

Scaling, Structure, and Transport in Materials

*Why size matters, and when it
doesn't*

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August 30, 2022

Outline

- The Quantum Capacitor
- Scale invariance and self similarity in certain things
 - Fractals, Critical Phenomena, Benford's Law, etc.
 - Materials application: Aerogel
- Failure of gradient theories in transport at small scales
 - The continuum approximation, and its impact on our intuition
 - Effects of discrete ordering on large things
- How does our intuition change as we go small?
 - Classical Effects (mainly 4/5/08)
 - Phase change
 - Viscosity and mechanical motion
 - Importance of surface tension
 - Heat transport
 - Surface dominated effects at the nanoscale
 - Quantum Effects (mainly 4/7/08)
 - Confinement and zero-point energy
 - Exchange symmetry of identical particles
 - Examples in real materials
 - Devices at the quantum limit

Single Electron Capacitor

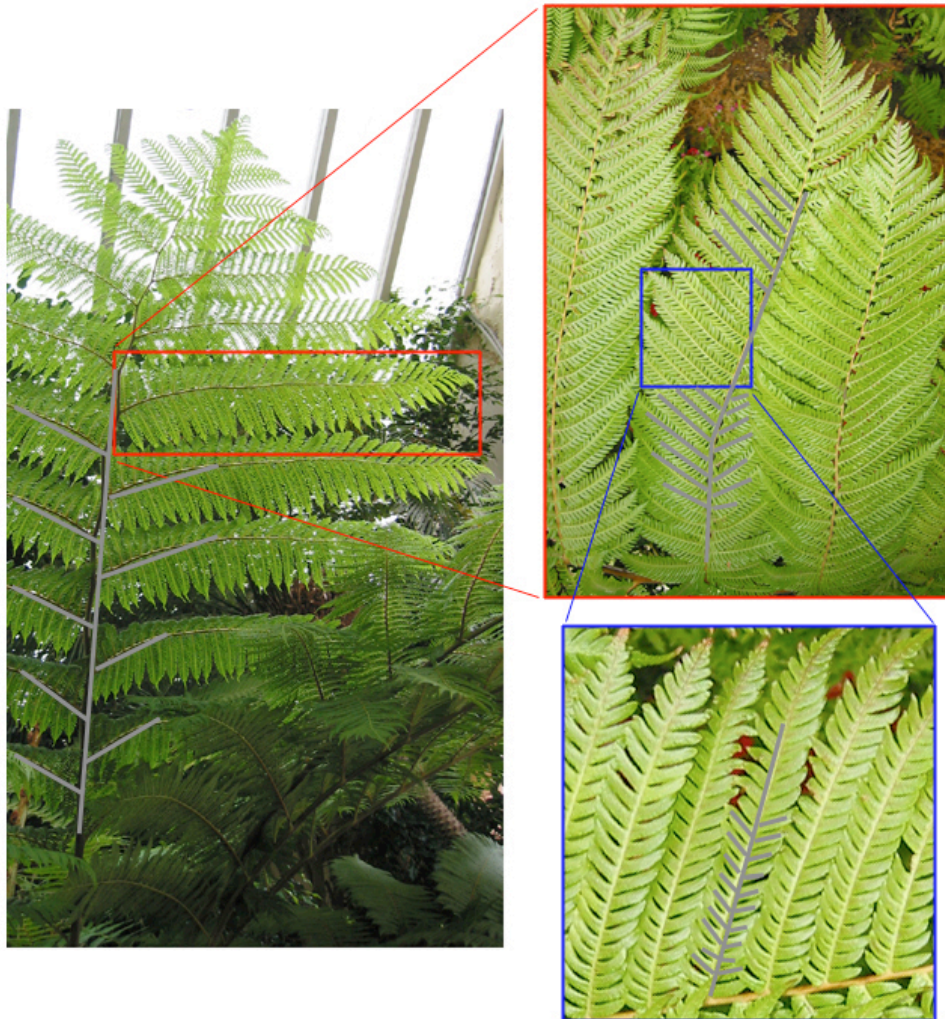
- See the short paper by R.V. Duncan
- $E_n = n^2 e^2 / (2C)$ which must be $\gg k_B T$
- Furthermore, $\Delta E \Delta t \sim h$
 $\Delta t = RC$, $\Delta E \ll (E_2 - E_1)$
 $R \gg h / e^2$, the Von Klitzing Constant

Scale invariance and structural self-similarity

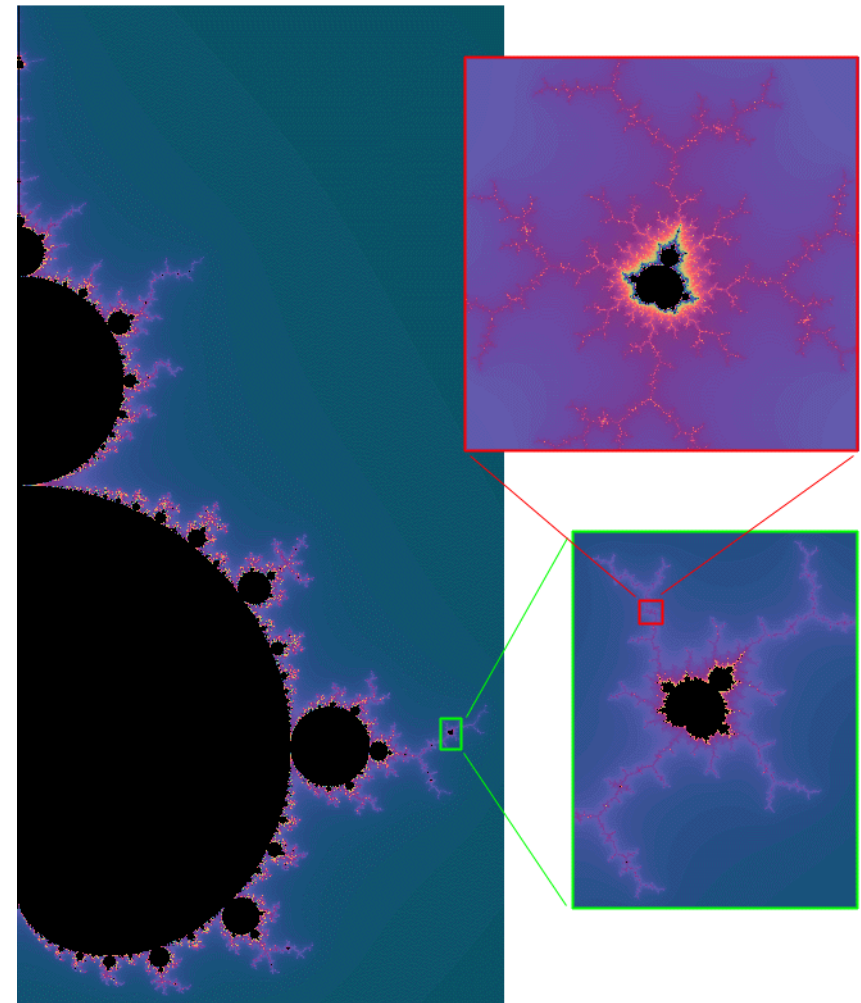
From Paul Bourke, <http://local.wasp.uwa.edu.au/~pbourke/fractals/selfsimilar/>

Many examples: Static terrain, Dynamic 1/f noise,

Ferns :

