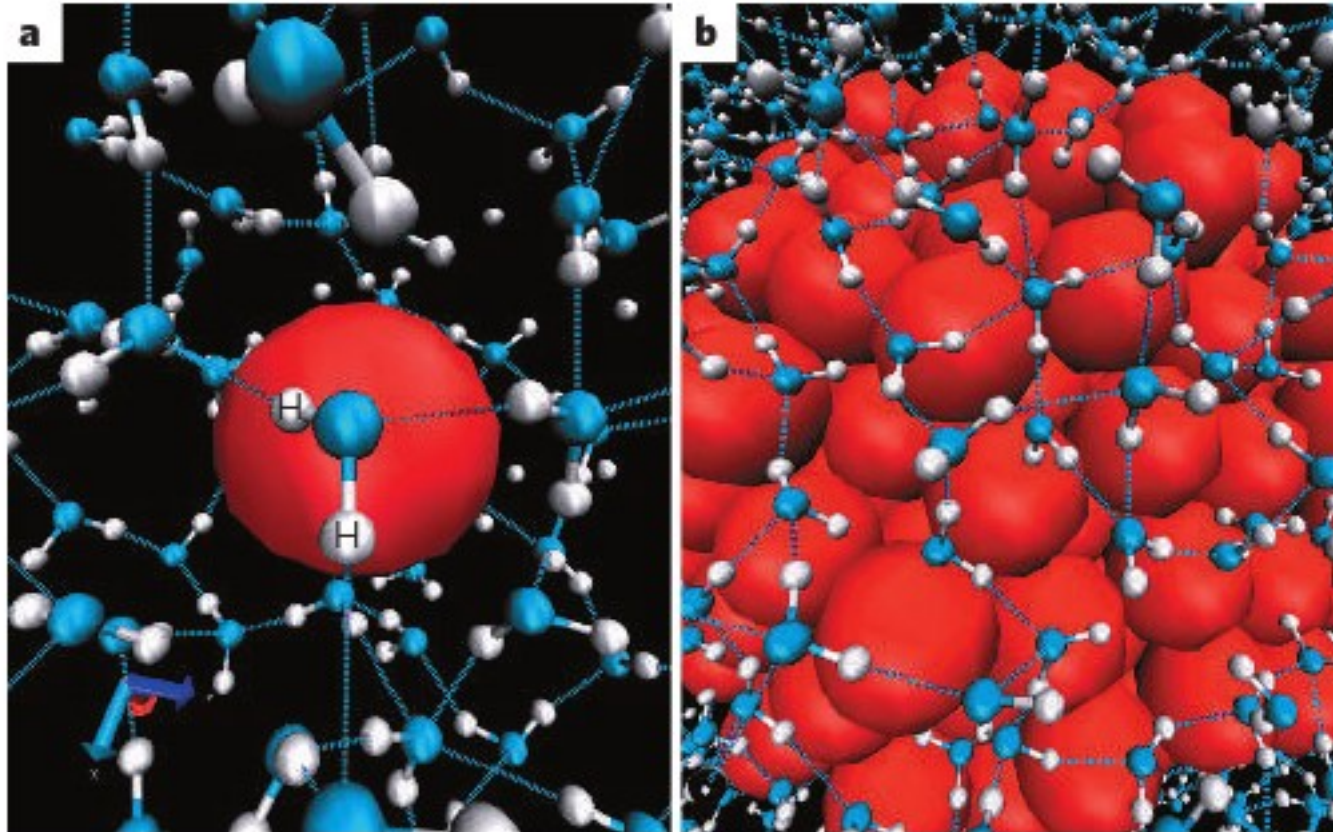
$$\beta\mu_{\text{cav}}(d) = \frac{3\eta}{(1-\eta)}d + \frac{3\eta(2-\eta)(1+\eta)}{2(1-\eta)^2}d^2 + \frac{\eta(1+\eta+\eta^2-\eta^3)}{(1-\eta)^3}d^3 - \ln(1-\eta).$$

$$\Delta G_{\text{rep}} \propto T$$

Equilibrium concentration of gases in liquids decreases with increasing temperature!



Why does detergent work? Hydrophobic assembly!



Water preserves hydrogen-bond network around small solutes and breaks it around large solutes. There are on average 3 H-bonds for each water on the surface of a large solute.

