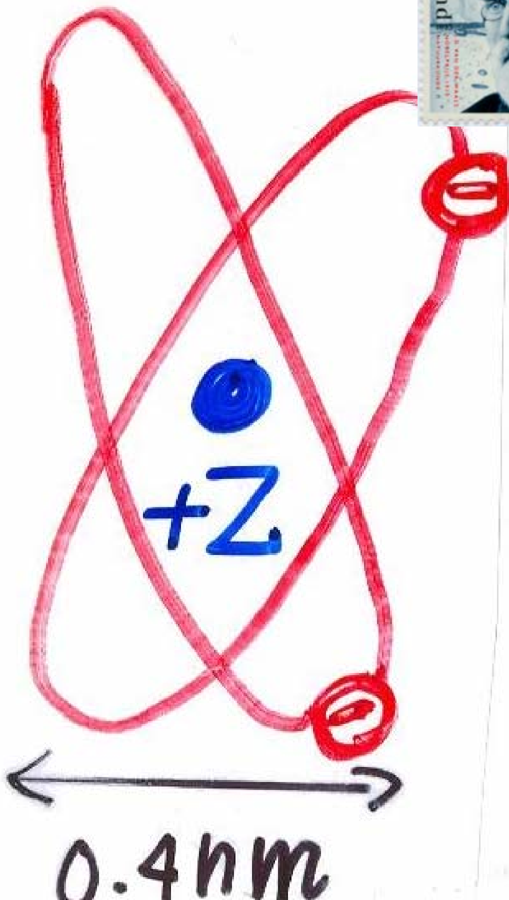
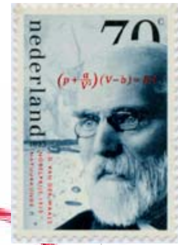
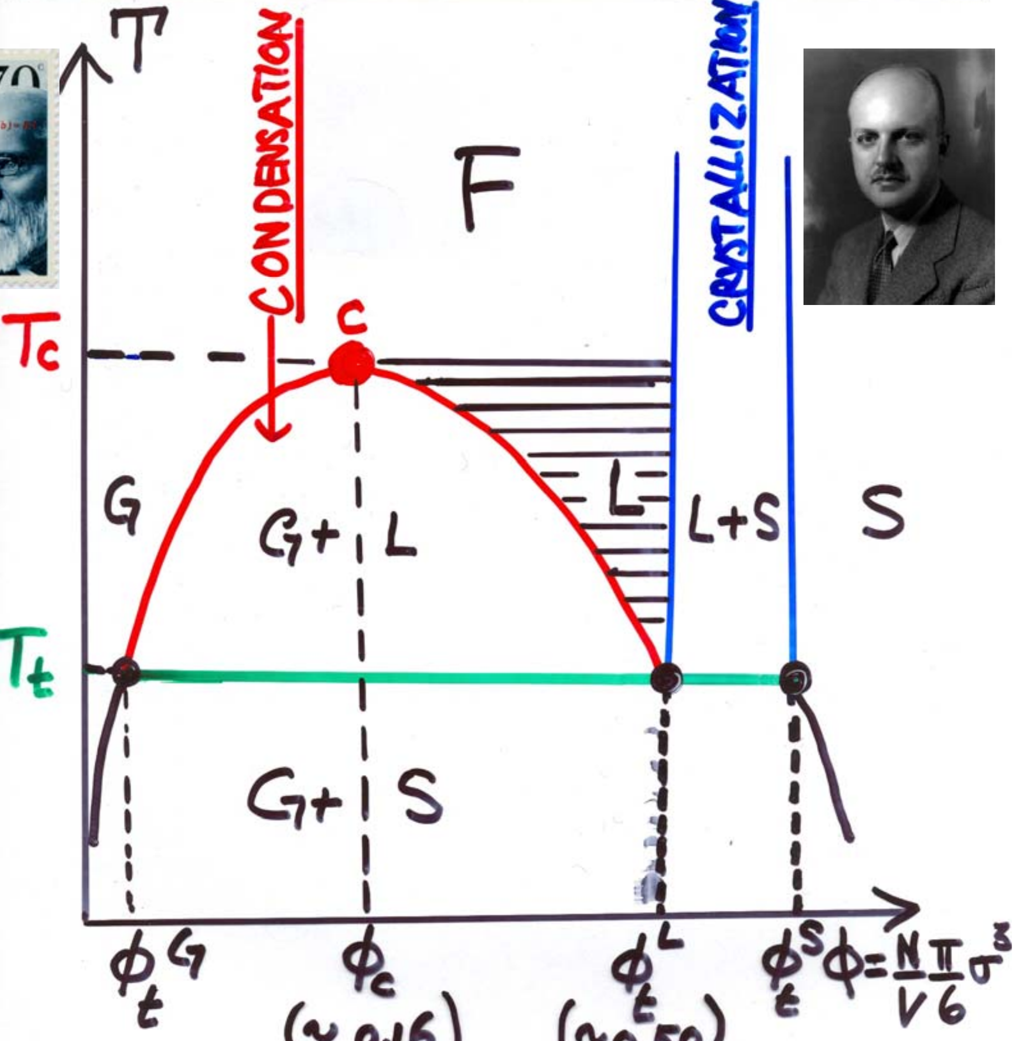
# The Program

- Lecture 1: Phase transitions in atomic and molecular systems
- Lecture 2: Colloids as atoms
- Lecture 3: Hard spheres
- Lecture 4: Hard spheres + attraction
- Lecture 5: Rods
- Lecture 6: Platelets