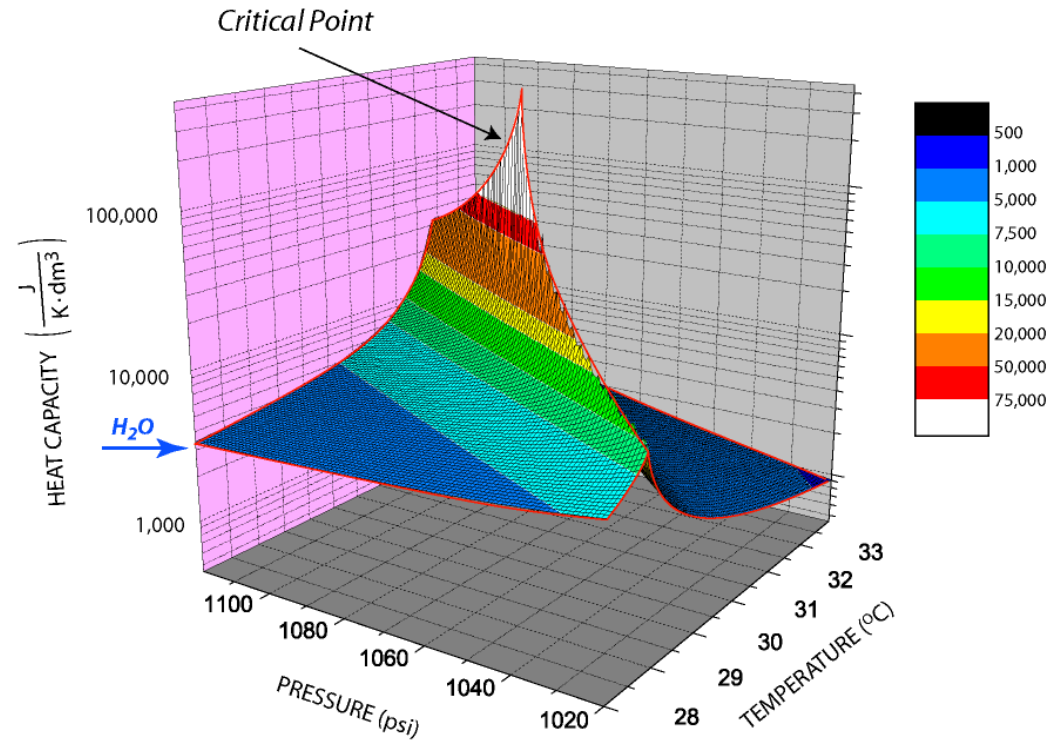
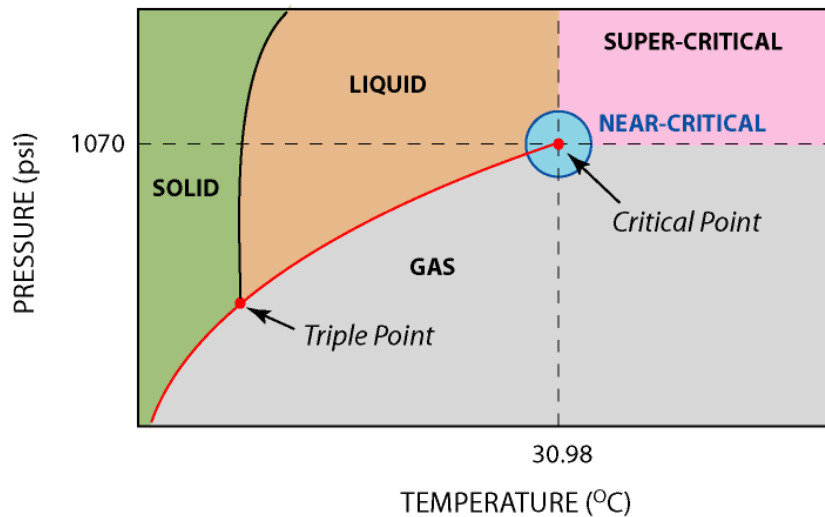


Mandelbrot Sets:



In almost all pure substances...

CO₂ in this case:



The heat capacity, isothermal compressibility, thermal expansion coefficient, etc. all become very large at the Critical Point, as does the magnetic susceptibility near a magnetic critical point (Curie Point). Only at the critical point do the fluctuations between the ordered and disordered phases become very large, diverging as the critical point is approached. This leads to universality and scale-invariance of the thermodynamic properties near critical points.

Aerogel

- Nice video:
<http://www.youtube.com/watch?v=5PfelqRpOQk>
- Picture at the right is from Wikipedia:
<http://en.wikipedia.org/wiki/Image:Aerogelbrick.jpg>
- Many applications!



Aerogel: example of critical drying

- Liquid – vapor density difference goes to zero at the critical point.
- Large fluctuations of the liquid phase fraction are solidified as the sample is dried, resulting in a fractal distribution of open space regions.
Aerogel is 1% of the solid glass density.
- Drying at the critical point permits the liquid to be drawn off the solidified matrix without collapsing it through surface tension.

Thermodynamic self-similarity near critical points

$$C_V = A^{+/-} \left(\frac{|T - T_c|}{T_c} \right)^{-\alpha} + B^+$$

Specific heat near the superfluid transition in ^4He .
Buckingham and Fairbank, 1965,
and Lipa et al., 1992.

Similar behavior for all materials
In the same 'universality class'
Which depends only on
dimensionality and number of
components in the order parameter

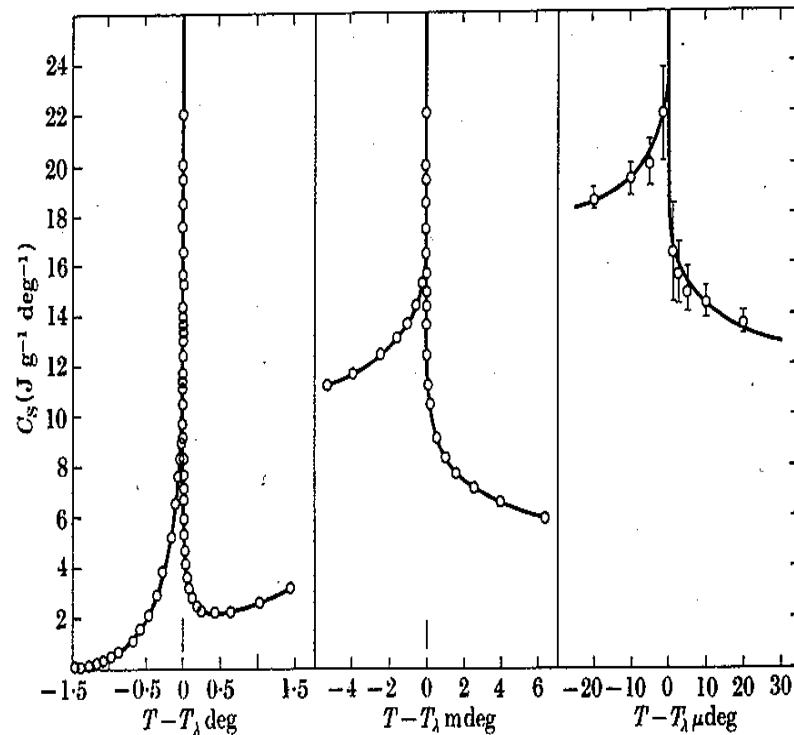


Fig. 1.16. Specific heat of ^4He as a function of $T - T_\lambda$ in K. Notice that the shape of the specific heat curve is rather like the Greek letter λ , whence the origin of the term ' λ -transition'. The fact that the specific heat is only about ten times its 'normal' value even at temperatures only a few microdegrees from T_λ is correlated with the fact that the critical-point exponent is extremely small (in fact, α is probably zero, corresponding to a logarithmic divergence). The width of the small vertical line just above the origin indicates the portion of the diagram that is expanded in width in the curve directly to the right. After Buckingham and Fairbank (1965).