Cross-over in hydrophobic solvation

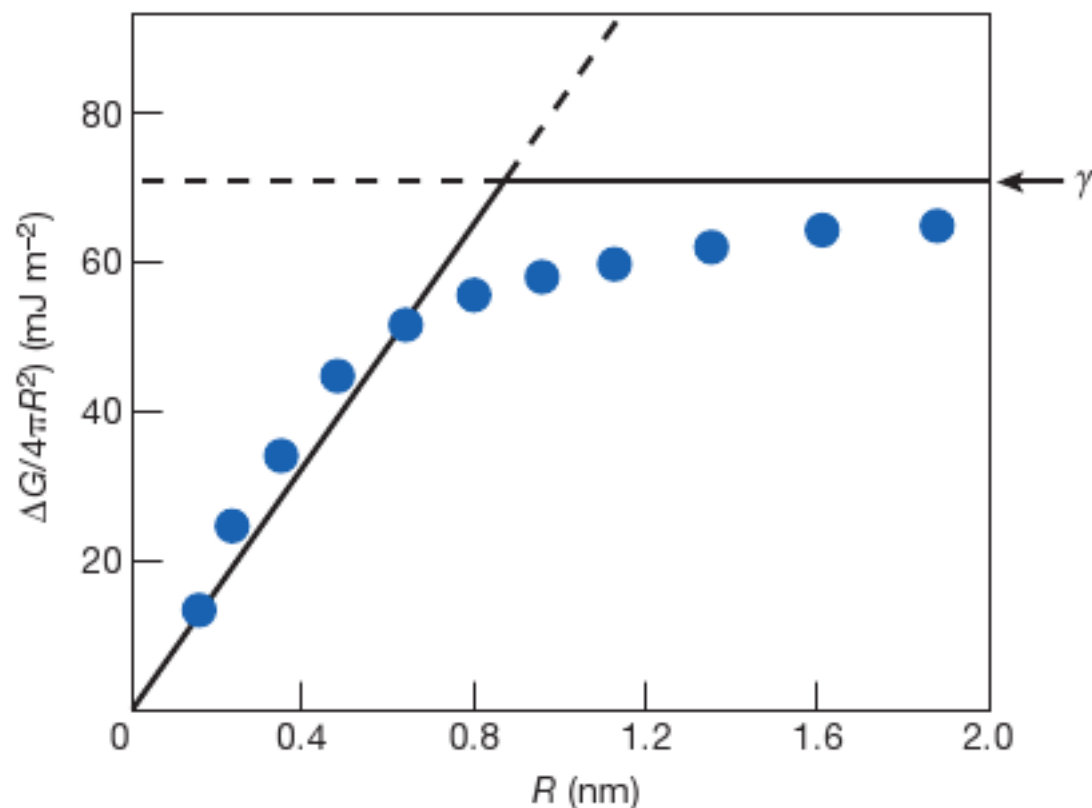
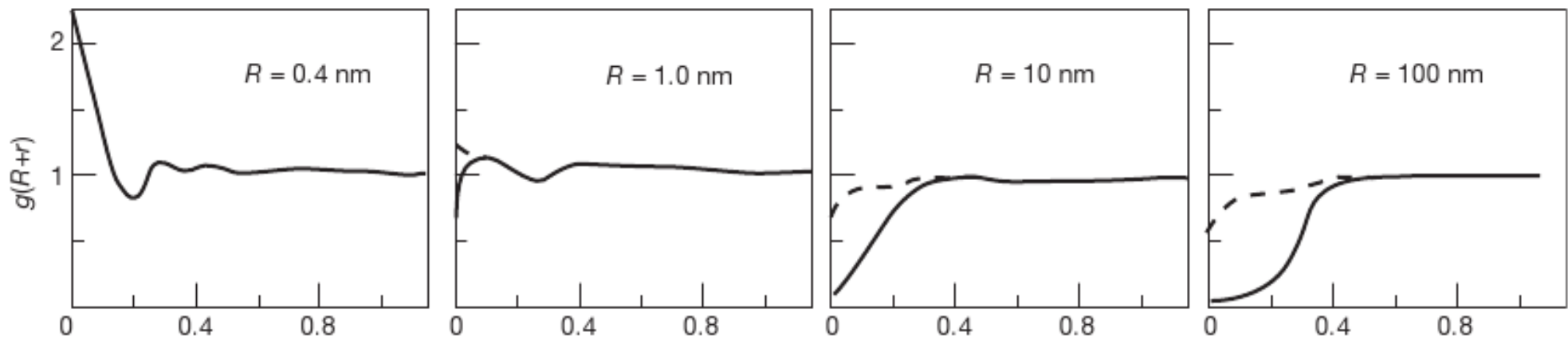
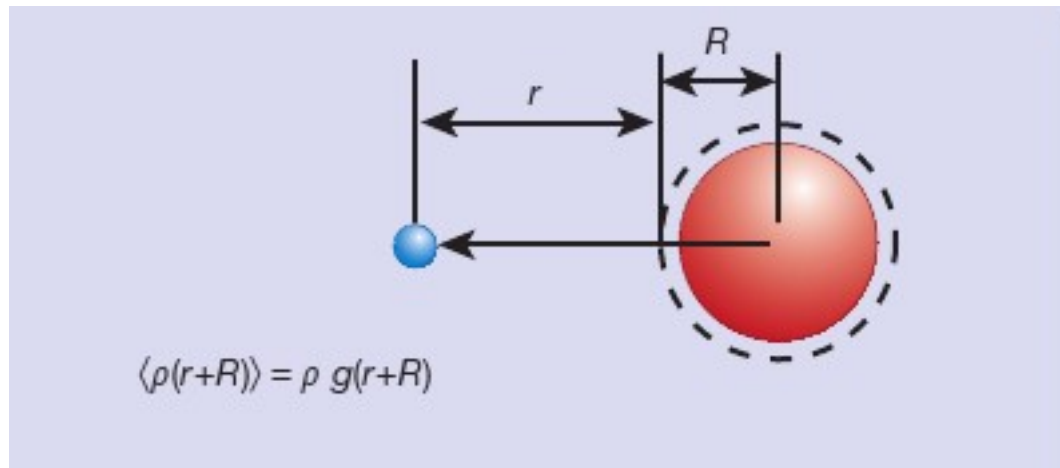


