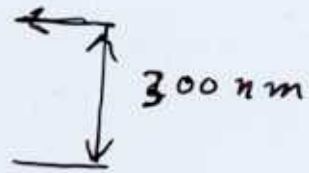
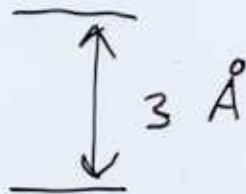


A COLLOID :



AN ATOM :



→ MOLECULES MAY BEHAVE LIKE COLLOIDS  
IN SOME RESPECTS BUT NOT IN OTHERS.

e.g. TMV



PHASE  
BEHAVIOR

COLLOID  
ONLY OVERALL  
SHAPE, CHARGE  
AND FLEXIBILITY  
MATTER

BIOLOGICAL  
FUNCTION:

PRECISE SEQUENCE  
IS IMPORTANT  
"NOT COLLOID"

PROTEIN



PRECISE  
STRUCTURE  
MATTERS



ONLY "OVERALL"  
STRUCTURE  
MATTERS

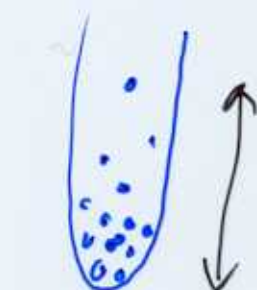
IS A BRICK A COLLOID?

COLLOIDS CAN BE DESCRIBED BY  
STATISTICAL MECHANICS

→ RELEVANT ENERGIES  $O(kT)$

---

e.g. BAROMETRIC HEIGHT DISTRIBUTION



COLLOIDS

$$P(h) \sim e^{-mgh/kT}$$



BRICKS

CRITERION:

$$\langle h \rangle = \frac{kT}{mg}$$

SHOULD NOT  
BE LESS  
THAN  $R$

FOR BRICKS:  $\langle h \rangle \approx 10^{-20}$  cm (ON EARTH)  
(1 kg)

$$\langle h \rangle = kT/mg = kT / \left[ \frac{4\pi}{3} \rho R^3 g \right] \approx R$$

$$\rightarrow \frac{\pi}{6} g \rho \sigma^3 = kT$$

|  
( $\sigma = 2R$ )



$$\sigma \approx 1 \mu$$

(ON EARTH)

# FORCES BETWEEN COLLOIDS.

## SPECIFIC EXAMPLES

### 1°) "HARD-CORE" REPULSION

COLLOIDS HAVE A SHAPE

(THAT IS NOT OBVIOUS.)

SMALL MOLECULES USUALLY DO NOT  
HAVE A SHAPE — DON'T TELL MSI.)

WHY DO COLLOIDS HAVE A SHAPE?

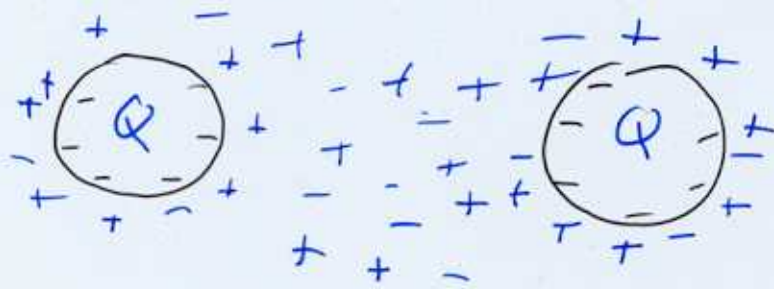
- a) THEY ARE "FAIRLY" SOLID
- b) THEY CANNOT INTERPENETRATE
  - PAULI
  - SHORT-RANGED COULOMB REPULSION
  - "STERIC" STABILIZATION

→ IT IS POSSIBLE TO MAKE  
MANY COLLOIDAL SHAPES



etc.

# COULOMB INTERACTION



STRAIGHT FORWARD ?

No!

1) COULOMB REPULSION IS  
SCREENED BY COUNTERIONS + ADDED SALT

SCREENING DISTANCE :

$$\kappa^{-1} = \sqrt{\frac{4\pi}{\epsilon kT} \sum_i \rho_i q_i^2}$$

↑  
DIEL.  
CONST

↑  
DENSITY OF  
SALT ION  $i$

CHARGE OF  
ION  $i$

COLLOID - COLLOID PAIR INTERACTION

$$V(R) = \left( \frac{Q e^{\kappa R}}{1 + \kappa R} \right)^2 \frac{e^{-\kappa R}}{\epsilon \kappa}$$

PURELY REPULSIVE

HOWEVER:

THERE MAY BE ATTRACTIONS  
BETWEEN LIKE CHARGED COLLOIDS

THESE ARE EITHER DUE TO  
A CONFINING WALL\*

OR

TO A NON-ADDITIVE "VOLUME"  
TERM IN THE POTENTIAL  
ENERGY\*\*

OR

TO CORRELATED CHARGE  
FLUCTUATIONS ("DISPERSION FORCES")\*\*\*

\* KEPLER / FRADEN, BOWEN / SHARIF, GOULDING / HANSEN

\*\* VAN ROIJ / HANSEN

\*\*\* RAY / MANNING, - - - - -

---

HOWEVER, AS A FIRST  
APPROXIMATION, DLVO IS  
USUALLY FINE.

SO: COULOMB FORCES ARE "SOLVENT MEDIATED".

NEXT: DISPERSION FORCES.

SURELY, THOSE ARE SIMPLE?

ATOMS:

$$U_{DISP}(r) \approx - \frac{3\epsilon_1\epsilon_2 h^2 \nu_1 \nu_2}{4\pi r^6} \equiv - \frac{C_{DISP}}{r^6}$$

NOW ADD COLLOID



CHANGE IN DISPERSION INTERACTION:

$$\Delta U_{DISP} \propto -\beta_s \alpha_s \underbrace{(\beta_c \alpha_c - \beta_s \alpha_s)}_{\text{REPLACE SOLVENT BY COLLOID}}$$

TWO COLLOIDS:

$$\text{INTERACTION} \propto - (\beta_c \alpha_c - \beta_s \alpha_s)^2$$

ATTRACTIVE

HOWEVER: NEED NOT BE ATTRACTIVE



SPECIAL CASE :

$$\rho_s \alpha_s = \rho_c \alpha_c \rightarrow \text{NO DISPERSION FORCES}$$

RECALL : CLAUSIUS - MOSOTTI

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \rho \alpha$$

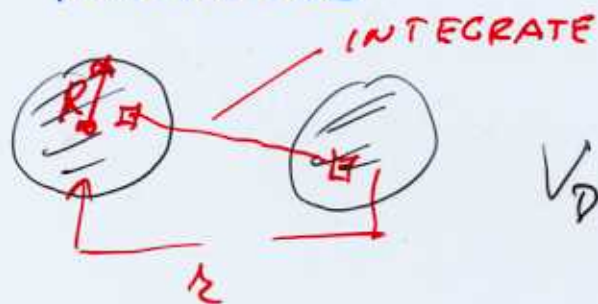
$$\rightarrow \rho_s \alpha_s = \rho_c \alpha_c \text{ IMPLIES } n_c = n_s$$

"REFRACTIVE INDEX MATCHING"

(COMMON IN LIGHT-SCATTERING EXPS.)

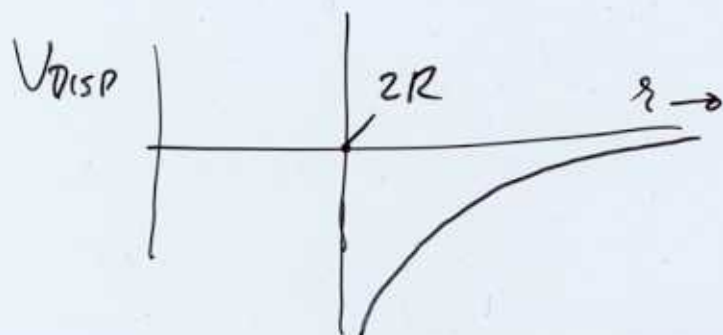
How DOES  $V_{\text{DISP}}$  DEPEND ON  $\lambda$ ?