How do we describe self-similarity?

- $P(N)$ such that $P(bN) = A(b) P(N)$
- Solution: $P(N) = \text{constant} * N^{-\alpha}$
 - Only the power law function is self-similar
 - $P(N)$ may be the frequency of an event of size N , or other self-similar phenomena
- Per Bak: Self-organized criticality (SOC)
 - How Nature Works (Springer-Verlag, 1996)
- Usually $\alpha = 1$, but sometimes it does not
 - In earthquake data, $\alpha \approx 2$.

Example: Benford's Law and Information Security

- $P(N) = N^{-1}$ where P is the probability of obtaining a number N in broad context data.
- $p(n)$ is the probability of first digit n

$$p(n) = \int_n^{n+1} N^{-1} dN = \log\left(\frac{n+1}{n}\right) = \log(1 + n^{-1})$$

How size matters as you go small

- Viscid forces dominate at very small sizes, and random motion wins out over weight and buoyancy
- Little things in motion generate low Re flow, and motion is dominated by viscid drag, not momentum through the fluid.
- Diffusion spreads out as $(2Dt)^{1/2}$ and D becomes large for small things.
- Surface tension becomes very important at small length scales, resulting in new methods of self-assembly
- Heat flow becomes much more efficient, both through diffusion and radiation, but heat convection becomes insignificant
- Quantum confinement leads to zero-point energy, and quantum symmetry for identical particles result in counter-intuitive properties

What happens when we scale to very small systems?

- Gradient theories of transport (Fourier's Law, Ohm's Law, etc.) fail at length scales shorter than the mean free path of electrons and phonons, for $< \sim 50$ nm
 - Electronic band theory fails
- Discrete molecular structure replaces continuum models, for < 1 nm
 - Elasticity and other bulk properties emerge from inter-molecular forces and symmetry

How to 'Think Nano'

- Consider how known classical phenomena scale as you reduce the system size
 - Heat transport
 - Mechanical motion and flow
 - EM fields and acoustic wave interactions
 - Information storage
- Systems become dominated by quantum effects
 - Confinement zero-point energy
 - Identical particle exchange symmetry considerations
 - It takes some time to become intuitive in this regard
- Ask yourself 'What is going on at the atomic level?'
- See Richard Feynman's paper, "Plenty of Room at the Bottom", December, 1959.

Solids are Anharmonic

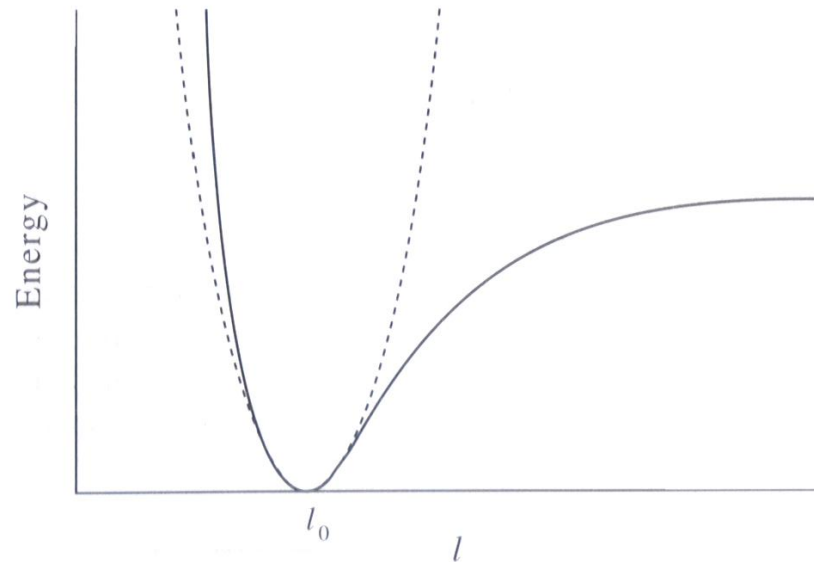


FIGURE 5.5

A comparison of the harmonic oscillator potential ($k(l - l_0)^2/2$; dashed line) with the complete internuclear potential (solid line) of a diatomic molecule. The harmonic oscillator potential is a satisfactory approximation at small displacements from the minimum.

$$E = \frac{1}{2} k (r - r_0)^2 + \beta (r - r_0)^3 + \dots$$

Hence thermal expansion

Lindemann's Theory of Melting

- $\langle E \rangle = k_B T_m = \frac{1}{2} f x_c^2$, where f is the force constant, x_c is the rms displacement.
- $F = Ya$, Y = Young's modulus and a = lattice spacing.
- So $k_B T_m = \frac{1}{2} Ya x_c^2$, now $x_c = \delta a$, **$\delta \approx 0.07$**
- Hence $T_m = Y\delta^2 a^3 / (2k_B)$, now $N_A a^3 = M/\rho$, (assuming a cubic lattice) so...

$$T_m = \frac{YM\delta^2}{2\rho R}$$

How well does This work?

See:
Martin &
O'Conner,
(1977)

Crystal	Parameters at the melting point			Values for α		
	$\sqrt{u_{\text{mean}}^2}$ (Å)	$\frac{\sqrt{u_+^2} + \sqrt{u_-^2}}{2}$ (Å)	d (Å)	from $\sqrt{u_{\text{mean}}^2}$	Present results from $\frac{\sqrt{u_+^2} + \sqrt{u_-^2}}{2}$	Other experime
Al	0.218	0.218	2.910 (a)	0.075	0.075 ± 0.001	0.082
Cu	0.219	0.219	2.608 (b)	0.084	0.084 ± 0.002	0.076
LiF	0.194	0.235	2.061 (c)	0.094	0.114 ± 0.001	
NaCl	0.327	0.328	2.928 (d)	0.112	0.112 ± 0.001	0.097
KCl	0.348	0.348	3.177 (d)	0.110	0.110 ± 0.001	0.107
KBr	0.380	0.384	3.380 (c)	0.112	0.114 ± 0.001	

(a) Simmons and Bulluffi (1960)

(b) Simmons and Bulluffi (1963)

(c) Extrapolation of thermal expansion results

(d) Pathak and Vasavad (1970)

(e) Gilvarry (1956) from results of Owen and Williams (1947)

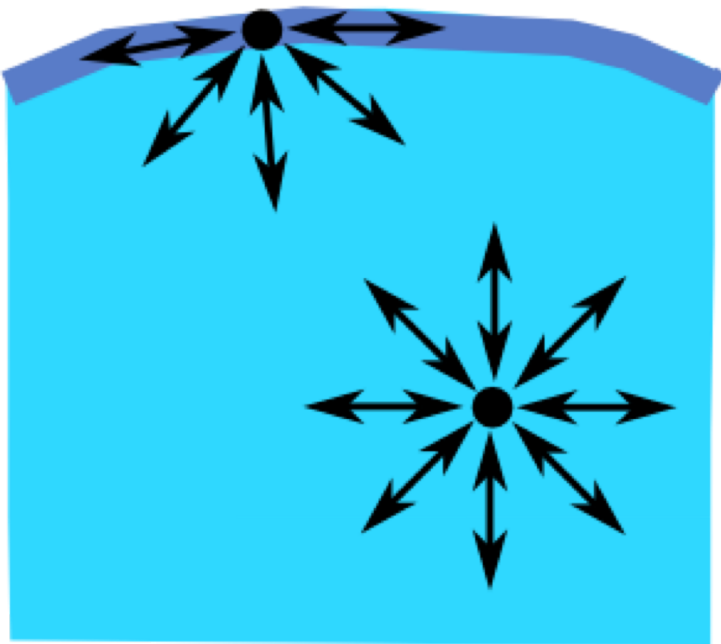
Fluid motion for small things

- Shear Viscosity η :
 - $F_{xz} / A = \eta \, dv_x/dz$
 - Larger force for more abrupt velocity change
 - If you are small then fluids are very ‘viscous’
- Reynolds Number: $Re = \rho av/\eta$
 - ‘a’ is the characteristic size of the flow channel
 - density ρ and flow speed v
 - turbulent for $Re >$ about 2,000
 - small channels provide low Re (laminar) flow
- Sphere of radius a moving at speed v
 - momentum = $4\pi\rho a^3v/3$, $F = 6\pi\eta av$
 - Stopping time $\sim a^2\rho/\eta$