# PHASE TRANSITIONS IN ATOMIC SYSTEMS

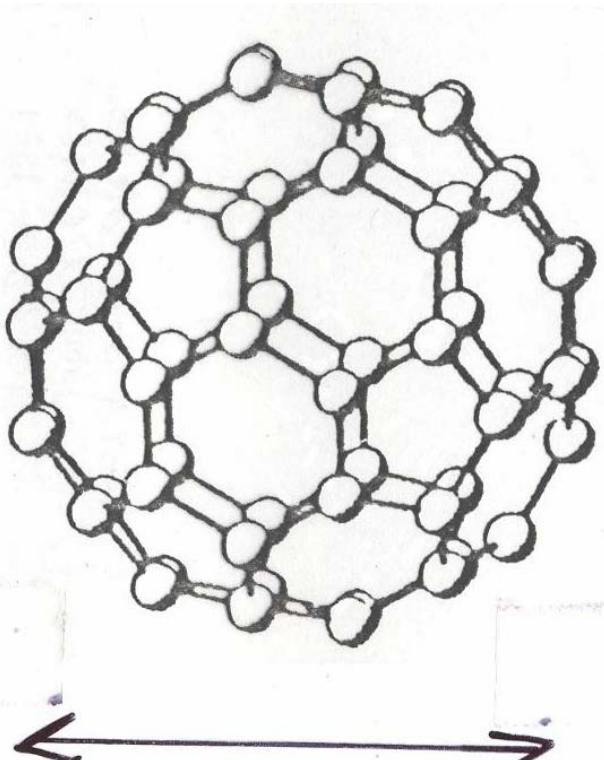


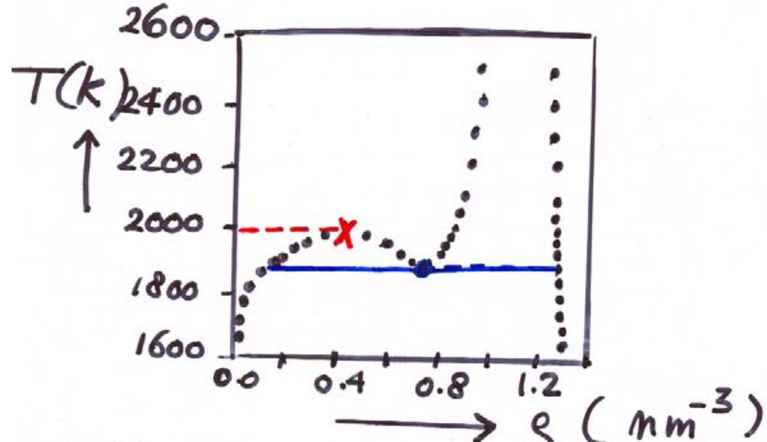

$$\frac{T_c}{T_t} \simeq 2 \qquad \frac{\phi_c}{\phi_t^L} \simeq \frac{1}{3}$$

M. Hasegawa, K Ohno, J. Chem. Phys. 111, 5955 (1999)



$\simeq 1 nm$

## Monte Carlo simulation study of the high-temp. phase diagram of model $C_{60}$ molecules

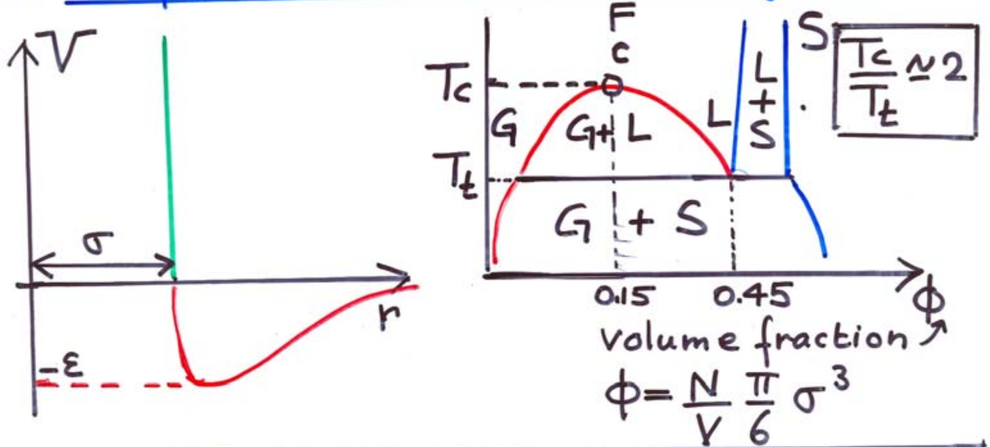



Based on the same Girifalco potential as Hagen et al. but not truncated at $r = 2\sigma$

| | | |
|---|---|---|
| × $T_c = 1980 K$ | $\rho_c = 0.44 nm^{-3}$ | $\phi_c = \frac{\pi}{6}\sigma^3 \rho_c = 0.20$ |
| $T_t = 1880 K$ | $\rho_t^{\ell} = 0.74 nm^{-3}$ | $\phi_t^{\ell} = 0.34$ |
| $T_c / T_t = 1.05$ | $\rho_t^{\ell} / \rho_c = 1.7$ | |