COLLOIDS ARE NOT POINT PARTICLES



$$V_{\text{DISP}}(\lambda) \approx -\frac{A}{6} \left[ \frac{2R^2}{\lambda^2 - 4R^2} + \frac{2R^2}{\lambda^2} + \ln \left( \frac{\lambda^2 - 4R^2}{\lambda^2} \right) \right]$$

$A =$  "HAMAKER CONSTANT"  $\leftrightarrow (\rho_c \alpha_c - \rho_s \alpha_s)^2$

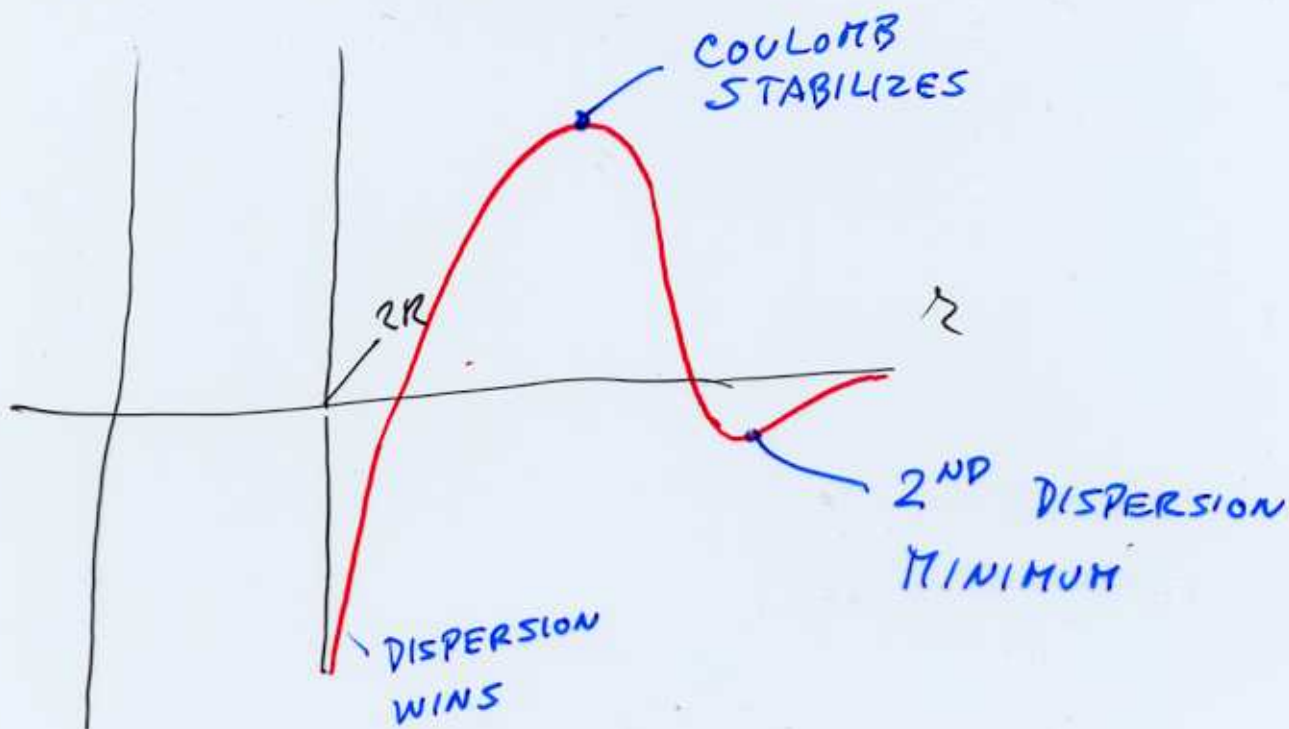




DLVO:

DISPERSION + SCREENED COULOMB.

$$V_{DLVO}(r) = \left( \frac{Qe^{-kr}}{1+kr} \right)^2 \frac{e^{-kr}}{\epsilon r} - \frac{A}{\delta} \left\{ \frac{2R^2}{r^2 - 4R^2} + \frac{2R^2}{r^2} + \ln \left( \frac{r^2 - 4R^2}{r^2} \right) \right\}$$



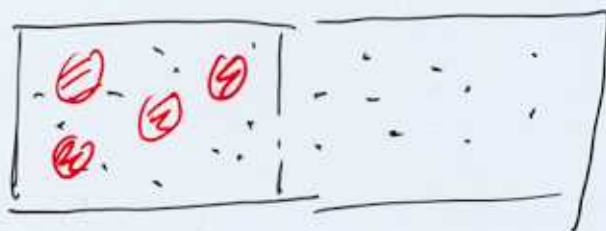
IF THE COULOMB BARRIER  $\gg kT$

→ (META) STABLE

OTHERWISE: IRREVERSIBLE AGGREGATION

(ADDING SALT TO MILK)

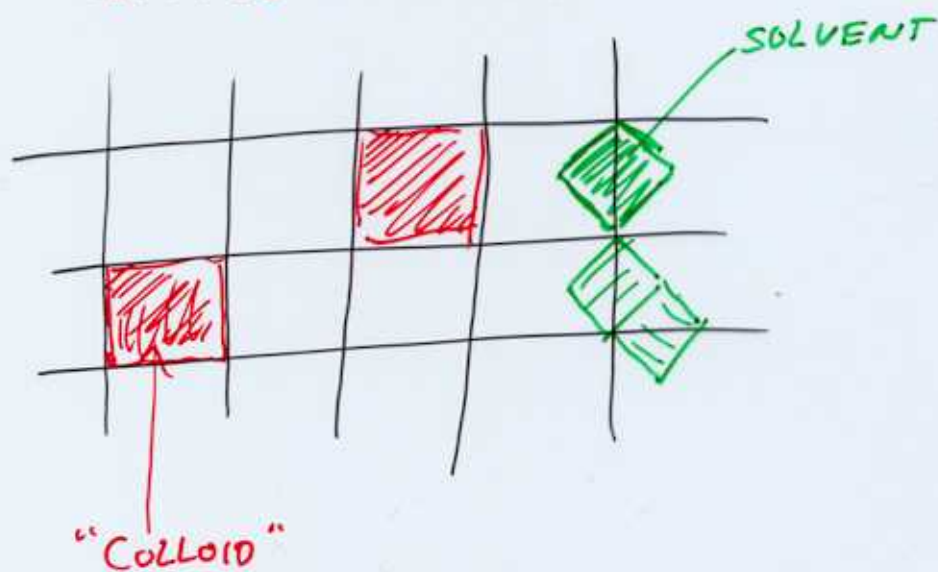
# DEPLETION - INTERACTION.



$$U_{\text{EFF}}(\vec{r}^{N_c}) = U_{\text{DIRECT}}(\vec{r}^{N_c}) - kT \ln \langle e^{-\beta U_{sc}} \rangle_{H_s, U, T}$$

## SIMPLE EXAMPLE.

"LATTICE COLLOID"



$N$  LATTICE SITES  
 $d$  DIMENSIONS

FIRST: CONSIDER ONLY COLLOID:

$$\left[ \frac{\quad}{\quad} \right] = \sum_{\{n_i\}} e^{\beta \mu_c \sum_i n_i}$$

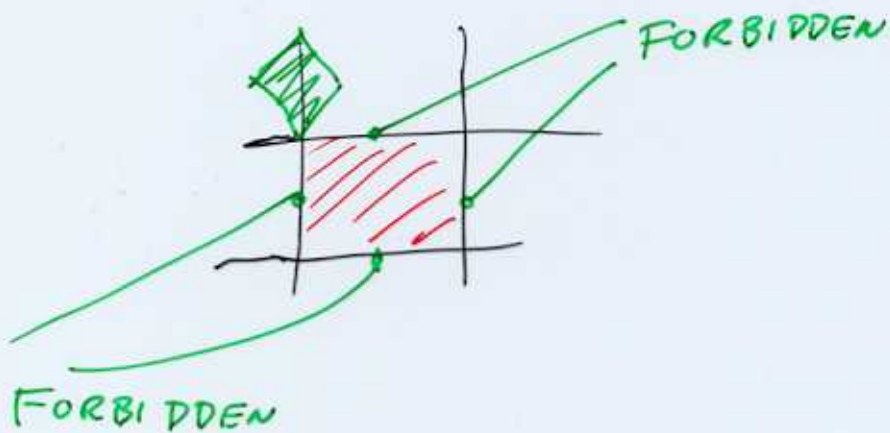
( $n_i$  IS EITHER 0 OR 1)

Now, ADD "SOLVENT"

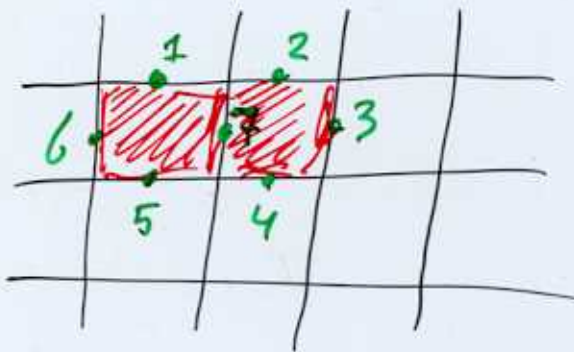
How MANY SITES ARE AVAILABLE?