Random 'Brownian' Motion

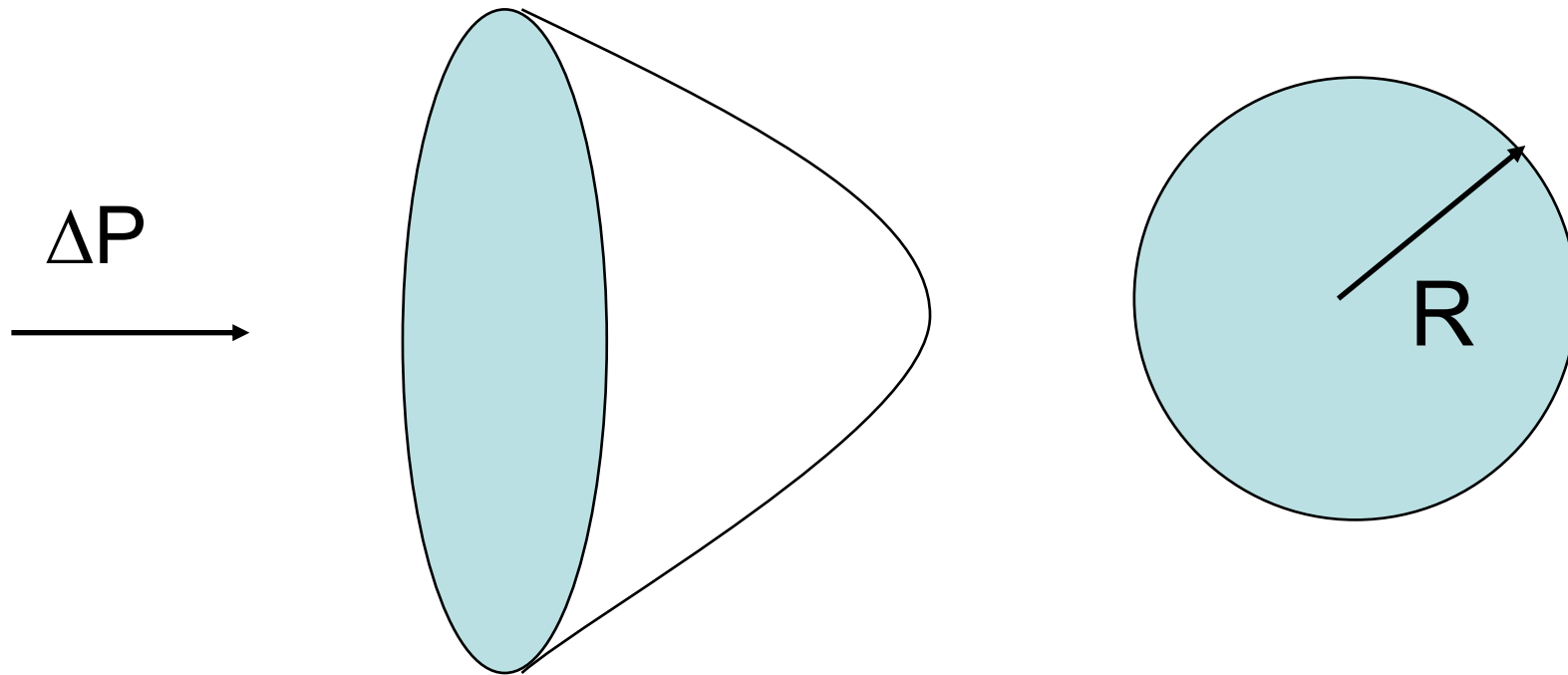
- $F_{\text{grav}} = mg = \rho L^3 g$
- $F_{\text{random}} = \delta P L^2$
- Random fluid forces begin to dominate when $\delta P = \rho L g$, so when $L < \delta P / (\rho g)$
- Typically $\delta P = 0.001 \text{ mb} = 0.1 \text{ Pa}$, so for $\rho = 3 \text{ g/cm}^3 = 3,000 \text{ kg/m}^3$, random motion dominates in air for $L < 3 \text{ microns}$

Cohesion, adhesion, and surface tension



γ = surface tension = force per unit length exerted on the circumference of the cohesive liquid = work (energy) per unit area.

Blowing bubbles: Young-Laplace



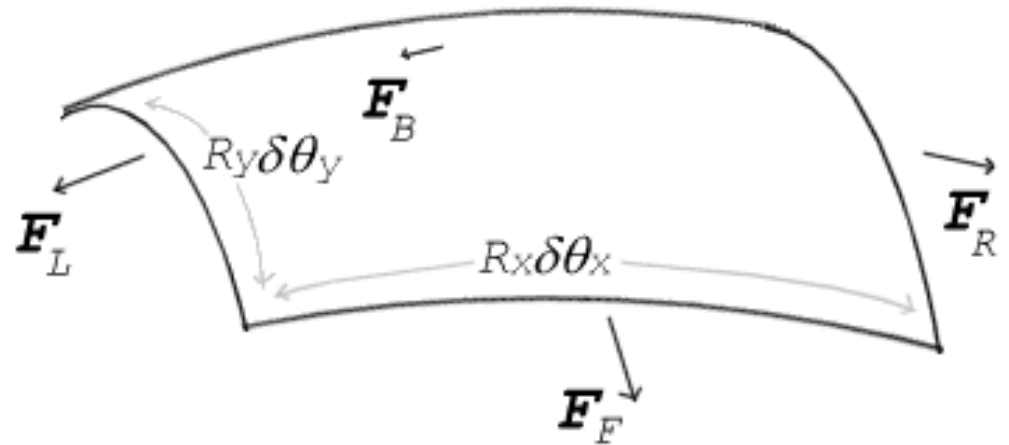
$$(2 * 2\pi R)\gamma = \pi R^2 \Delta P$$

$$\Delta P = 4\gamma/R \quad (2\gamma/R \text{ if a water drop})$$

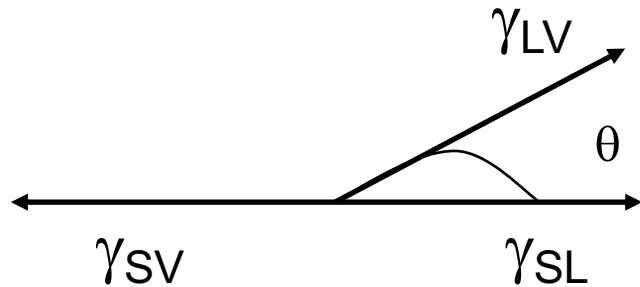
Young-Laplace Theory

- This pressure difference is large in tiny drops: for H₂O: $R = 1\mu\text{m}$, $\Delta P = 1.44\text{ atm}$
- Surfactants can decrease γ by a factor of 0.1 or more
- More generally:

