project:
CB - 1

Crystal Binding

Cohesive Energy ≡ Energy required to separate crystal into component atoms

1 cal/gm °C
→ 18 cal/mole °C
Compare ICE

Heat fusion H_2O
80 Kcal/mole
Vaporization
540 Kcal/mole
heat 6×10² → +1800 Kcal/mole
1 cal = 4.18 J

		vs		
Ne	1.92 kJ/mole		Li	158 kJ/mole
Ar	7.74 kJ/mole		Na	107 kJ/mole

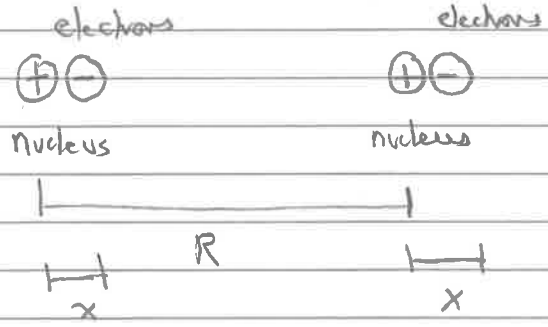
B 561 kJ/mole
C 711 kJ/mole

very small (not surprising ∵ filled shells → weak interactions)

Melting Tempr (similar point) → Ne 24.6 °K, Ar 83.8 °K B 2365 °K

Ne, Ar have **Van der Waals interaction**: interaction between 2 neutral atoms caused by induced dipole moments

Schematically:



$$U = e^2\left[\frac{+1}{R} + \frac{1}{R} + \frac{-1}{(R-x)} + \frac{-1}{(R+x)}\right]$$

$$= \frac{e^2}{R}\left[2 - \frac{1}{\left(1-\frac{x}{R}\right)} - \frac{1}{\left(1+\frac{x}{R}\right)}\right]$$

DiVOGA

project: CB-2

$$(1+x)^n = 1 + nx + \frac{n(n-1)}{2}x^2 + \dots$$

$$U = \frac{e^2}{R}\left[\overset{\checkmark}{2} - \left(\overset{\checkmark}{1} + \overset{\checkmark\checkmark}{\frac{x}{R}} + \frac{x^2}{R^2} + \dots\right) - \left(\overset{\checkmark}{1} - \overset{\checkmark\checkmark}{\frac{x}{R}} + \frac{x^2}{R^2} \dots\right)\right]$$

$$\left(1 - \frac{x}{R}\right)^{-1} \qquad \left(1 + \frac{x}{R}\right)^{-1}$$

$U \sim -\frac{2e^2}{R}\frac{x^2}{R^2}$ ← PE of 2 dipoles $\sim 1/R^3$

vs $1/R$ of 2 charges

But atoms are not <u>permanent</u> dipoles instead they have <u>induced</u> dipoles because of other atom Interaction is even weaker van der Waals $\sim 1/R^6$

Why? ~~p~~ dipole $\sim \vec{E}$ field

$\vec{E} \sim 1/R^2$ charge

$\sim 1/R^3$ dipole ← additional $1/R^3$

~~$1/R^3$ and~~

Why not get closer and closer?

Ultimately Repulsive force due to Pauli Exclusion principle of overlapping electron clouds. Turns out ~~a~~ combination can be very well fit by

$$U(r) = \frac{A}{R^{12}} - \frac{B}{r^6}$$ Lennard-Jones

$\frac{A}{R^{12}}$ ← Pauli repulsion

$\frac{B}{r^6}$ ← dipole-dipole attraction

BACK

Ionic crystals NaCl atoms which do have net charge

Binding is due to electrostatic energies of charges $\pm q$

separated by R : $-q^2/R$ Madelung Energy

much much bigger than $\sim 1/R^6$ van der Waals

Again there is ultimately repulsion due to overlap

Empirically $+\frac{A}{R^2} - \frac{B}{R}$ $B = Z_i Z_j e^2$ } A bit like Kepler problem $-1/R$ from gravity and $+1/R^2$ from angular momentum barrier!

Pauli Repulsion ($\frac{A}{R^2}$)

$\pm q$ charges ($\frac{B}{R}$)

ASIDE BOTTOM USES SAME $1/R^{12}$ AS Van der Waals! (why not $1/R^{12}$ again ?! → not simple to derive/explain empirical)

Covalent Bond

together (Co) valence (valent)

electrons have opposite spin ↑ ↓ to avoid Pauli repulsion

METALS binding driven by lowering of energy when electrons delocalize (metal) $KE \sim + \frac{(\Delta p)^2}{2m} \sim + \frac{1}{2m}\left(\frac{h}{\Delta x}\right)^2$

lowest for Δx large

project:
CB-4

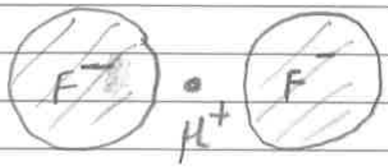
finally $\boxed{\text{Hydrogen Bond}}$

H loses e^- (partially) to atoms like F, O, N

and (approximately) bare of e^- H atom (proton)

sits between atoms.