1°) NO COLLOIDS: → EVERY LINK  
 $dN$  SITES

2°) ONE COLLOID: LOSE  $2d$  SITES



3°) TWO COLLOIDS: LOSE  $2 \times 2d$  SITES  
EXCEPT WHEN THEY TOUCH  
→ LOSE  $(2 \times 2d - 1)$  SITES





$$\left[ \begin{array}{c} - \\ - \end{array} \right]_{\text{MIXTURE}} = \sum_{S_i} e^{-\beta(H \sum S_i - J \sum_{\langle i,j \rangle} S_i S_j)}$$

OH NO ... IT IS THE ISING MODEL!

LET US CHOOSE  $\mu_s, \mu_c$  SUCH THAT  $H=0$

THEN: PHASE - TRANSITION FOR  $J > J_{crit}$

TWO STATES:

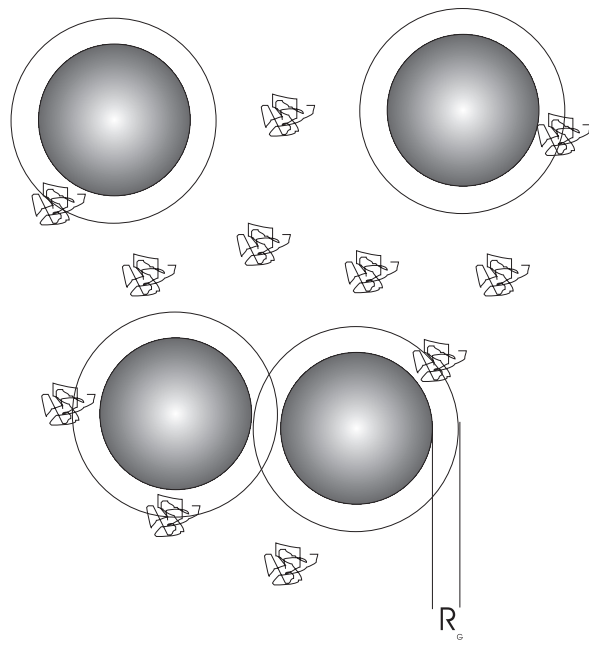
S "UP"  $\leftrightarrow$   $\langle n_i \rangle$  LARGE

S "DOWN"  $\leftrightarrow$   $\langle n_i \rangle$  SMALL

DE-MIXING TRANSITION.

THIS SIMPLE MODEL ILLUSTRATES

- 1° DEPLETION FORCES ARE RELATED TO THE ENTROPY CHANGE OF THE SOLVENT
- 2° THEIR RANGE IS COMPARABLE TO THE SOLVENT SIZE
- 3° THEY CAN BE ATTRACTIVE EVEN IF ALL DIRECT INTERACTIONS ARE REPULSIVE



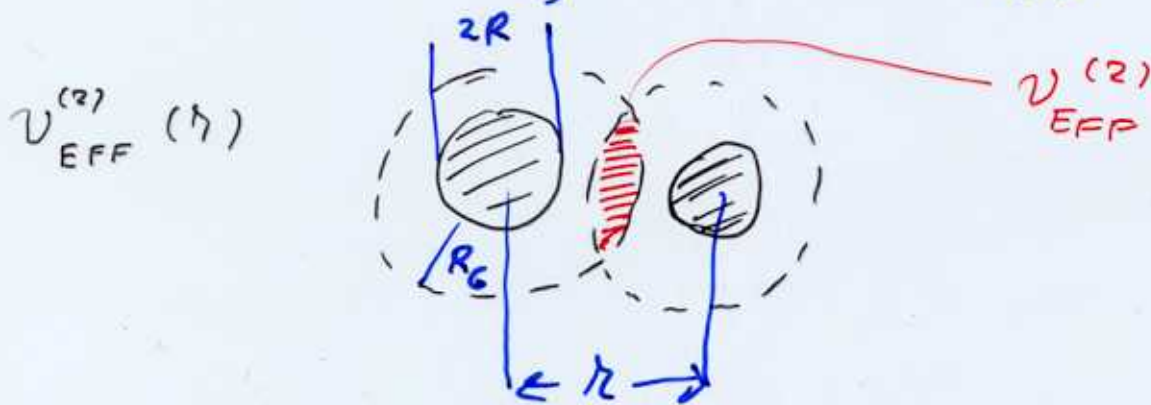
$$\boxed{\quad} = \frac{1}{N_c!} \int d\vec{r}^{N_c} e^{-\beta U_{cc}} \sum_{N_p=0}^{\infty} \frac{e^{\beta \mu_p N_p}}{N_p!} \int d\vec{r}^{N_p} e^{-\beta(U_{cp} + U_{pp})} \quad \leftarrow = 0$$

$$= \frac{1}{N_c!} \int d\vec{r}^{N_c} e^{-\beta U_{cc}} \sum_{N_p} \frac{e^{\beta \mu_p N_p}}{N_p!} \underbrace{\left( \int d\vec{r} e^{-\beta U_{cp}} \right)^{N_p}}_{\text{III}} \left[ V_{\text{EFF}}(\vec{r}^{N_c}) \right]^{N_p}$$

$$= \frac{1}{N_c!} \int d\vec{r}^{N_c} e^{-\beta [U_{cc} - \beta^{-1} \mu_p V_{\text{EFF}}(\vec{r}^{N_c})]}$$

$$\rightarrow V_{\text{EFF}}(\vec{r}^{N_c}) = U_{cc}(\vec{r}^{N_c}) - \beta^{-1} \mu_p V_{\text{EFF}}(\vec{r}^{N_c})$$

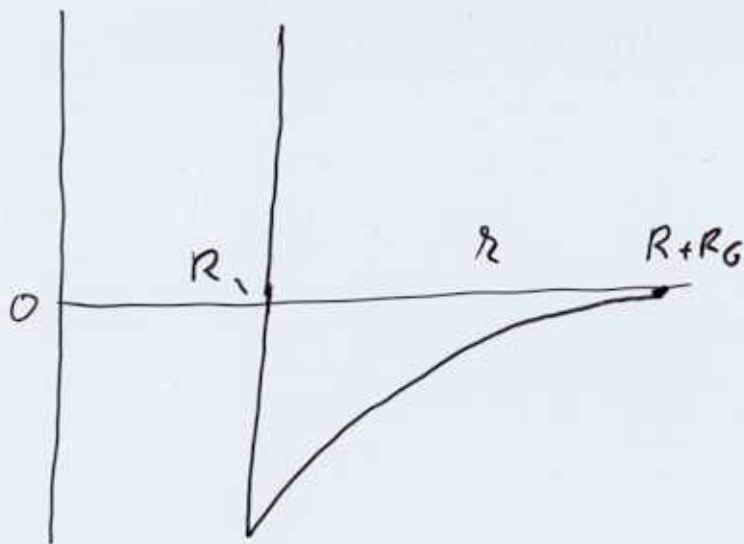
$$V_{\text{EFF}}(\vec{r}^{N_c}) = \sum_{i,j} V_{\text{EFF}}^{(2)}(r_{ij}) + \sum_{i,j,k,h} V^{(3)} + \dots$$



$$V_{\text{EFF}}^{(2)}(r) = \frac{4\pi}{3} (R+R_c)^3 \left\{ 1 - \frac{3r}{4(R+R_c)} + \frac{1}{16} \left( \frac{r}{R+R_c} \right)^3 \right\}$$

$(2R < r < 2(R+R_c))$

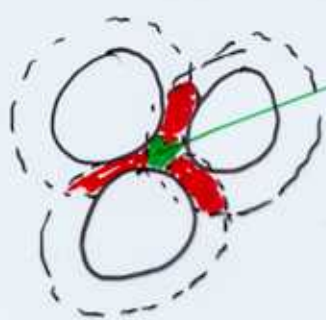
$U_{\text{EFF}}^{(2)}(r)$



### REMARKS

1°) RYSAKURA - OOSAWA POTENTIAL AGREES WELL WITH SIMULATIONS ON HARD COLLOIDS + IDEAL POLYMERS

2°) FOR LONG POLYMERS, "MANY-BODY" EFFECTS BECOME IMPORTANT



3-body correction

$$\begin{aligned} U^{(2)} &< 0 \\ U^{(3)} &> 0 \\ U^{(4)} &< 0 \\ &\dots \end{aligned}$$