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



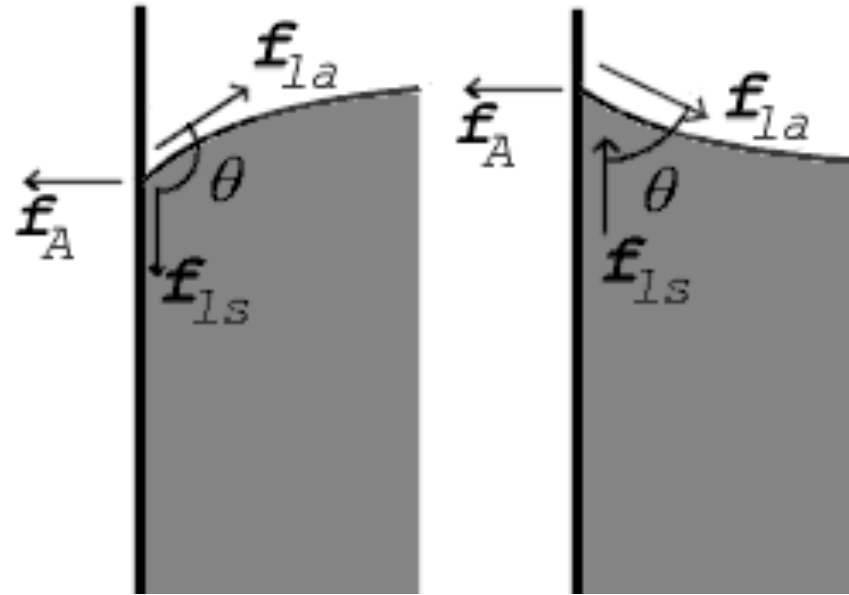
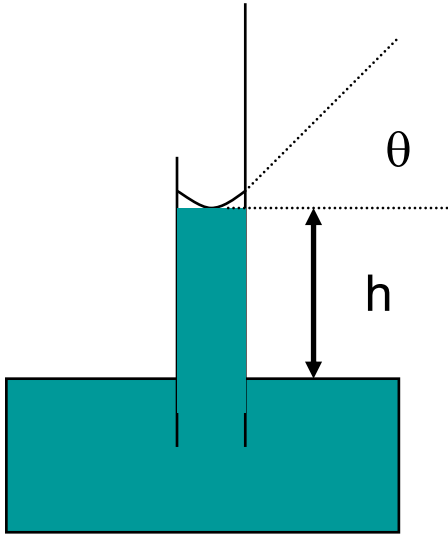
Surface Tension



$$\gamma_{LV}\cos\theta + \gamma_{SL} = \gamma_{SV}$$

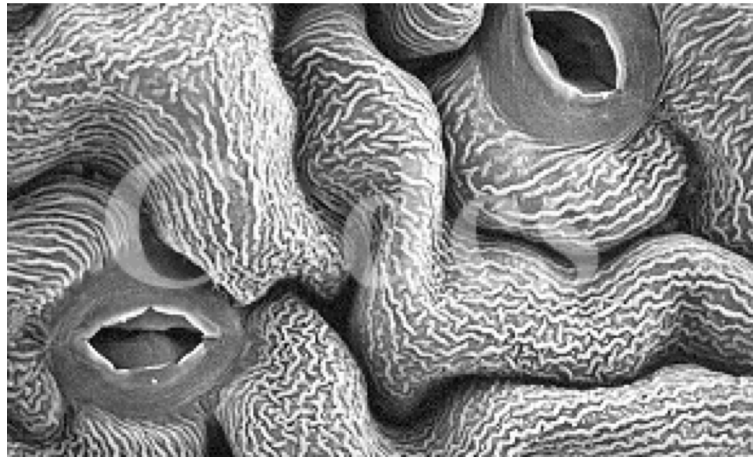
$\gamma_{LV}\sin\theta$ is the unbalanced force exerted on the surface, which exerts a huge pressure on the surface as the droplet shrinks. This force is often used in nano-engineering. Remember, critical drying made this force go to zero.

Capillary Action



$$\rho_L g h = 2\gamma \sin\theta / R$$

Why don't trees suck air and die?



Each opening is about
2 nm in diameter

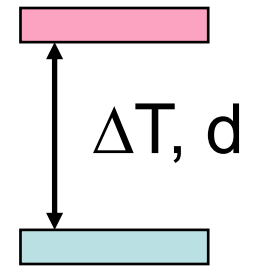
Image of Stomates (the tiny tubules in leaves) from the Image Gallery, Electron Microscopy Center, Department of Biology, Northeastern University.

<http://www.dac.neu.edu/biology/em/imagegallery.html>

$$P_{air} - P_{sap} \geq \frac{2\gamma_l}{R} = \frac{2(4 \times 10^{-2} \text{ N/m})}{2 \times 10^{-9} \text{ m}} \sim 3.2 \times 10^7 \text{ N/m}^2 \sim 320 \text{ atm}$$

Heat transfer at small distances

- ‘Conduction time’ to relax a thermal gradient $\sim d^2/D_T$
 - $D_T = \kappa/\rho C_p$ is the thermal diffusivity
 - As $d \rightarrow$ small, conduction becomes fast!
- Temperature gradient needed to start convection $\sim 1/d^3$ so convection doesn’t occur at small length scales
- Radiation heat transfer $P/A = \varepsilon\sigma T^4$, so power out $dQ/dt \sim a^2$, but heat capacity $Q \sim a^3$ so $dt = dQ/Q \sim 1/a$ so radiation cools very effectively as $a \rightarrow 0$ (nanoscale)



Heat Transfer Summary

- Hence, all intuition regarding heat transfer in large systems changes at the nanoscale
 - Conduction becomes much more efficient
 - Convection becomes insignificant
 - Radiation cools effectively at much smaller temperature differences

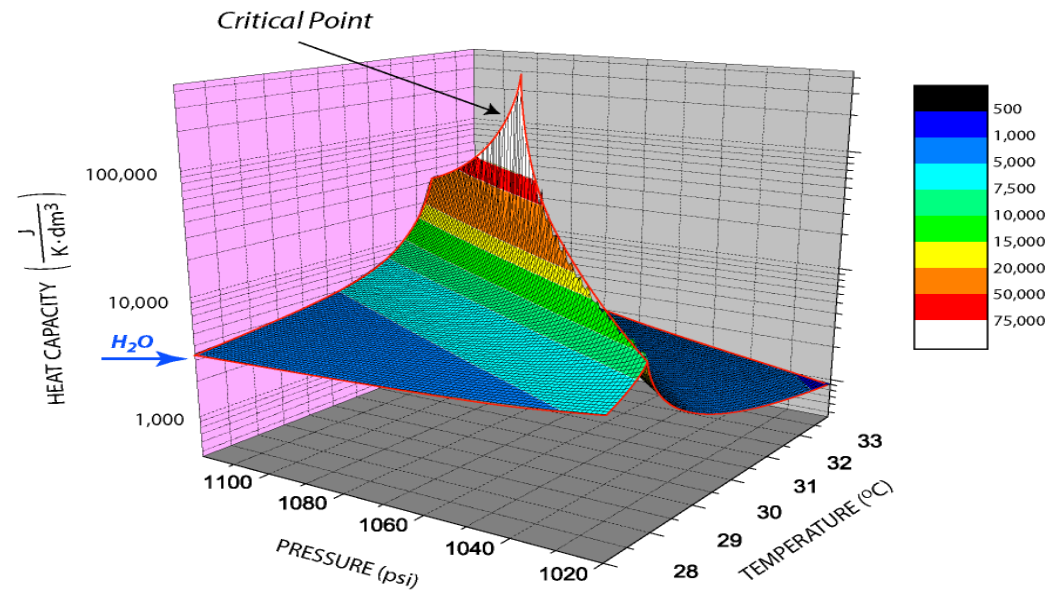
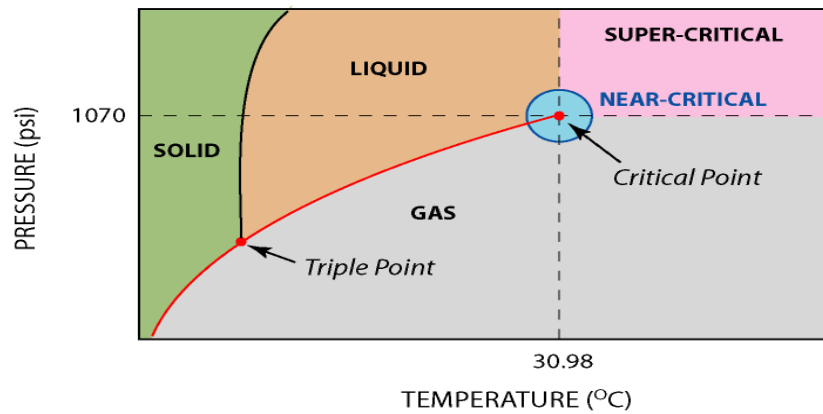
Summary: How size matters