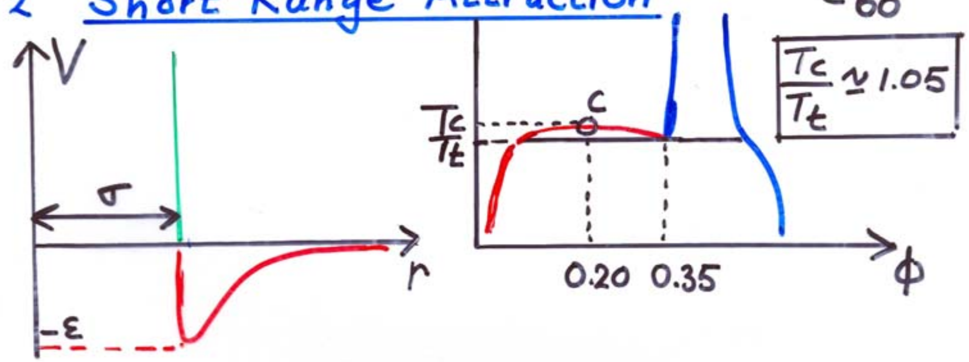
# SUMMARY LECTURE 1

## 1. Simple Atomic and Molecular Systems

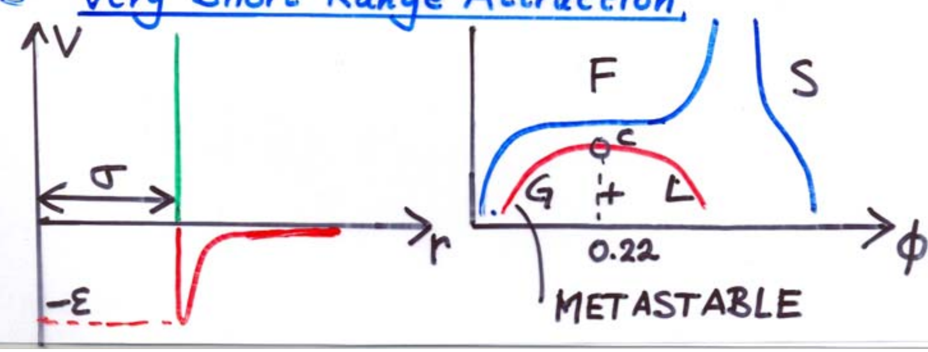



## 2 Short Range Attraction

$C_{60}$

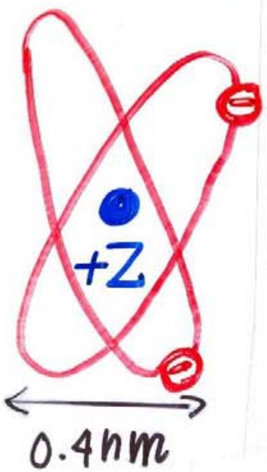


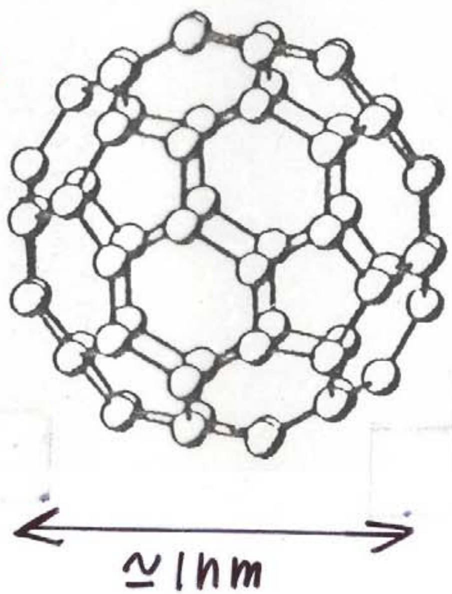

## 3 Very Short Range Attraction

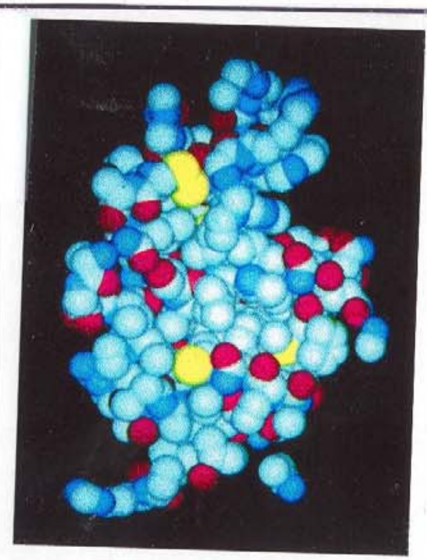


| 0.1 nm | 1 nm | 10 nm | 100 nm | 1000 nm |
|---|---|---|---|---|

| ATOMS | MOLECULES | MACROMOLECUS, VIRUSES, COLLOIDS | |
|---|---|---|---|
| ARGON | $C_{60}$ | GLOBULAR PROTEINS | COLLOIDAL SILICA, PMMA,.... |