---

BUT ACTUALLY,

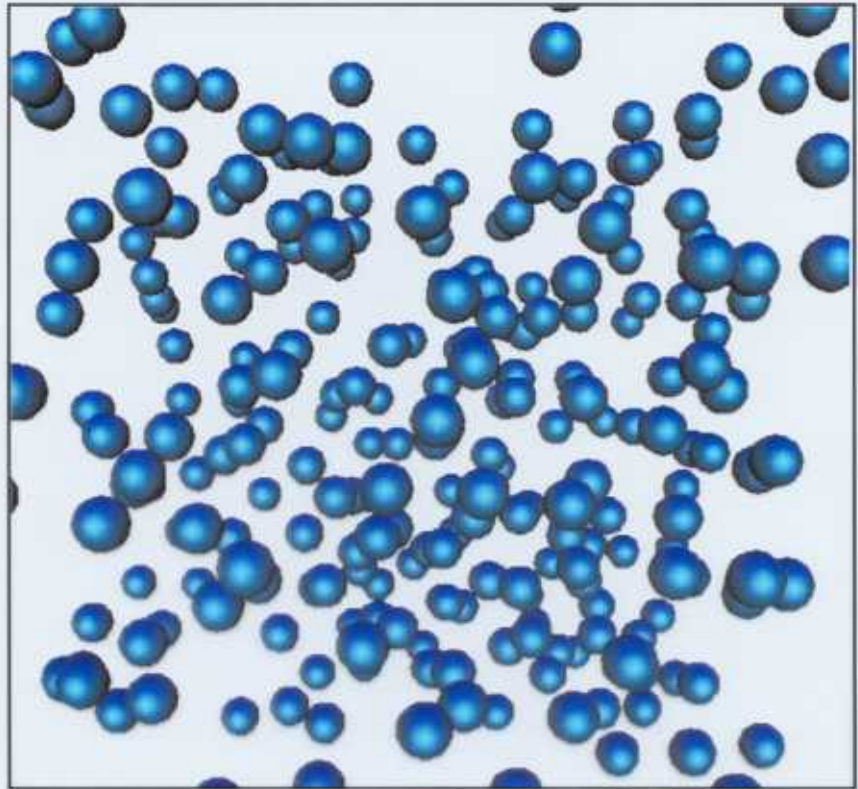
YOU HAVE KNOWN DEPLETION

FORCES FOR A LONG TIME...

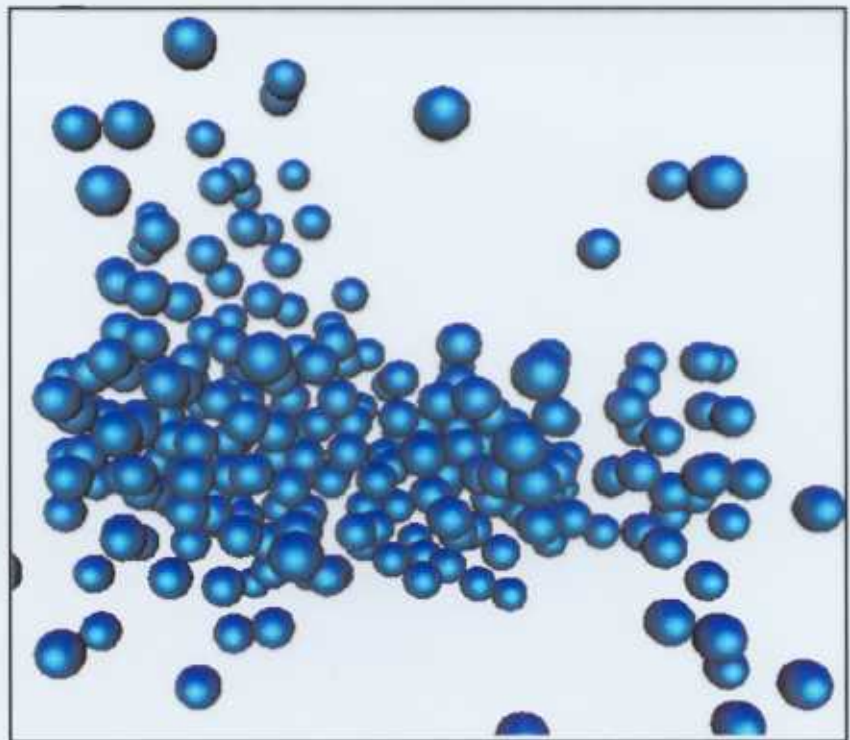


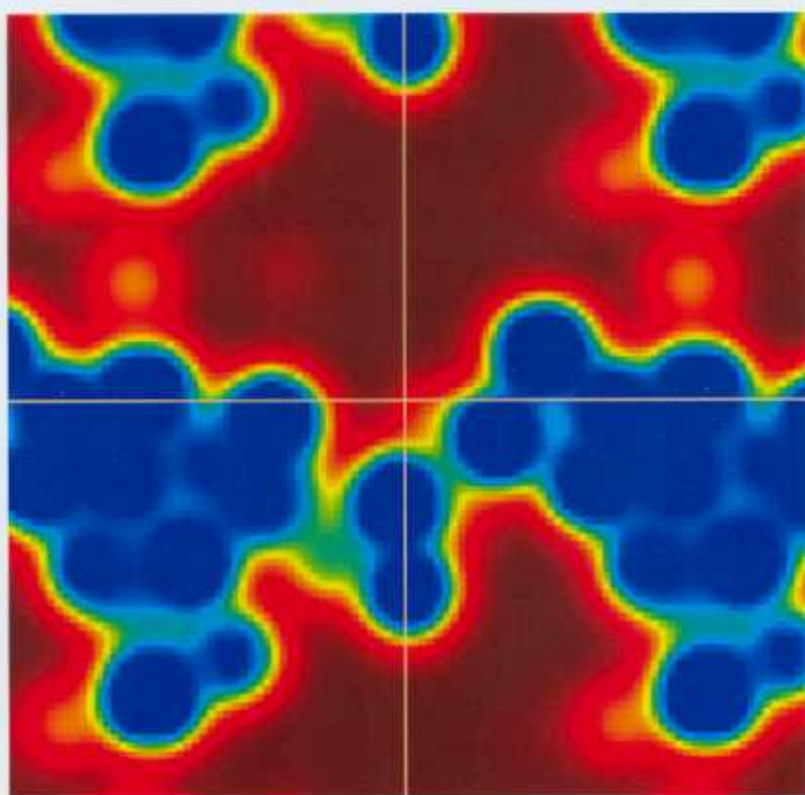
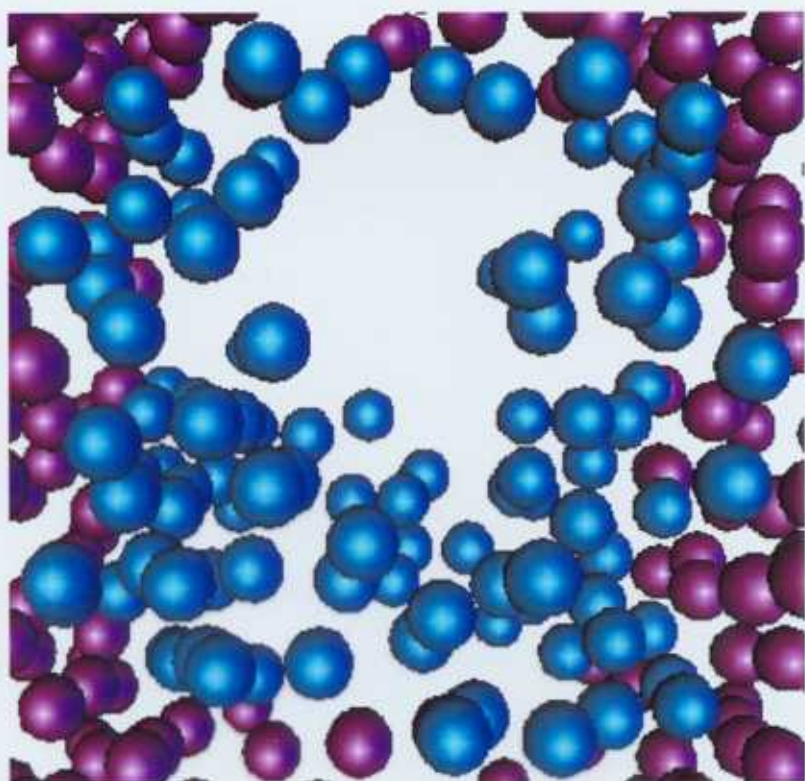
# Polymer induced phase separation

low polymer  
density



high polymer  
density





## SUMMARY:

IN SOME RESPECTS,  
COLLOIDS ARE LIKE GIANT  
ATOMS

BUT:

- a) WE CAN CONTROL  
THEIR INTERACTIONS
- b) AND THEIR SIZE  
(- DISTRIBUTION!)
- c) AND THEIR SHAPE.