- Viscid forces dominate at very small sizes, and random motion wins out over weight and buoyancy
- Little things in motion generate low Re flow, and motion is dominated by viscid drag, not momentum through the fluid.
- Diffusion spreads out as $(2Dt)^{1/2}$ and D becomes large for small things.
- Surface tension becomes very important at small length scales, resulting in new methods of self-assembly
- Heat flow becomes much more efficient, both through diffusion and radiation, but heat convection becomes insignificant
- Now on to: Quantum confinement leads to zero-point energy, and quantum symmetry for identical particles result in counter-intuitive properties

Introduction to Quantum Theory

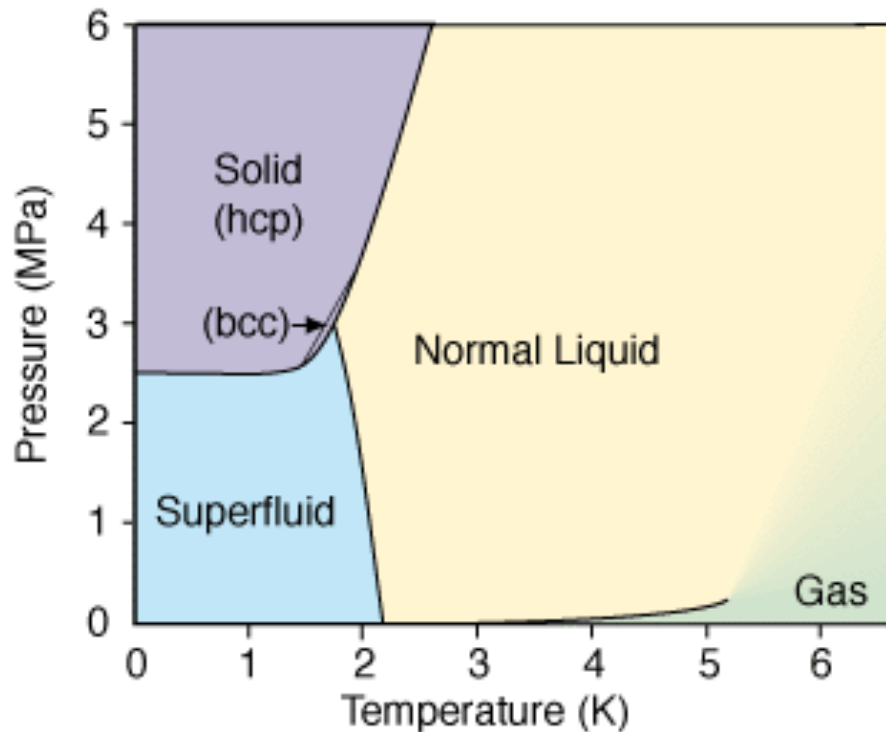
- Wave/particle duality: $\lambda = h/p$, $h = 6.7 \times 10^{-34}$ Js
 - ‘Wave’ when $\lambda >$ observer size d
 - ‘Particle’ in the opposite limit: $d \gg \lambda$
- Zero-point energy E_0
 - $p = h/\lambda$, $\lambda \sim d$, so $p = h/d$
 - $E_0 = p^2 / (2m) \sim h^2 / (2md^2)$
 - When is $E_0 \geq kT$?
- Identical particles are indistinguishable
 - Bosons: $\Psi(1,2) = \Psi(2,1)$
 - So ‘ground state’ is $\Psi(1,2) = \phi_0(1) \phi_0(2)$
 - Fermions: $\Psi(1,2) = -\Psi(2,1)$
 - So $\Psi(1,2) = [\phi_0(1)\phi_1(2) - \phi_0(2)\phi_1(1)] / \sqrt{2}$
 - This becomes more complex when we consider spin

'Classical' Phase Diagrams



But Helium Phase Diagrams are Different Due To Quantum Effects

Helium-4 (boson):



The superfluid phase and the lack of freezing under vapor pressure are quantum effects.

Why doesn't ^4He freeze?

- Van der Waals binding energy is small
 $U / k \sim 5\text{K}$
- Consider a ^4He particle confined so that $\lambda = 2d$, where d is the inter-particle spacing
 $d = 0.22\text{ nm}$, $p = h/(2d)$ (deBroglie with $\lambda = 2d$)
 $E_0 = p^2/(2m) = 1.7 \times 10^{-22}\text{ J}$
 $E_0 / k = 12\text{ K}$
- Below about 12 K the He atoms' kinetic energy does not change, and it is bigger than the solid binding energies

Why does ${}^4\text{He}$ form a superfluid?

- deBroglie $\lambda = h/p$
- $p^2 / (2m) = 3/2 kT$, so $p_{\text{rms}} = (3mkT)^{1/2}$
- So $\lambda_{\text{th}} = h/p_{\text{rms}} = h / (3mkT)^{1/2}$
- Now $\lambda_{\text{th}} > d$ for $T < 2.3 \text{ K}$
- Helium atoms are indistinguishable bosons, so for $T < 2 \text{ K}$ a single huge quantum state forms, called a superfluid
- Be careful – ${}^4\text{He}$ atoms are strongly interacting, so the situation is not this simple, but it is in BEC