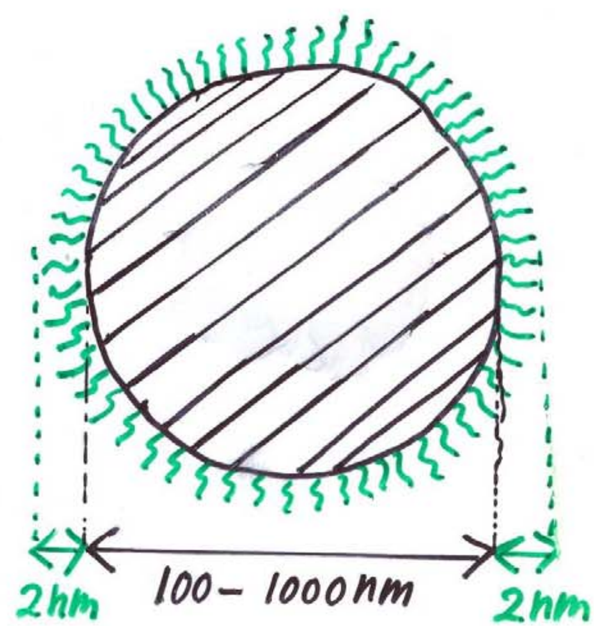


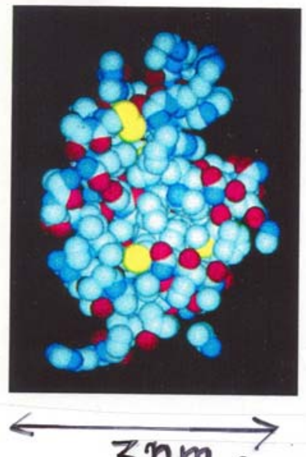



Space-filling model of lysozyme

M= 14600
Ellipsoidal Shape
4.5 x 3 x 3 nm
$V_0$= 21 $nm^3$

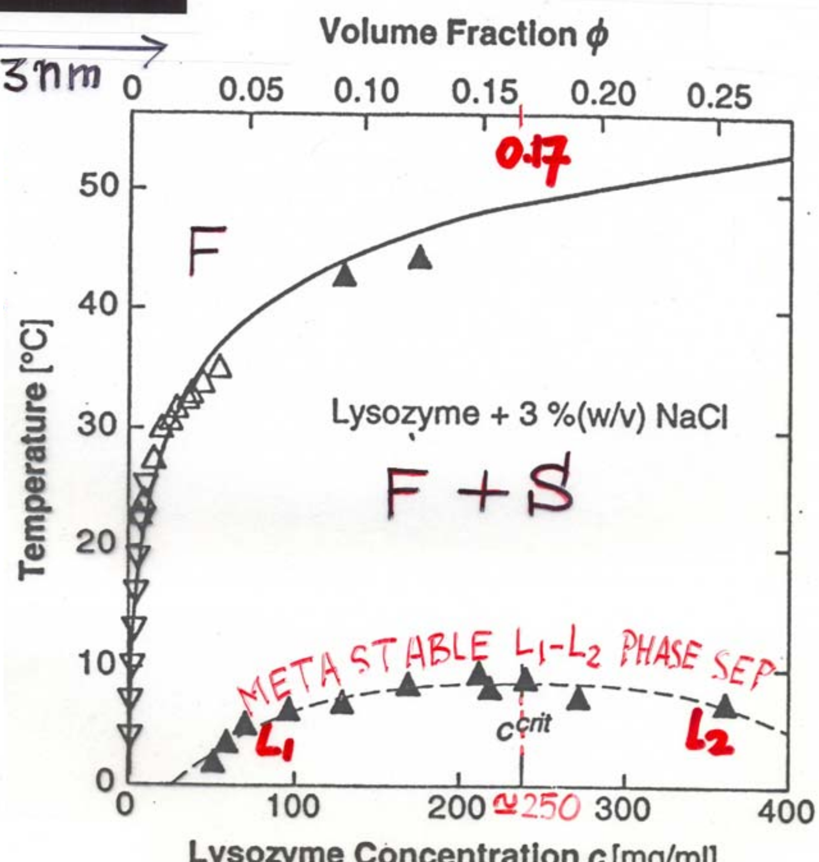


# PHASE DIAGRAMS OF GLOBULAR PROTEINS



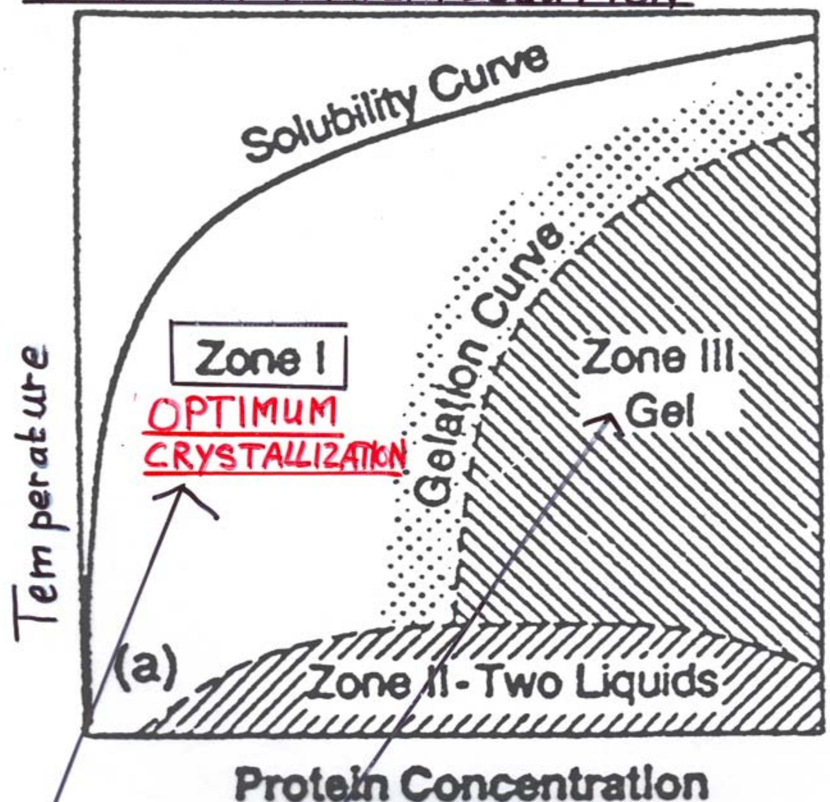

## LYSOZYME

M = 14400
Ellipsoidal Shape
4.5 X 3 X 3 nm



M. Muschol and F. Rosenberger J. Chem. Phys 107, 1953 (1997)

"MORPHOLOGY" PHASE DIAGRAM
GLOBULAR PROTEIN SOLUTION



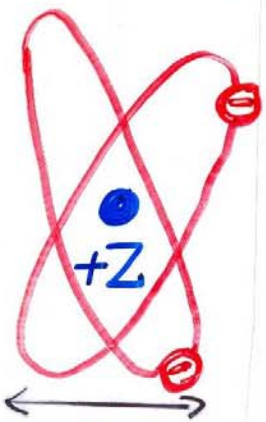

Zone I Optimum Crystallization

CRAGGS | CRYSTALLIZING AGGREGATES

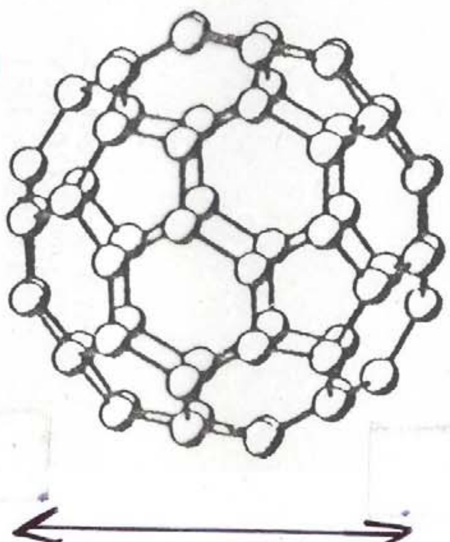
versus

PRAGGS | PRECIPITATING AGGREGATES

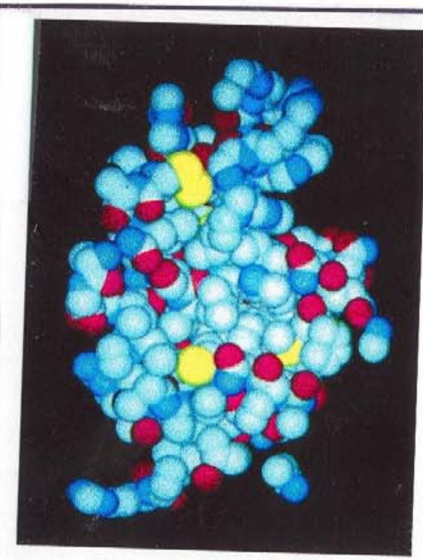
| 0.1nm | 1nm | 10nm | 100nm | 1000nm |
|---|---|---|---|---|
| ATOMS | MOLECULES | MACROMOLECUS, VIRUSES, COLLOIDS | | |
| ARGON | $C_{60}$ | GLOBULAR PROTEINS | | COLLOIDAL SILICA, PMMA,... |




0.4nm

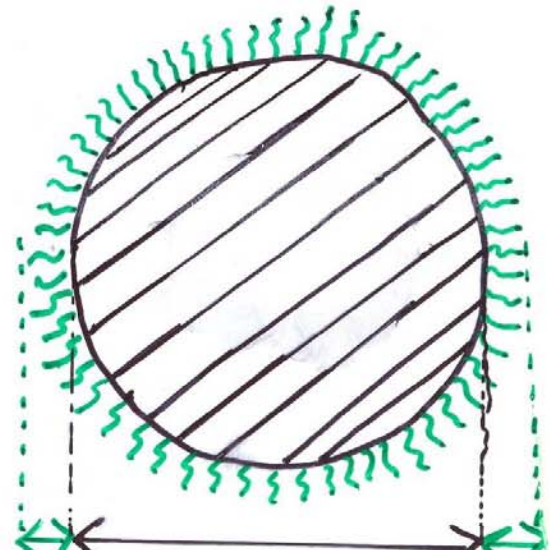


≃1nm



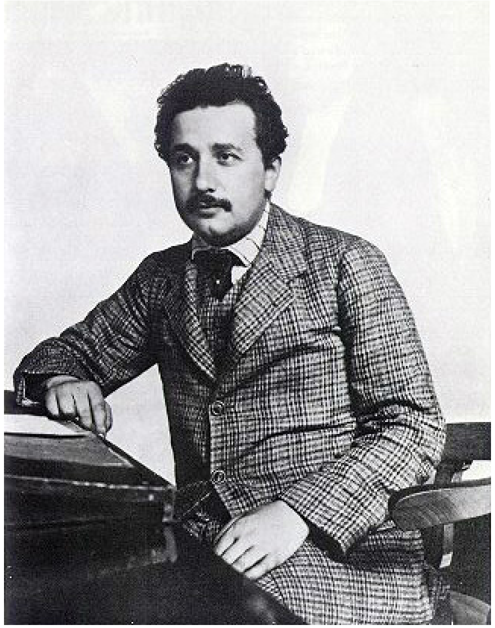
Space-filling model of lysozyme

M= 14600
Ellipsoidal Shape
4.5 x3 x3 nm
$V_0$= 21 nm$^3$



2nm 100– 1000nm 2nm

# Colloids as Atoms



Albert Einstein
(1879-1955)

# Ann. d. Physik, 17, 549 (1905)

**5. *Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen;***
***von A. Einstein.***

Vom Standpunkte der molekularkinetischen Wärmetheorie aus kommt man aber zu einer anderen Auffassung. Nach dieser Theorie unterscheidet sich eingelöstes Molekül von einem suspendierten Körper *lediglich* durch die Größe, und man sieht nicht ein, warum einer Anzahl suspendierter Körper nicht derselbe osmotische Druck entsprechen sollte, wie der nämlichen Anzahl gelöster Moleküle. Man wird anzunehmen haben, daß

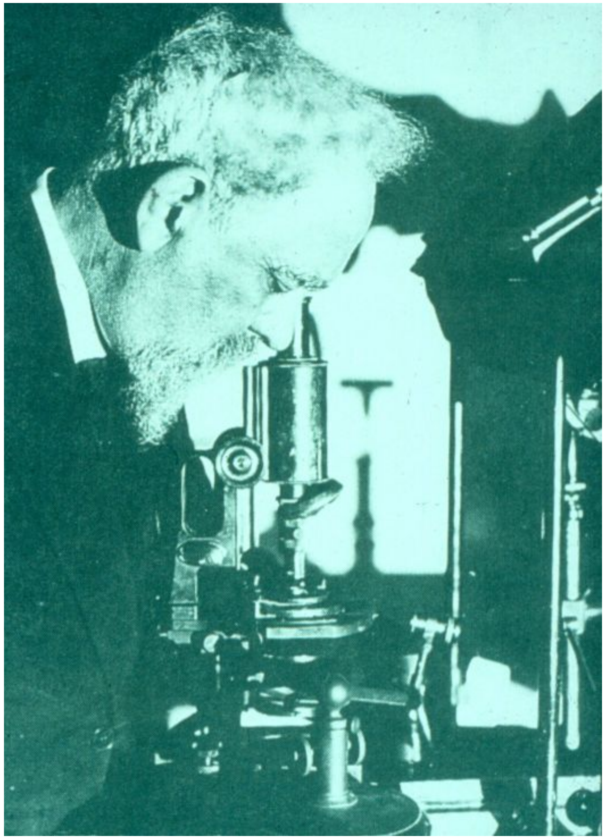
“According to this theory a dissolved molecule is differentiated from a suspended body *solely* by its dimensions, and it is not apparent why a number of suspended particles should not produce the same osmotic pressure as the same number of molecules.”