HF_2^-



H bond:
Impt in water/ice/DNA

project:
CLT-1

We got into discussion of central limit theorem

For discrete $P(\pm 1) = 1/2$ (coin toss, random walk)

$$P(x) = \frac{1}{2^N} \binom{N}{\frac{N+x}{2}} \qquad x = \sum_{1}^{N} x_N$$

$x = -4$ LLLL

$x = -2$ LLLR LLRL LRLL RLLL

$x = 0$ LLRR LRLR LRRL RLLR RLRL RRLL

more "paths" to $x=0$

Suppose some "force" favors large excursion $E(x) = -\frac{1}{2} k x^2 \frac{1}{N}$

Which effect wins? What to minimize

"free energy" $$F(x) = E(x) - T \ln \underbrace{\binom{N}{\frac{N+x}{2}}}_{\text{"entropy"} \equiv \# \text{ paths}}$$

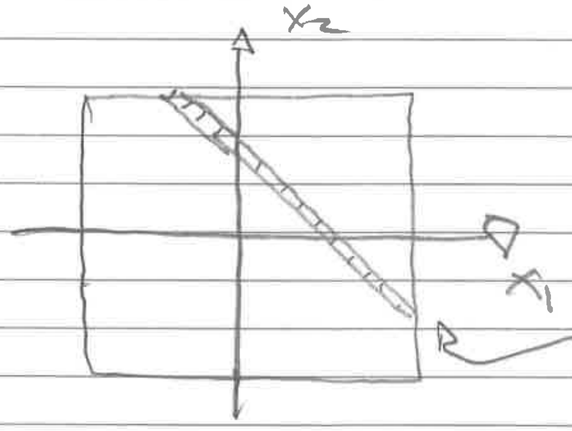
depending on value of T can favor $x=0$ or $x \neq 0$

"phase transition"

project:

CLT-2

$P(x_i) = 1/2 \qquad -1 < x_i < 1$



$x = x_1 + x_2$

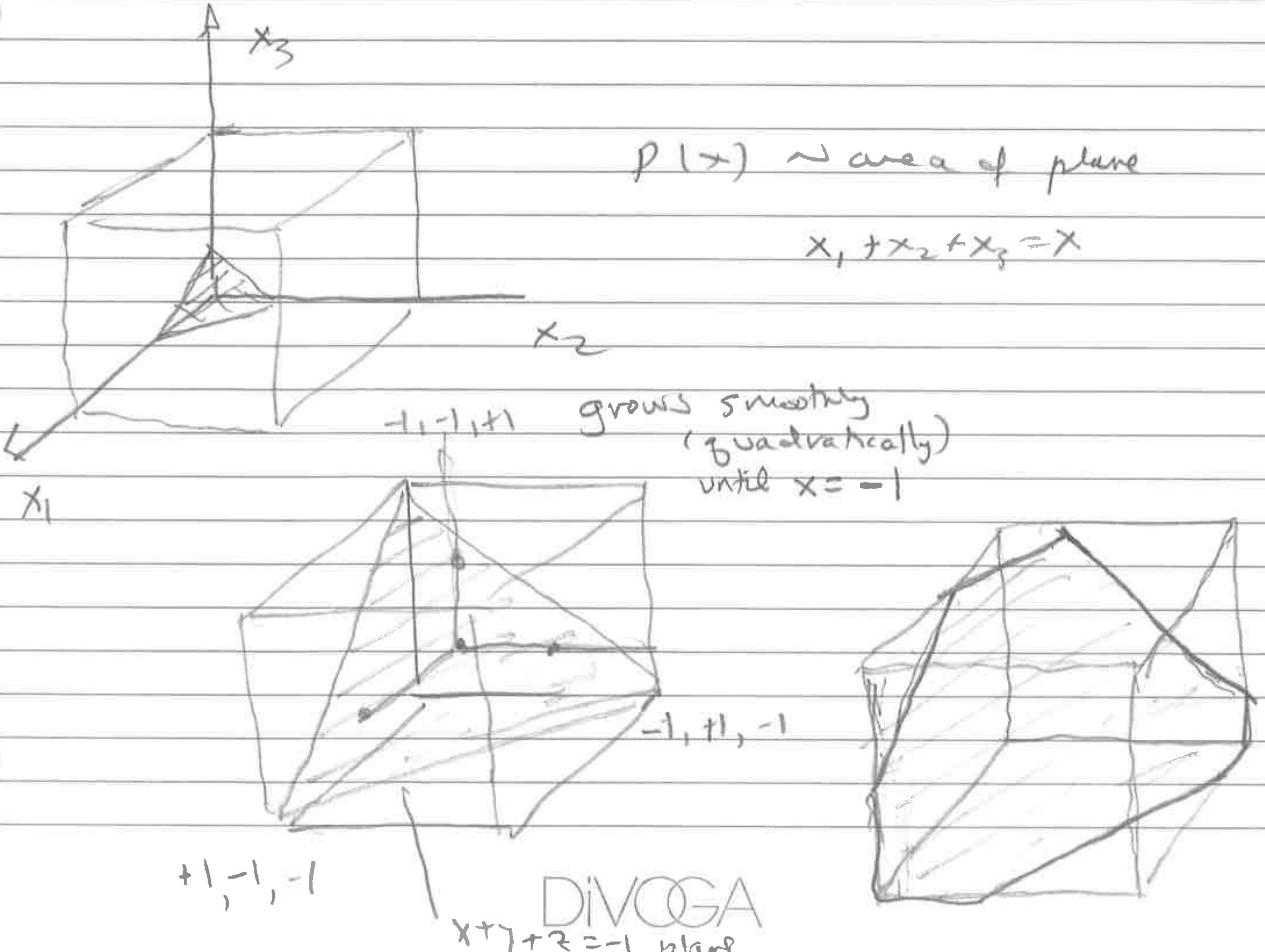
$P(x) \approx$ length of this $x_1 + x_2 = x$ line