Fermi Energy

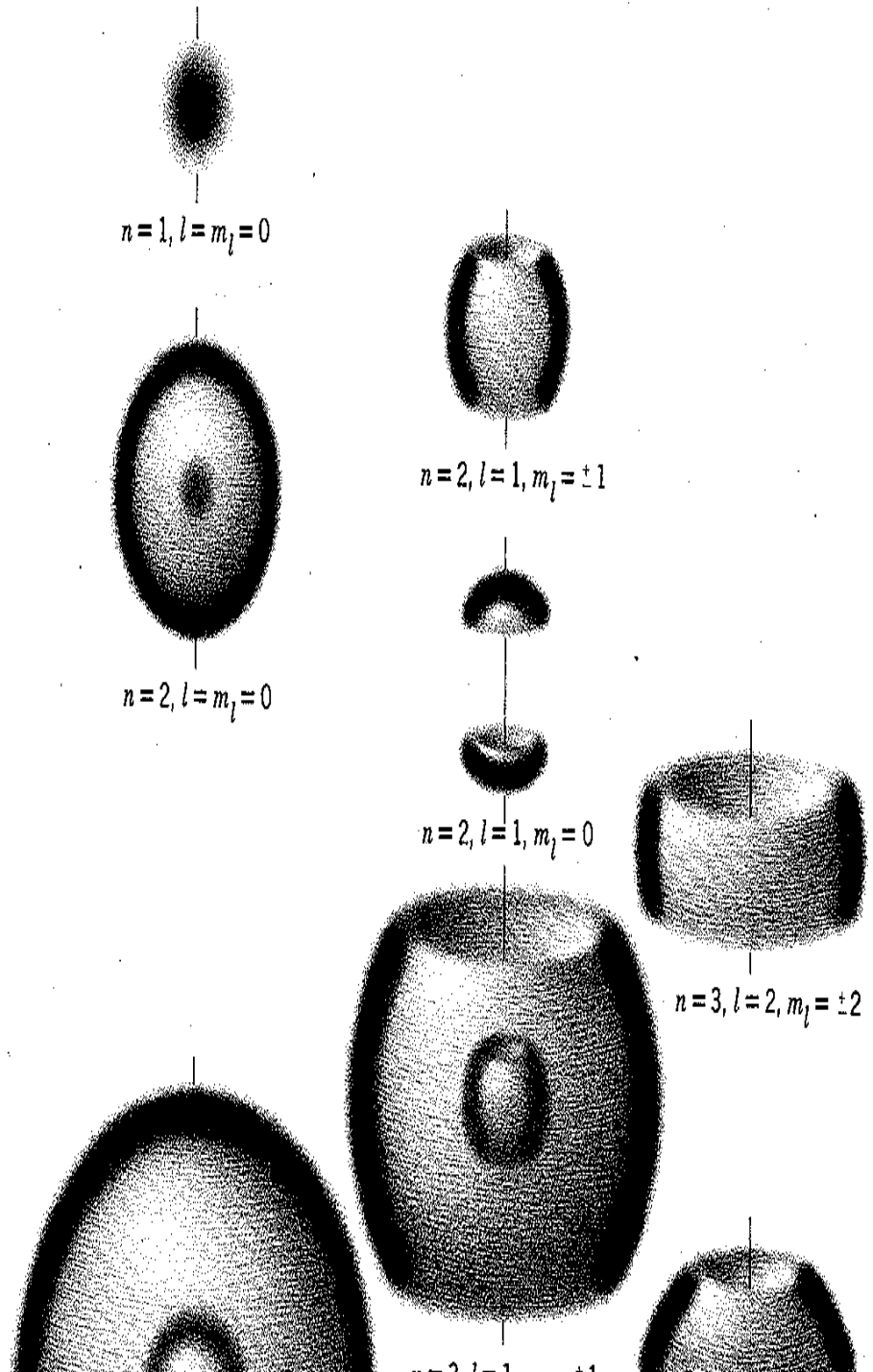
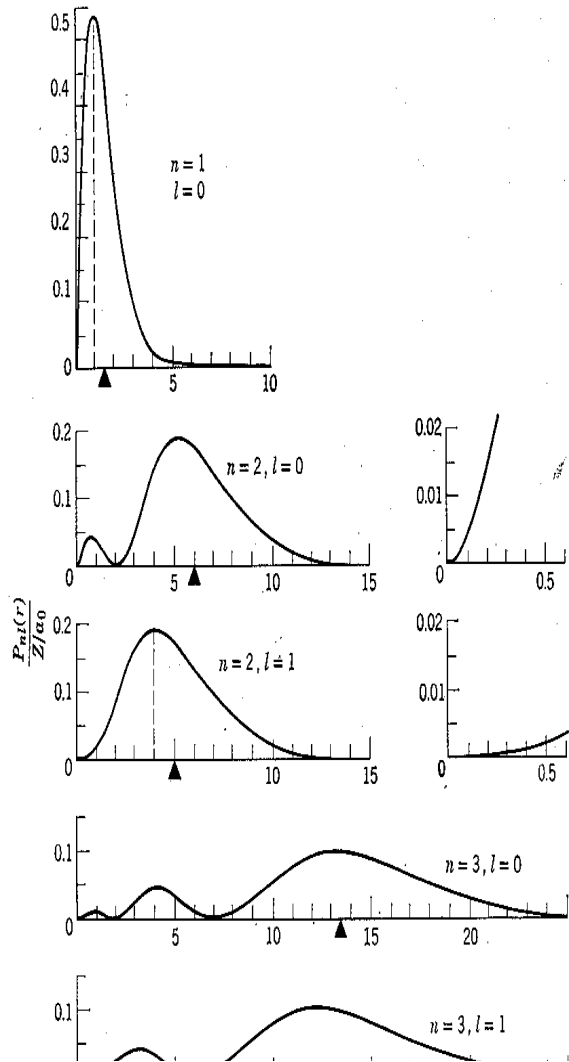
- Pauli exclusion principle

All Fermions such as electrons must be in a distinct quantum state (this comes from anti-symmetric exchange symmetry)

$E_f \sim n^{2/3}$ in three dimensions

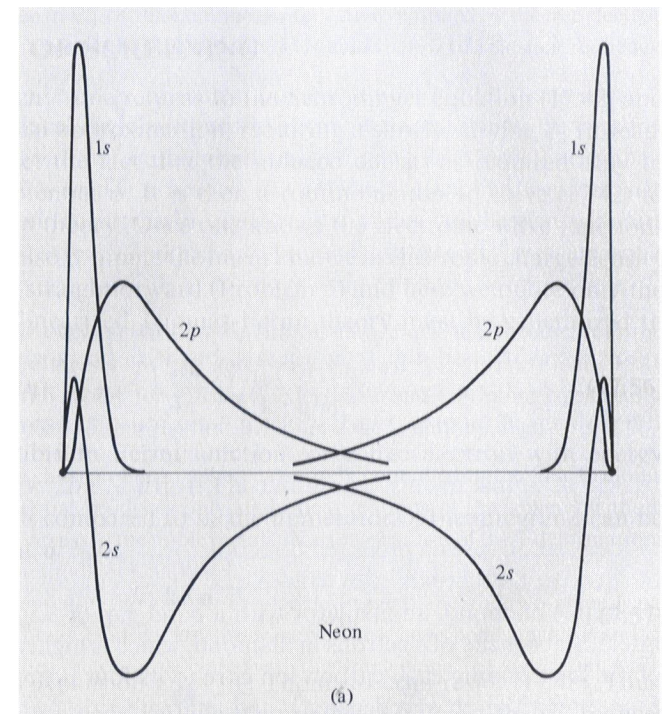
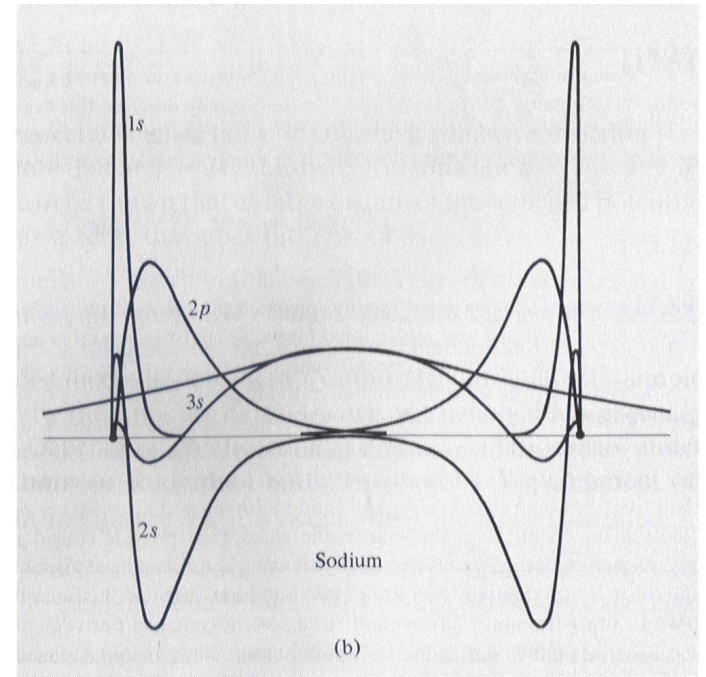
Why is a neutron stable in many nuclei while it has a 1,000 s half-life in free space?