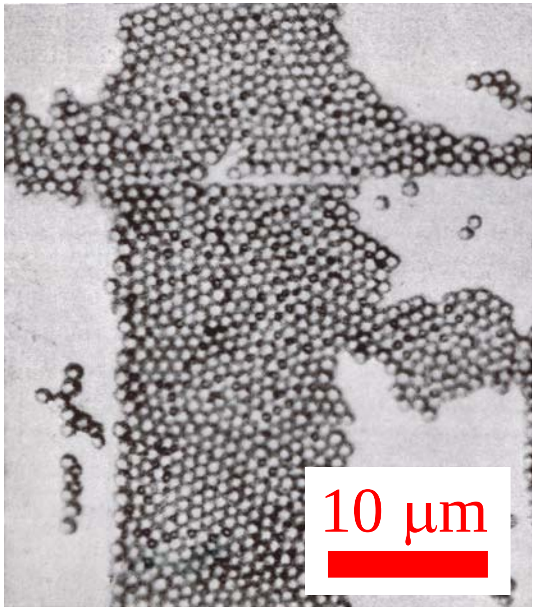
# Colloids as Atoms

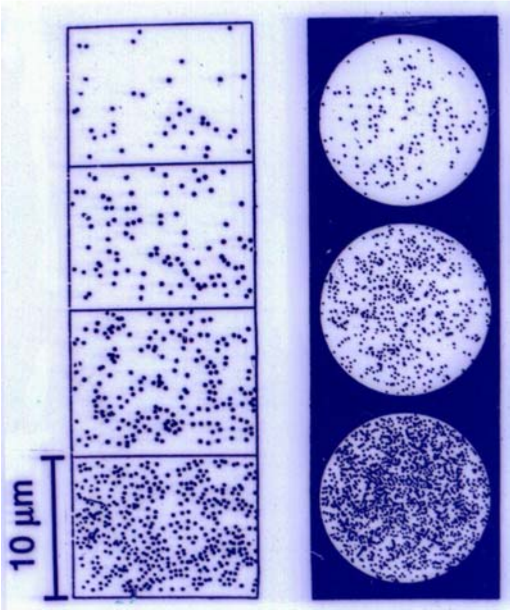
Jean Perrin (1870-1942)

Nobel Prize Physics 1926

"For his work on the discontinuous structure of matter, and especially for his discovery of sedimentation equilibrium."



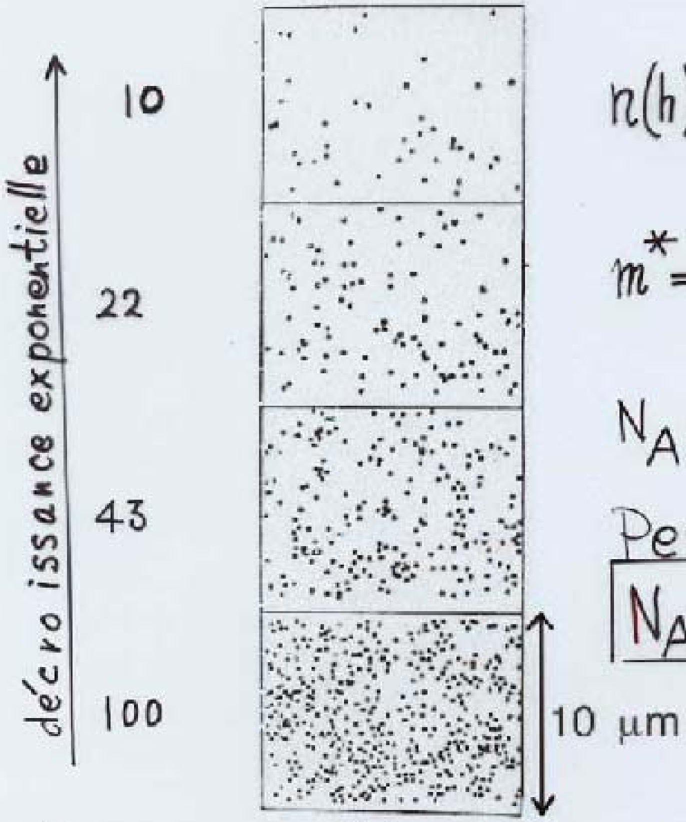


## Les grandes expériences de Jean Perrin
## 1907 – 1913
## Mouvement Brownien et Réalité Moléculaire

### Extensions des lois des gaz aux émulsions diluées

Observation de la répartition en hauteur d' une émulsion verticale




$$n(h) = n(0)\exp\left(-\frac{m^* g h}{k_B T}\right)$$

$$m^* = \frac{\pi}{6}\sigma^3(\rho_p - \rho_0)$$

$$N_A = \frac{R}{k_B}$$

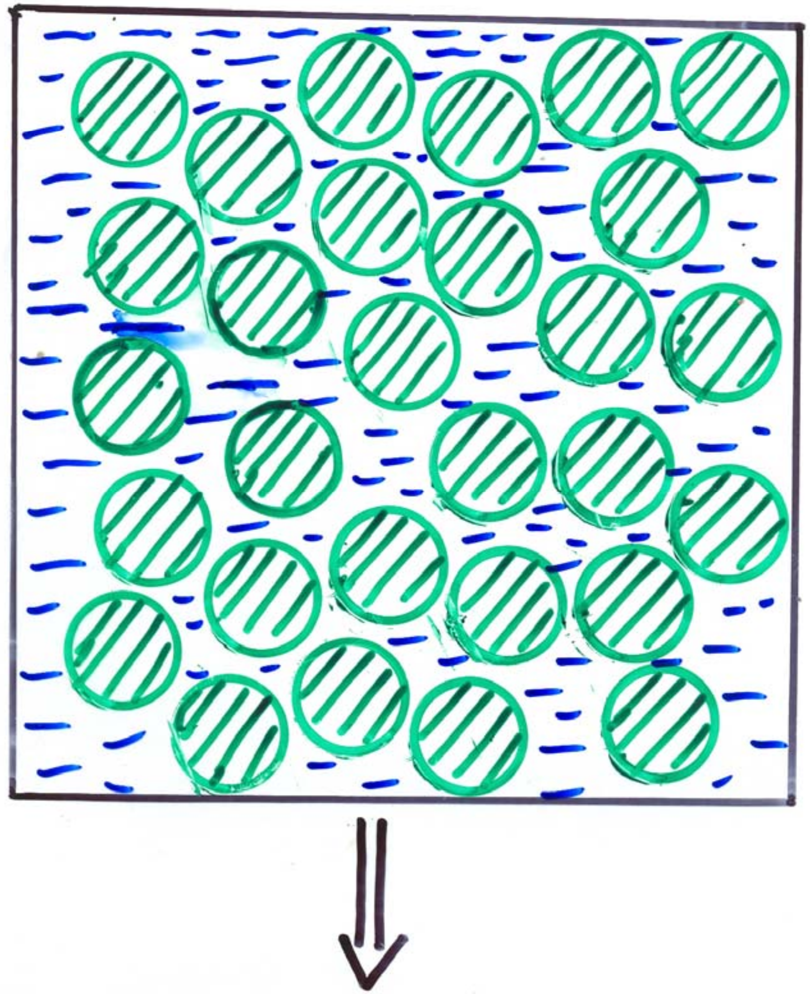
Perrin :