Figure 2 | Solvation free energy, ΔG , for a spherical cavity in water as a function of the cavity size. The results are for ambient conditions (room temperature and 1 atm pressure). The circles show the results of detailed microscopic calculations²⁵. The liquid–vapour surface tension is shown by γ . The solid lines show the approximate scaling behaviour of $\Delta G/4\pi R^2$ for small R , and the asymptotic behaviour for large R . This approach can be used to infer the typical length characterizing the crossover behaviour, but not the quantitative behaviour of ΔG in the crossover regime.

Wet or dry?



Hydrophobic assembly, now you can get it!

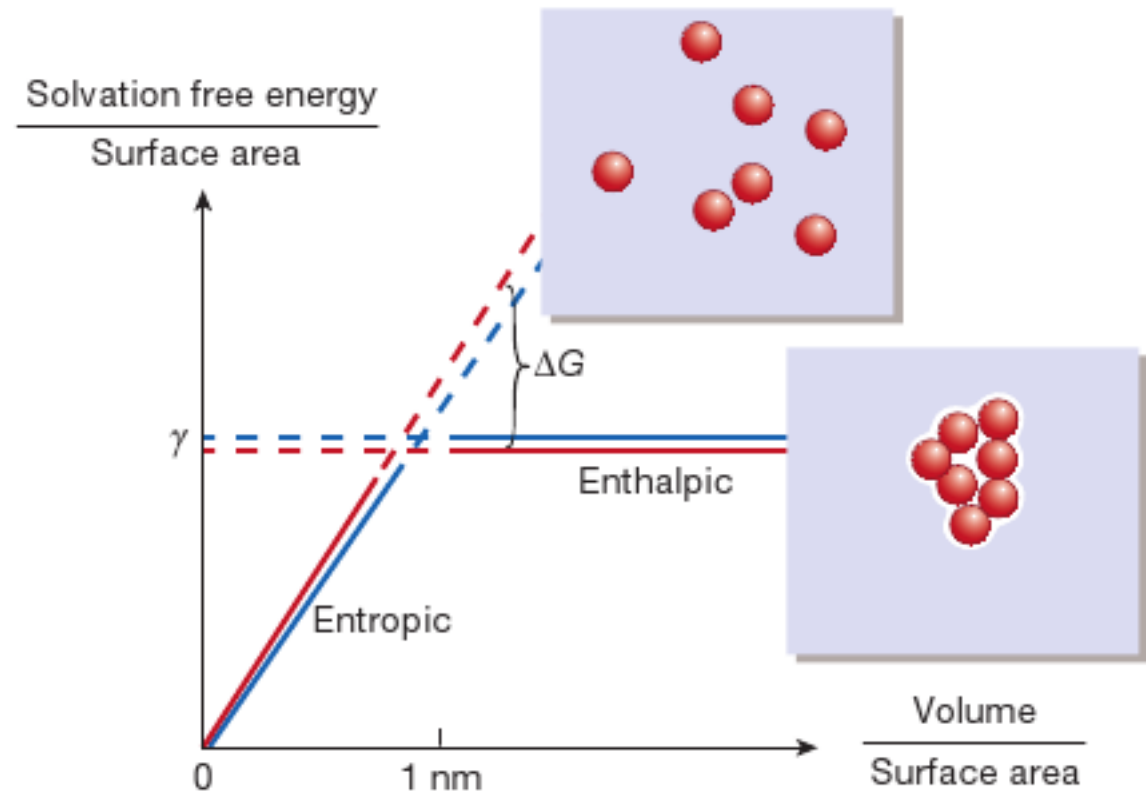


Figure 4 | The driving force, ΔG , for assembling a cluster of small hydrophobic particles. For large enough clusters, ΔG is a favourable driving force. The horizontal and sloping lines indicate the behaviour of the solvation free energy for the assembled and disassembled cluster, respectively. Red lines indicate the free energies at a higher liquid temperature; blue lines indicate the free energies at a lower temperature. The liquid-vapour surface tension is indicated by γ . 'Volume' and 'surface area' denote the volume excluded to water, and the solvated surface area of that volume, respectively.