(max at $x=0$)

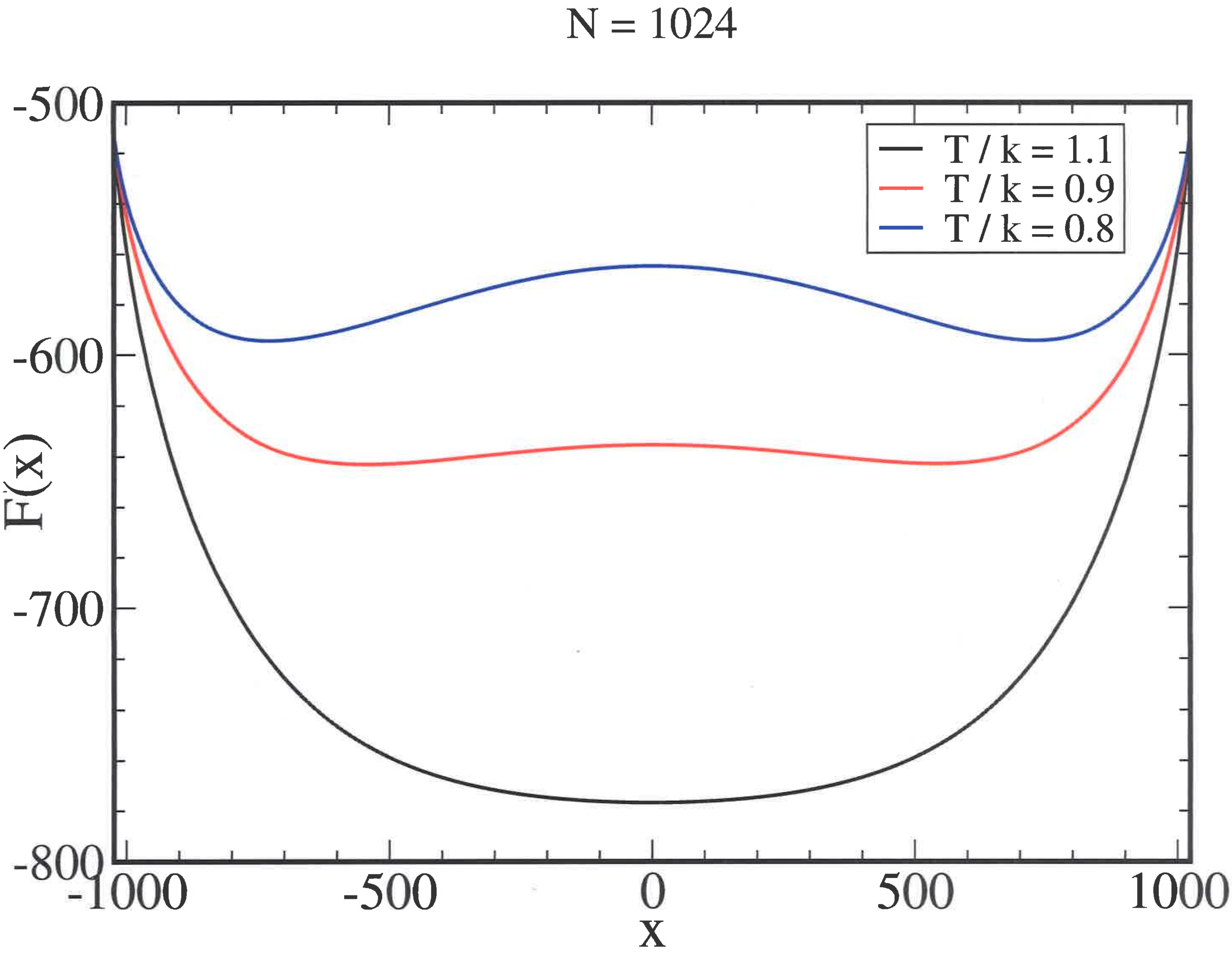
Similarly for $x = x_1 + x_2 + x_3$

$P(x) \sim$ area of plane

$x_1 + x_2 + x_3 = x$



grows smoothly
(quadratically)
until $x = -1$


N = 1024
F(x)
-500
-600
-700
-800
-1000
-500
0
500
1000
x
T / k = 1.1
T / k = 0.9
T / k = 0.8