$$N_A = 6.82\ 10^{23}$$

$(6.02\ 10^{23})$

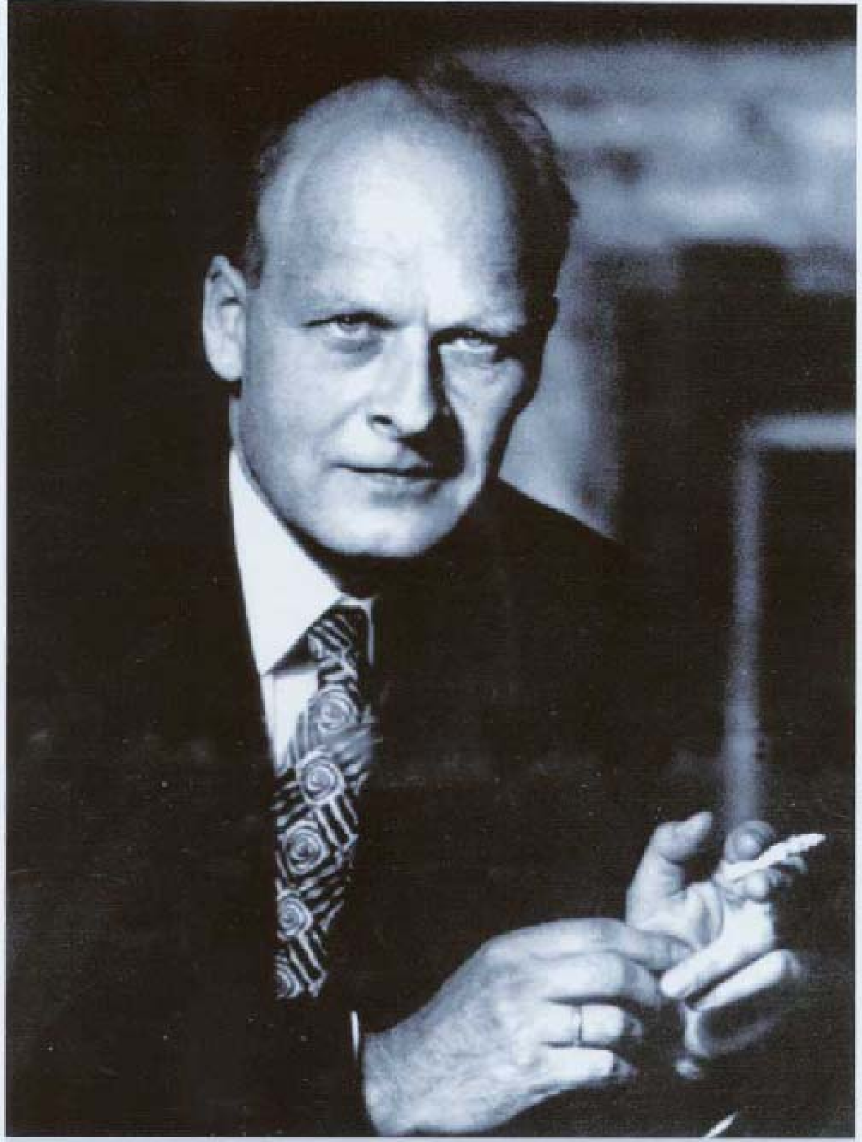
Répartition d'équilibre de grains de gomme-gutte (3000 grains) ($\sigma = 0.6\ \mu m$)

(CONCENTRATED)
COLLOIDAL SUSPENSIONS



O PARTICLE INTERACTIONS
+
O STATISTICAL PHYSICS

LARS ONSAGER (1903-1976)



Nobel Prize Chemistry 1968

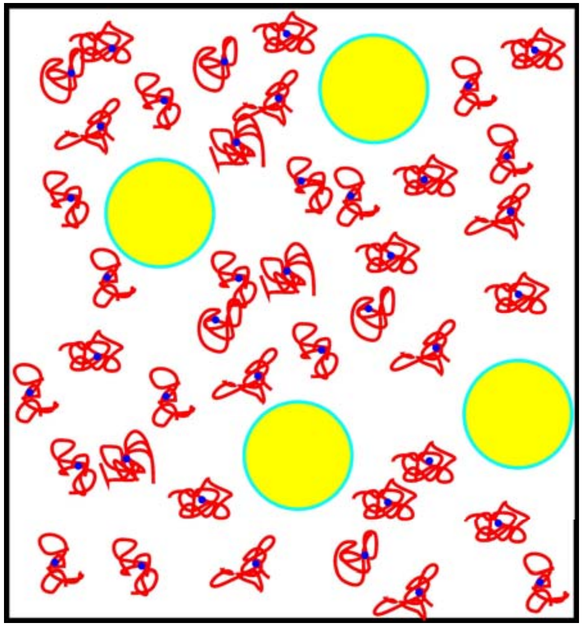
"For the discovery of the Reciprocity Relations, which are fundamental for the Thermodynamics of Irreversible Processes"

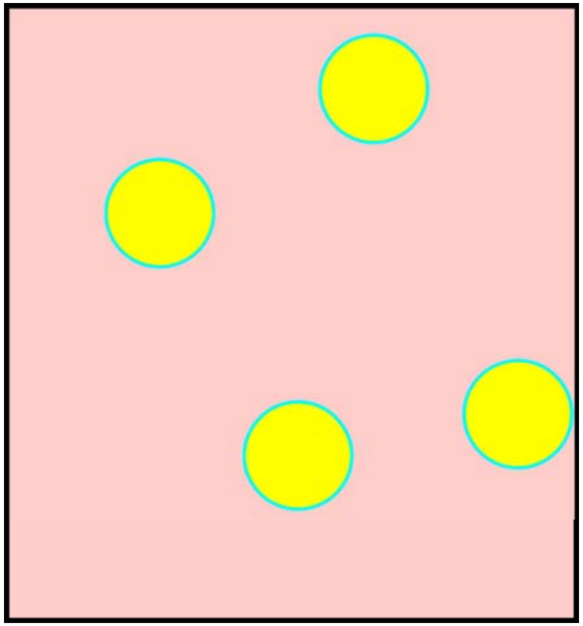
KEY CONCEPT

# COLLOID - ATOM ANALOGY.

THE SAME CONCEPTS AND METHODS OF THE STATISTICAL MECHANICS OF SIMPLE LIQUIDS CAN BE APPLIED TO COLLOIDAL SUSPENSIONS ONE MUST SIMPLY REPLACE THE BARE POTENTIAL $V(r)$ BY THE POTENTIAL OF THE AVERAGE FORCE $W(r)$