# COLLOID DYNAMICS

IN 20 MINUTES.

ONLY ONE MESSAGE

CONSERVED QUANTITIES

CAN BE TRANSPORTED

BUT YOU NEVER GET  
RID OF THEM.

## HONOUR LIST OF CONSERVED QUANTITIES

1. MASS
2. ENERGY
3. MOMENTUM (INCL. ANGULAR)
4. CHARGE

⋮

# BOLTZMANN:

ENTROPY ( $S$ ) IS RELATED  
TO THE TOTAL NUMBER OF  
STATES ( $\Omega$ ) IN WHICH A  
SYSTEM CAN BE FOUND

$$S = k \ln \Omega$$

Boltzmann

NICE ....

BUT WHAT DOES IT MEAN?

INTUITIVE INTERPRETATION:

|                |                   |                  |
|----------------|-------------------|------------------|
| SMALL $\Omega$ | $\leftrightarrow$ | ORDERED STATE    |
| LARGE $\Omega$ | $\leftrightarrow$ | DISORDERED STATE |

EXAMPLE:

# COUNTER EXAMPLES:

LOOK AT MODEL SYSTEMS THAT  
HAVE NO ENERGY TO SPEND -

## HARD-CORE SYSTEMS

$$(E = E_{\text{KINETIC}} = \text{CONSTANT} \times T)$$

DO THEY ORDER ?

### 1. FREEZING:

ALDER/WAINWRIGHT, WOOD/JACOBSON (1957)

HARD SPHERES CAN CRYSTALLIZE

### 2. LIQUID CRYSTAL FORMATION:

NON-SPHERICAL HARD-CORE MOLECULES  
CAN FORM MOST LIQUID-CRYSTALLINE  
PHASES

NEMATICS

(ONSAGER 1942/1949)

SMECTICS

— SIMULATION






COLUMNAR

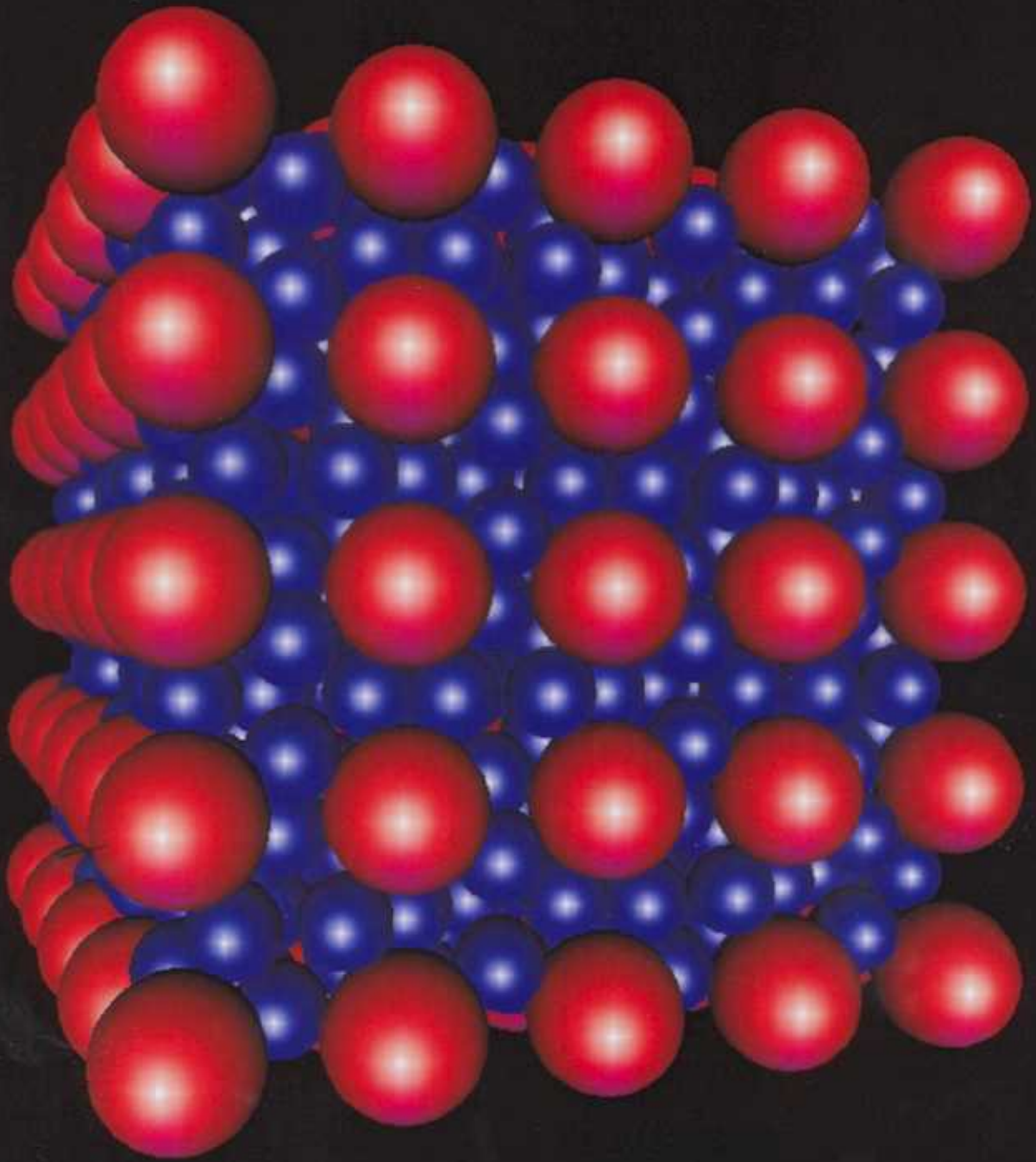
— SIMULATION

⋮

# LIQUID CRYSTALS

## A GLOSSARY

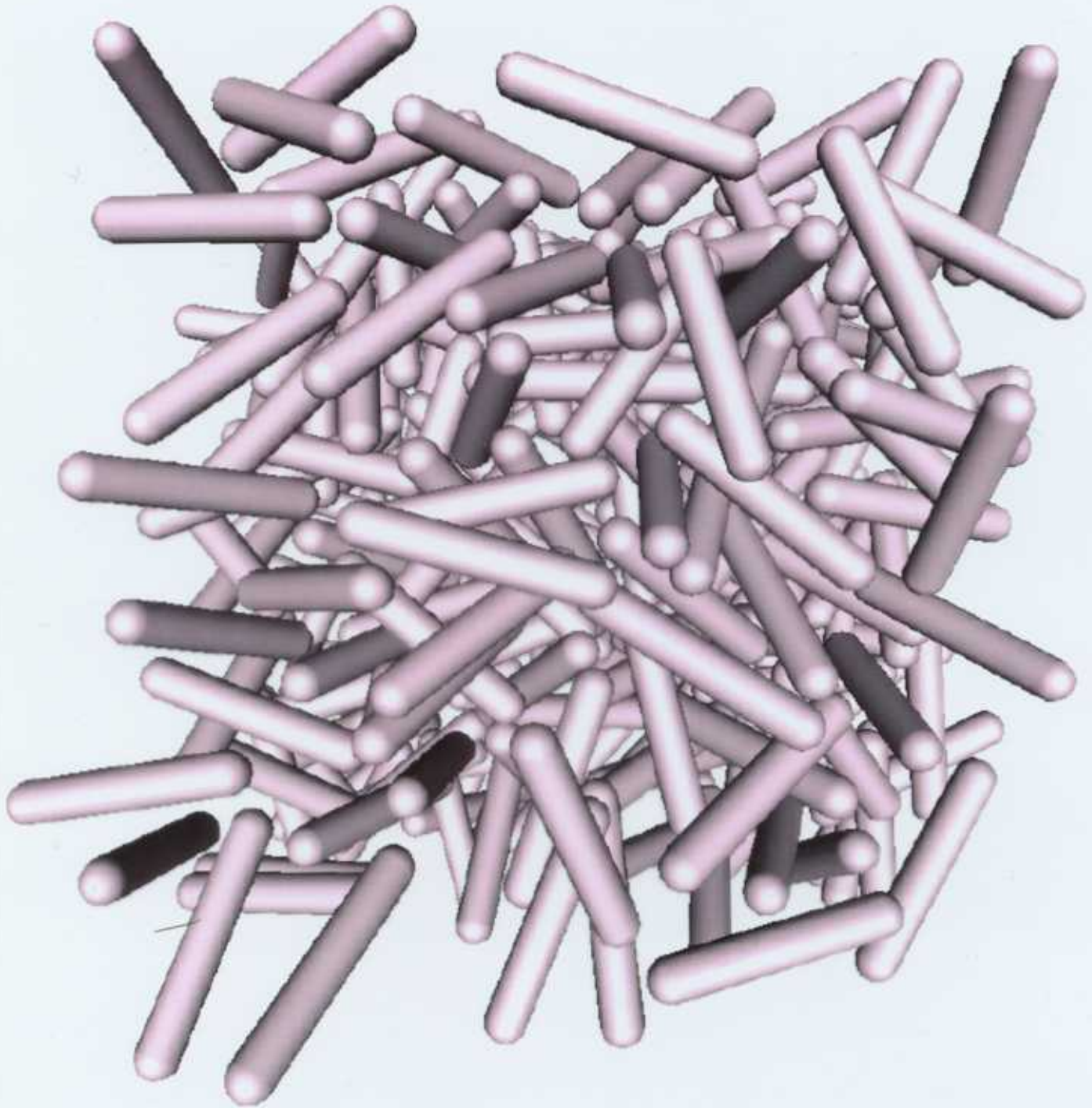
| NAME                                                                            | TRANSL. ORDER | ORIENT. ORDER | SNAPSHOT                                                                              |
|---------------------------------------------------------------------------------|---------------|---------------|---------------------------------------------------------------------------------------|
| ISOTROPIC LIQUID                                                                | NO            | NO            |    |
| NEMATIC LIQUID CRYSTAL                                                          | NO            | YES           |    |
| SMECTIC-A LIQUID CRYSTAL                                                        | 1D (LAYERS)   | YES           |    |
| COLUMNAR LIQUID CRYSTAL                                                         | 2D (COLUMNS)  | YES           |   |
| CRYSTALLINE SOLIDS                                                              | 3D            | YES           |  |
| THE REST:<br>CHOLESTERIC<br>SMECTIC-B, C, ...; H<br>HEXATIC<br>CUBATIC<br>..... |               |               |                                                                                       |