Hydrogenic Wavefunctions (Eisberg and Resnick)



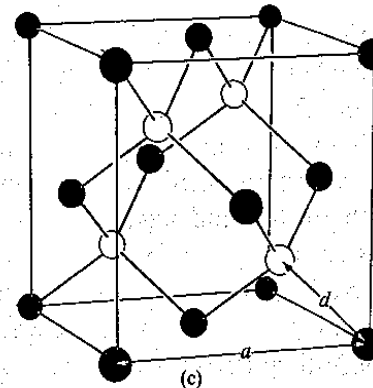
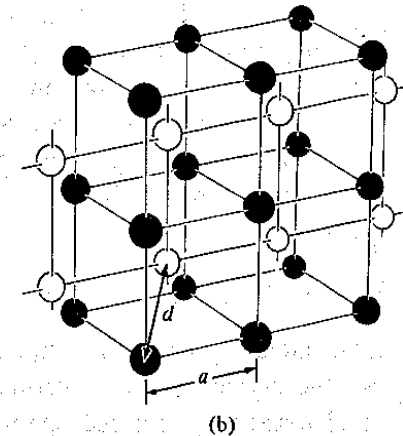
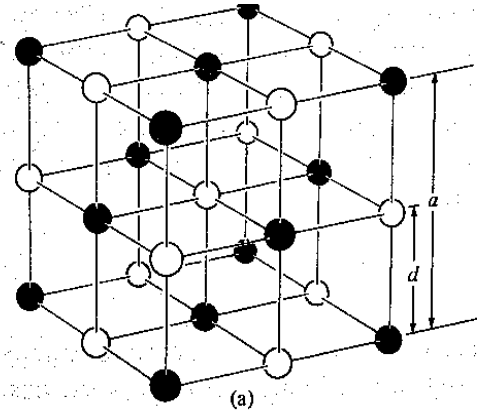
Basics of Chemical Bonding

Overlap of the outer (valence) electron orbitals permits the formation of a conduction band, but it is often not so simple. See Chapter 19 of Ashcroft and Mermin



Five Types of Crystals

- Molecular
- Ionic
- Covalent
- Metal
- 'Hydrogen'
- *Special Cases*
 - Sulfur
 - Selenium



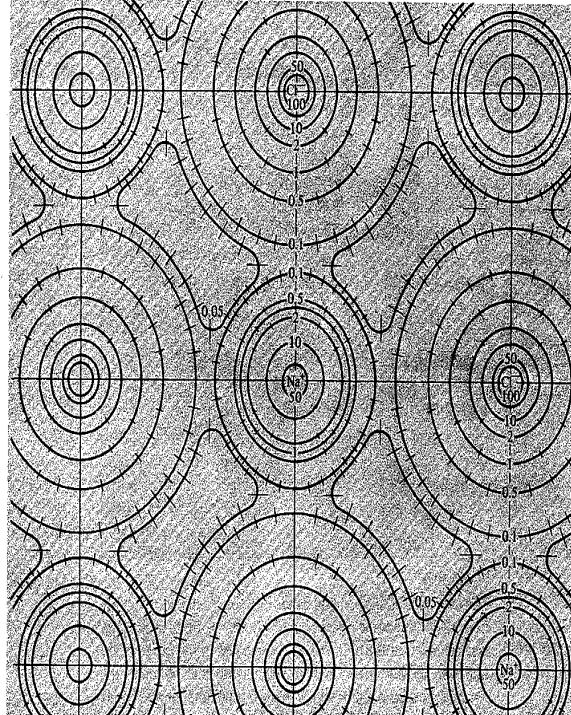
Molecular Crystals

- Solid Kr, Ar, Ne, also N₂, O₂
- Fluctuation creates dipole moment p_1
- Neighbor 'sees' an electric field $E \sim p_1/r^3$
- Creates a dipole moment $p_2 = \alpha E \sim \alpha p_1/r^3$
- So $\Delta E = - p_2 p_1 / r^3 \sim \alpha p_1^2 / r^6$
- $\langle p_1^2 \rangle \neq 0$, so attraction results
- Most of these molecular crystals melt at about 100K, so $\Delta E \sim 10^{-21}$ J or so

Ionic Crystals

RbBr: Br⁻: ↓3.5 eV, Rb⁺: ↑4.2 eV

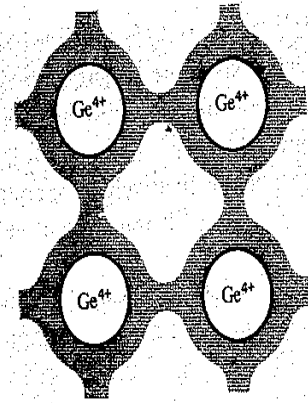
But $r \sim 0.34$ nm, so $-e^2/r \approx -4.2$ eV so it binds



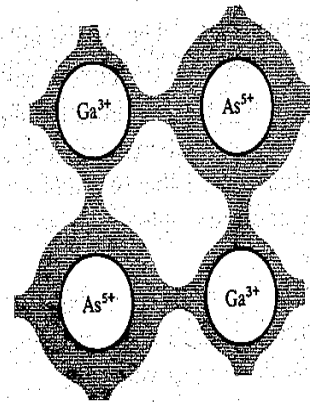
NaCl: electron density down to < 0.05 e per cubic angstrom!

Ionic to Covalent Crystals

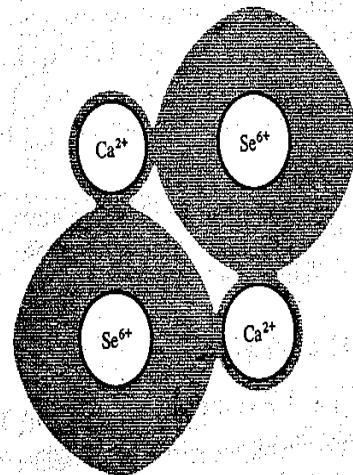
388 Chapter 19 Classification of Solids



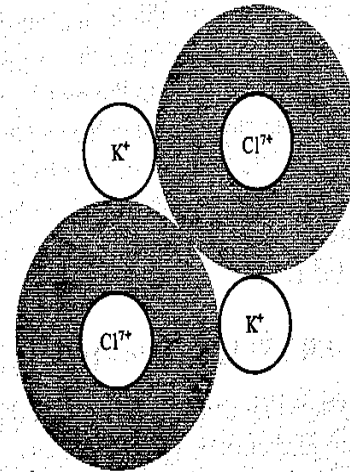
(a)



(b)



(d)



Metallic Crystals

- Dominated by the physics of the free electron gas
- Exception: Noble Metals (Cu, Ag, Au) with filled d-orbitals

METAL	SINGLY IONIZED IONIC RADIUS, r_{ion} (Å)	NEAREST-NEIGHBOR HALF DISTANCE IN METAL, r_{met} (Å)	$r_{\text{met}}/r_{\text{ion}}$
Li	0.60	1.51	2.52
Na	0.95	1.83	1.93
K	1.33	2.26	1.70
Rb	1.48	2.42	1.64
Cs	1.69	2.62	1.55
Cu	0.96	1.28	1.33
Ag	1.26	1.45	1.15
Au	1.37	1.44	1.05