# Concept of the potential of mean force



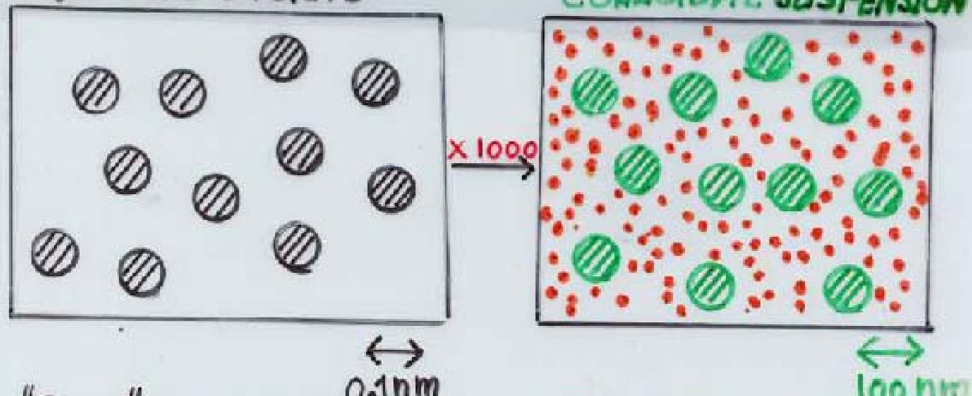


L. Onsager, Chem. Rev. 13 73-89 (1933)
"Theories of Concentrated Electrolytes"

# ANALOGY

SIMPLE ATOMIC LIQUIDS ⇄ CONCENTRATED COLLOIDAL DISPERSIONS

SIMPLE LIQUID | COLLOIDAL SUSPENSION




"BARE" POTENTIAL

$V$

FORCE

$$K = -\frac{\partial V}{\partial R}$$

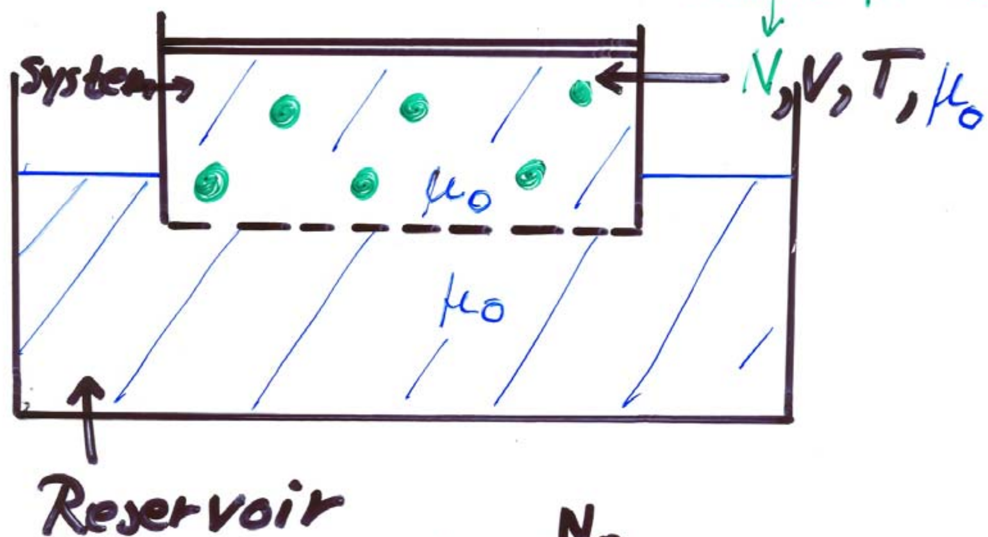
POTENTIAL OF MEAN FORCE

$W$

MEAN FORCE

$$\langle K \rangle = -\frac{\partial W}{\partial R}$$

# Potential of Mean Force




$$\Xi = \sum_{N_0 \geq 0} \left(e^{\mu_0/kT}\right)^{N_0} \times \frac{1}{N!\, N_0!} \int e^{-U(\vec{R}^N, \vec{R}^{N_0})} d\vec{R}^N d\vec{R}^{N_0}$$

$$\equiv \frac{1}{N!} \int e^{-W(\vec{R}^N, \mu_0)} d\vec{R}^N$$

# Potential of Mean Force

$$W(\vec{R}^N, \mu_0) = -kT \ln \left[ \sum_{N_0 \geq 0} \left(e^{\mu_0/kT}\right)^{N_0} \times \frac{1}{N_0!} \int e^{-U(\vec{R}^N, \vec{R}^{N_0})/kT} d\vec{R}^{N_0} \right]$$

$$\Rightarrow -\frac{\partial W}{\partial \vec{R}_j} = \frac{\sum_{N_0 \geq 0} \frac{\left(e^{\mu_0/kT}\right)^{N_0}}{N_0!} \int \left(-\frac{\partial U}{\partial \vec{R}_j}\right) e^{-U/kT} d\vec{R}^{N_0}}{\sum_{N \geq 0} \frac{\left(e^{\mu_0/kT}\right)^{N_0}}{N_0!} \int e^{-U/kT} d\vec{R}^{N_0}}$$

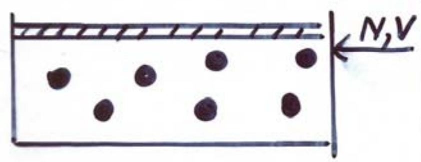
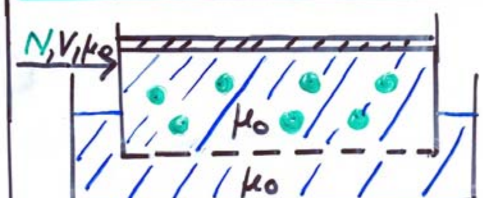
$$= \langle \vec{F}_j \rangle$$