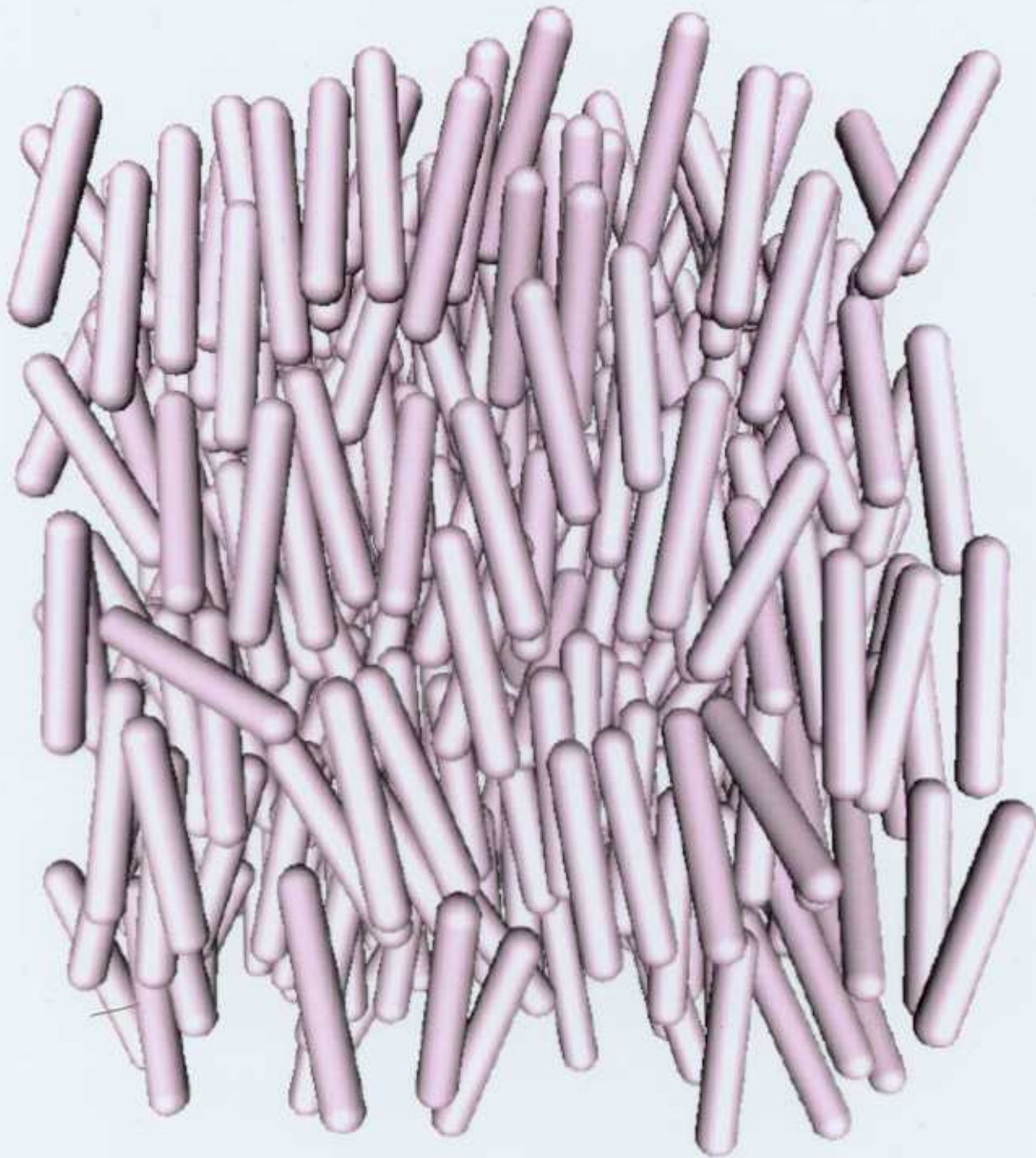


HARD SPHEROCYLINDERS

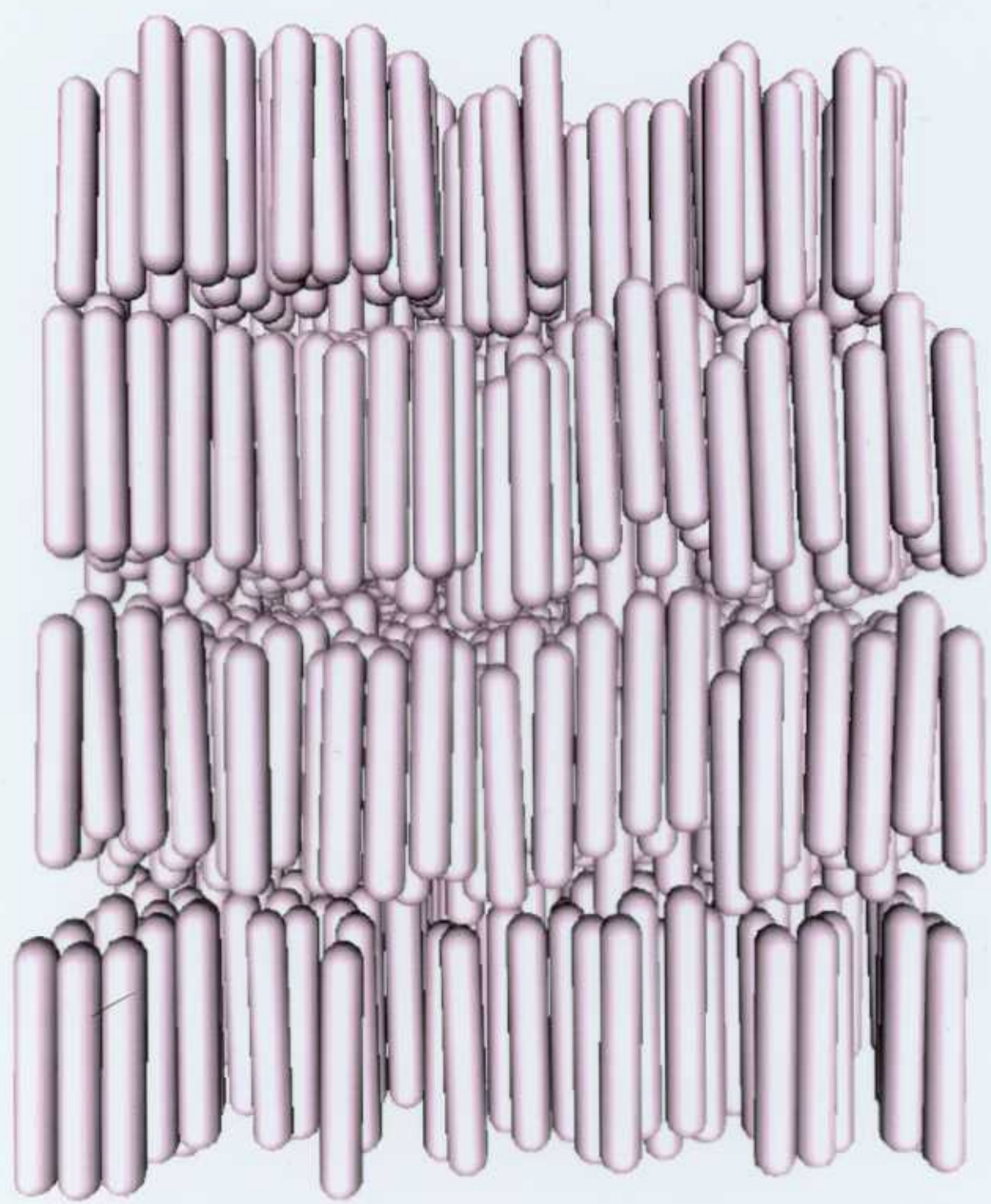
ISOTROPIC FLUID



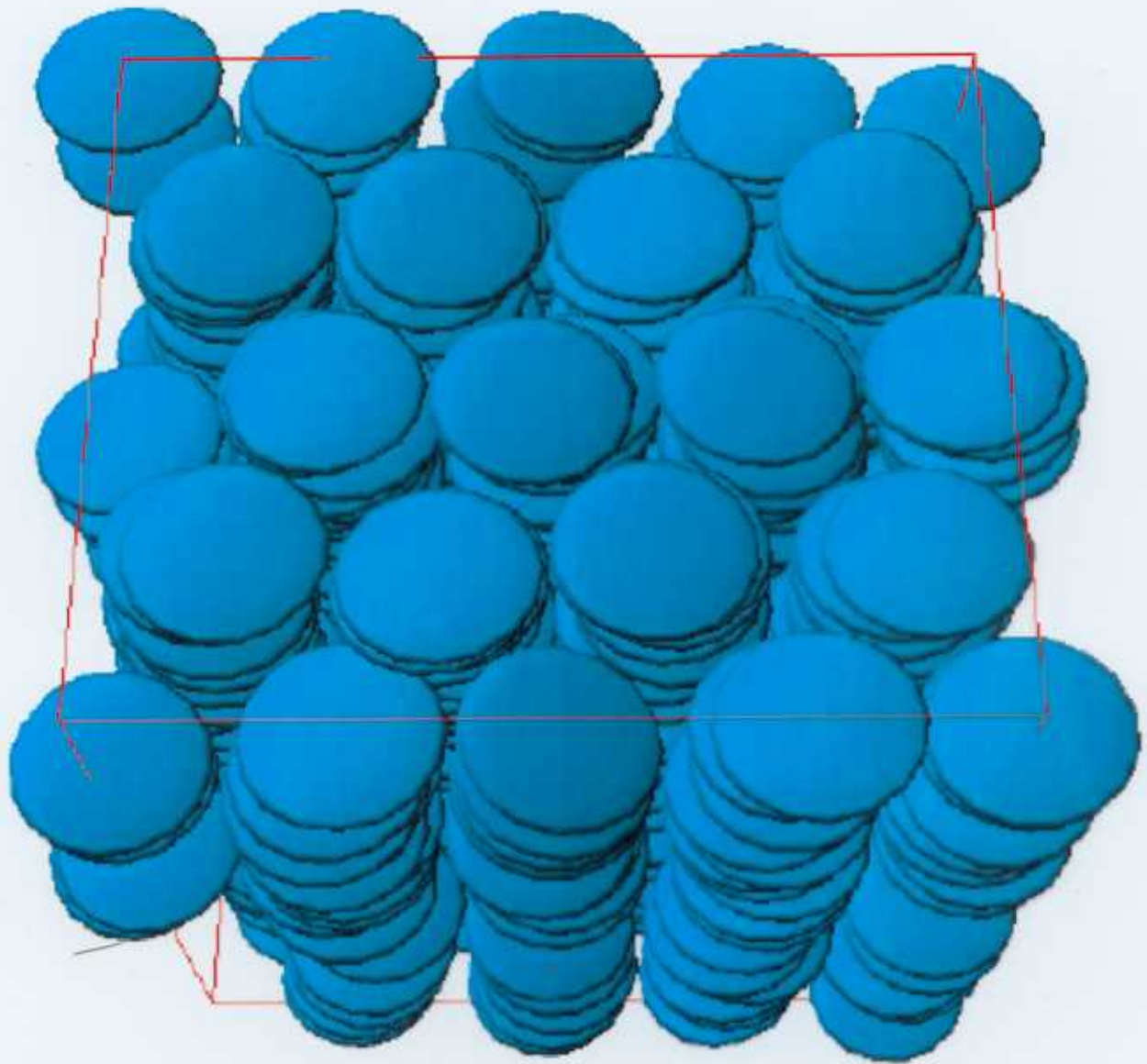
# NEMATIC FLUID



SMECTIC-A FLUID



# COLUMNAR PHASE



# 3D CRYSTAL



SO WHAT ?

THIS IS ONLY SIMULATION...

---

BUT NOW THERE ARE  
EXPERIMENTS ON HARD-PARTICLE  
SYSTEMS

HARD SPHERES —

SILICA COLLOIDS  
(VRIJ, LEKKERKERKER)

PMMA COLLOIDS  
(PUSEY, ZHU ET AL.)

HARD RODS —

BOEHMITE COLLOIDS

TMV VIRUS

L2 " . . . .

ORDER THROUGH DISORDER

IS REAL

# VAN DER WAALS:

1873

## ASSUMPTIONS -

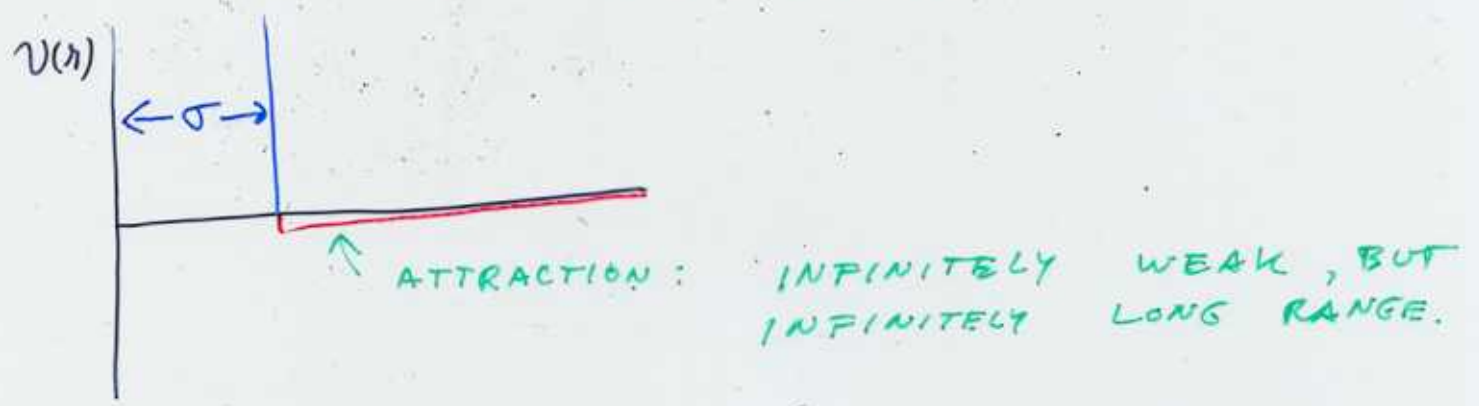
1. MOLECULES EXIST

2. THEY REPEL AT  
SHORT DISTANCES

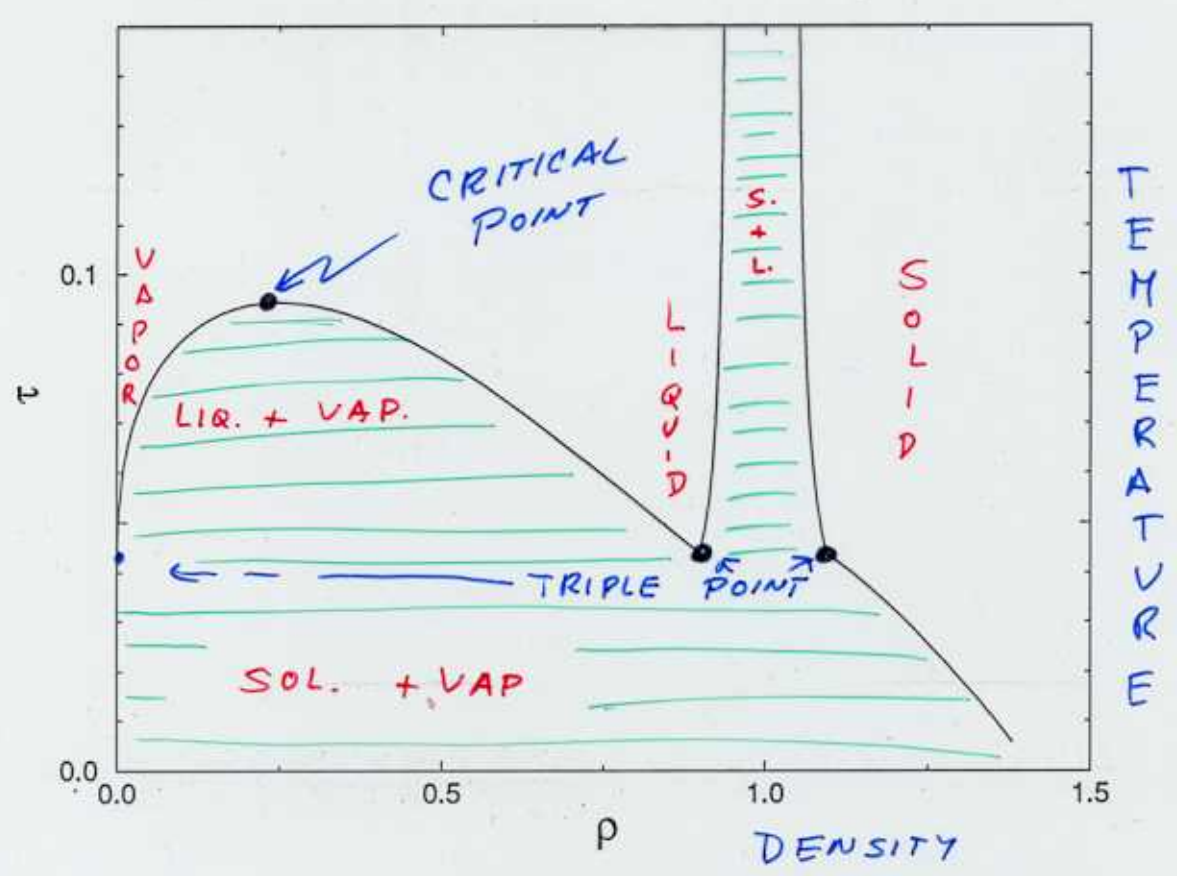
3. THEY ATTRACT AT  
LONGER DISTANCES

1+2+3 → LIQUID - VAPOR  
TRANSITION

WIDOM - LONGUET - HIGGINS  
 "EXACT"  
 PHASE DIAGRAM OF  
 "VAN-DER-WAALS IUM"



$$\frac{T_{\text{CRIT.}}}{T_{\text{TRIPLE}}} = 2.172 \dots$$





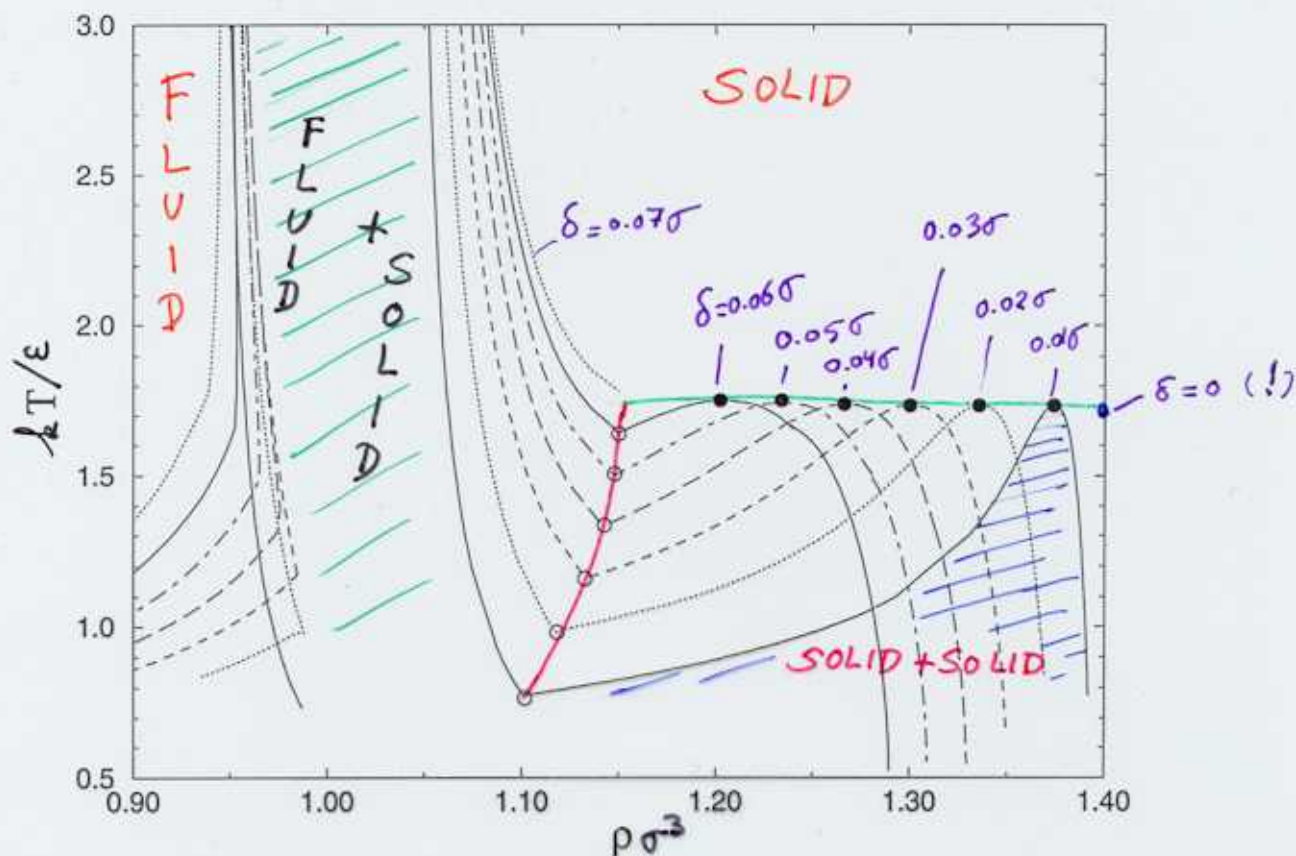
THE LIQUID-VAPOR TRANSITION  
IS NOT INEVITABLE.

IT OCCURS BECAUSE ALL\*  
SIMPLE FLUIDS HAVE A  
"LONG-RANGED" ATTRACTION

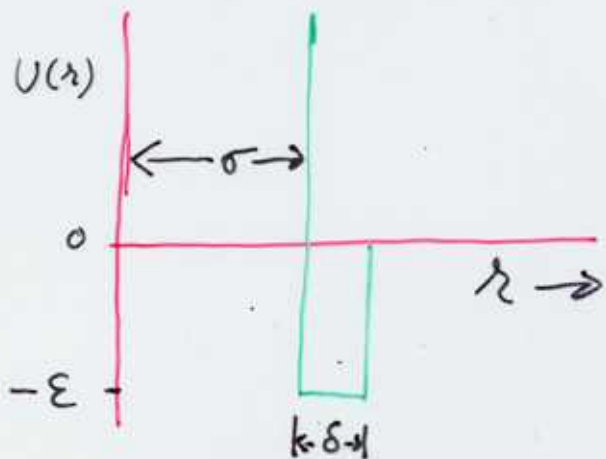
\* ALMOST

---

ALTERNATIVES :



SOLID - SOLID CRITICAL POINT IN SYSTEM WITH SHORT-RANGED ATTRACTION



SQUARE-WELL MODEL

SIMULATIONS: PETER BOLHUIS

SOLID - SOLID TRANSITION

IF  $\delta/\sigma \leq 0.06$