Mean Force

W: potential of the Mean Force

# STATISTICAL MECHANICS OF COLLOIDAL DISPERSIONS

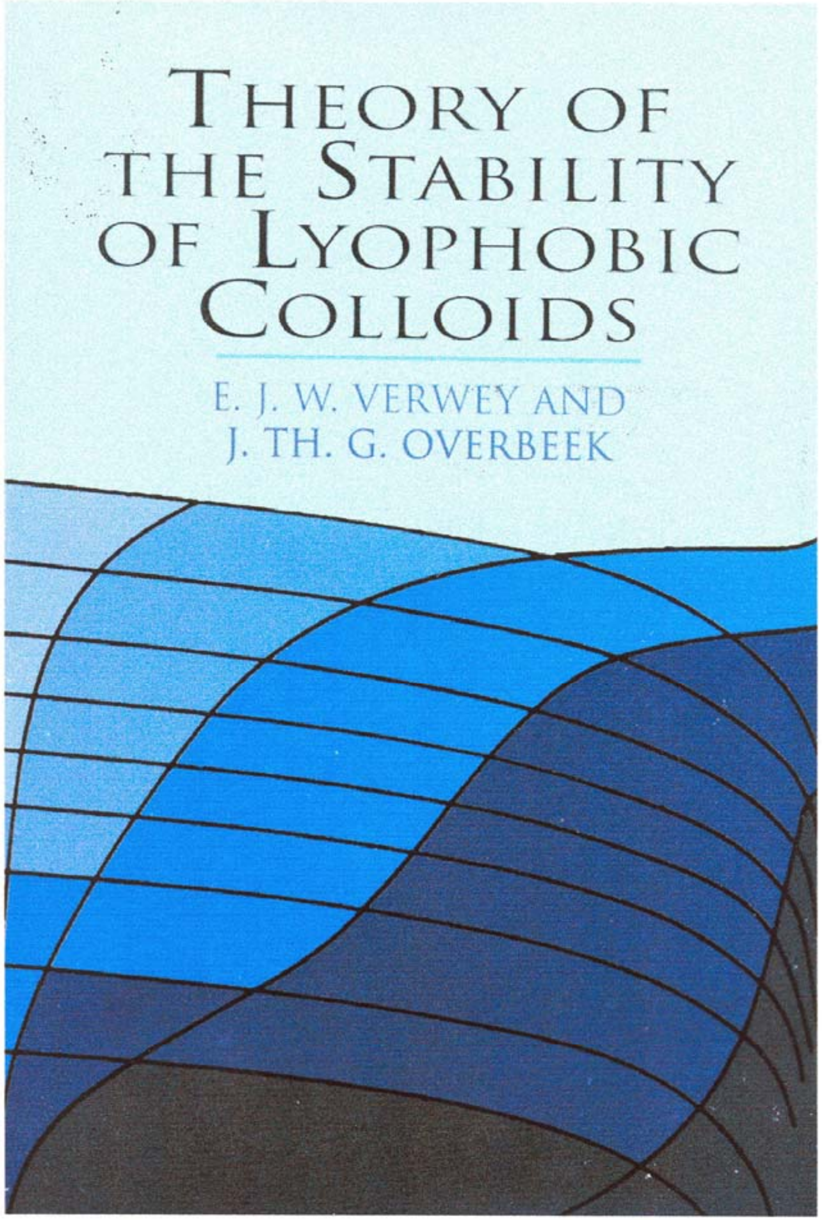
- Colloidal particles are equivalent to Atoms in that they undergo Thermal Motion
- This analogy was (correctly!) applied in an intuitive way by Einstein, Von Smoluchowski, Perrin .... in the early part of this century.
- A formal basis for this analogy was provided by Onsager (1933, 1949) and McMillan and Mayer (1945)

| SIMPLE (ATOMIC) FLUID | DISPERSION OF (SPHERICAL) COLLOIDAL PARTICLES |
|---|---|
|   |   |
| N Atoms in Volume V | N Colloidal Particles in V in Solvent with chemical potential $\mu_0$ |
| Bare Potential $U(\vec{R}_1 \dots \vec{R}_N)$ | Potential of Mean Force $W(\vec{R}_1 \dots \vec{R}_N, \mu_0)$ |
| $Z = \frac{1}{N!}\int \exp(-U/kT)\, d\Gamma$ | $\Xi = \frac{1}{N!}\int \exp(-W/kT)\, d\Gamma$ |
| $F = -kT \ln Z$ | $\Omega = -kT \ln \Xi$ |

Bottom Line: $W$ is rigorous and precise but the calculation of $W$ frequently seems to be mysterious.

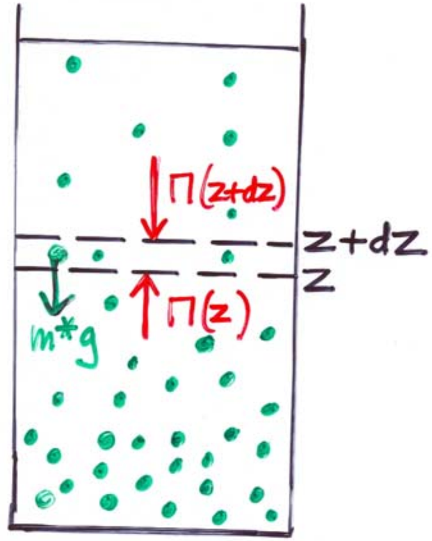
COMMERCIAL

BREAK




UNABRIDGED DOVER (1999) REPUBLICATION OF THE WORK PUBLISHED BY ELSEVIER 1948
$14.95 IN USA.

# SEDIMENTATION EQUILIBRIUM




## BALANCE

| OSMOTIC PRESSURE GRADIENT | | GRAVITY FORCE |
| --- | --- | --- |
| $\Pi(z) - \Pi(z+dz)$ | $=$ | $m^* g\, \rho\, dz$ |

$$-\frac{d\Pi}{dz}\, dz = m^* g\, \rho\, dz$$

$$-\frac{\partial \Pi}{\partial \rho}\frac{d\rho}{dz} = m^* g\, \rho$$

van 't Hoff $\frac{\partial \Pi}{\partial \rho} = kT$ →

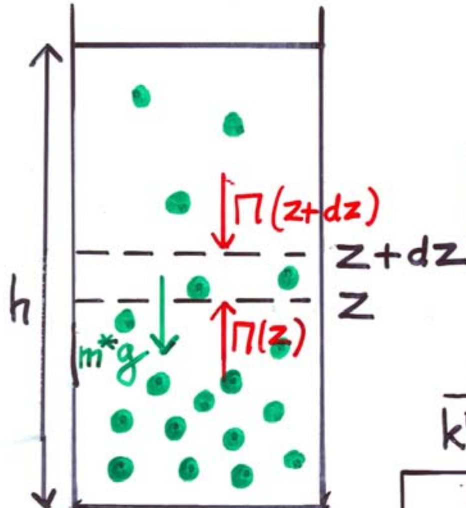
$$\frac{d\rho}{dz} = -\frac{m^* g}{kT}\rho \qquad \xi_g = \frac{kT}{m^* g}$$

$$\rho(z) = \rho(0)\exp\left(-z/\xi_g\right)$$

# A Test of the Hard-Sphere Equation of State

R. Piazza, T. Bellini, V. Degiorgio

(PRL 71, 4267, 1993)




## BALANCE

GRAVITY FORCE = OSMOTIC PRESSURE GRADIENT

$$m^* g \rho\, dz = \Pi(z) - \Pi(z+dz)$$

$$\frac{1}{kT}\frac{d\Pi}{dz} = -\left(\frac{m^* g}{kT}\right)\rho$$

$$\frac{1}{kT}\frac{d\Pi}{dz} = -\frac{\rho}{\xi_g}$$

gravitational length

$$\xi_g = \frac{kT}{m^* g}$$

$\xi_g \sigma^3 \simeq 1 - 10\ \mu m^4$

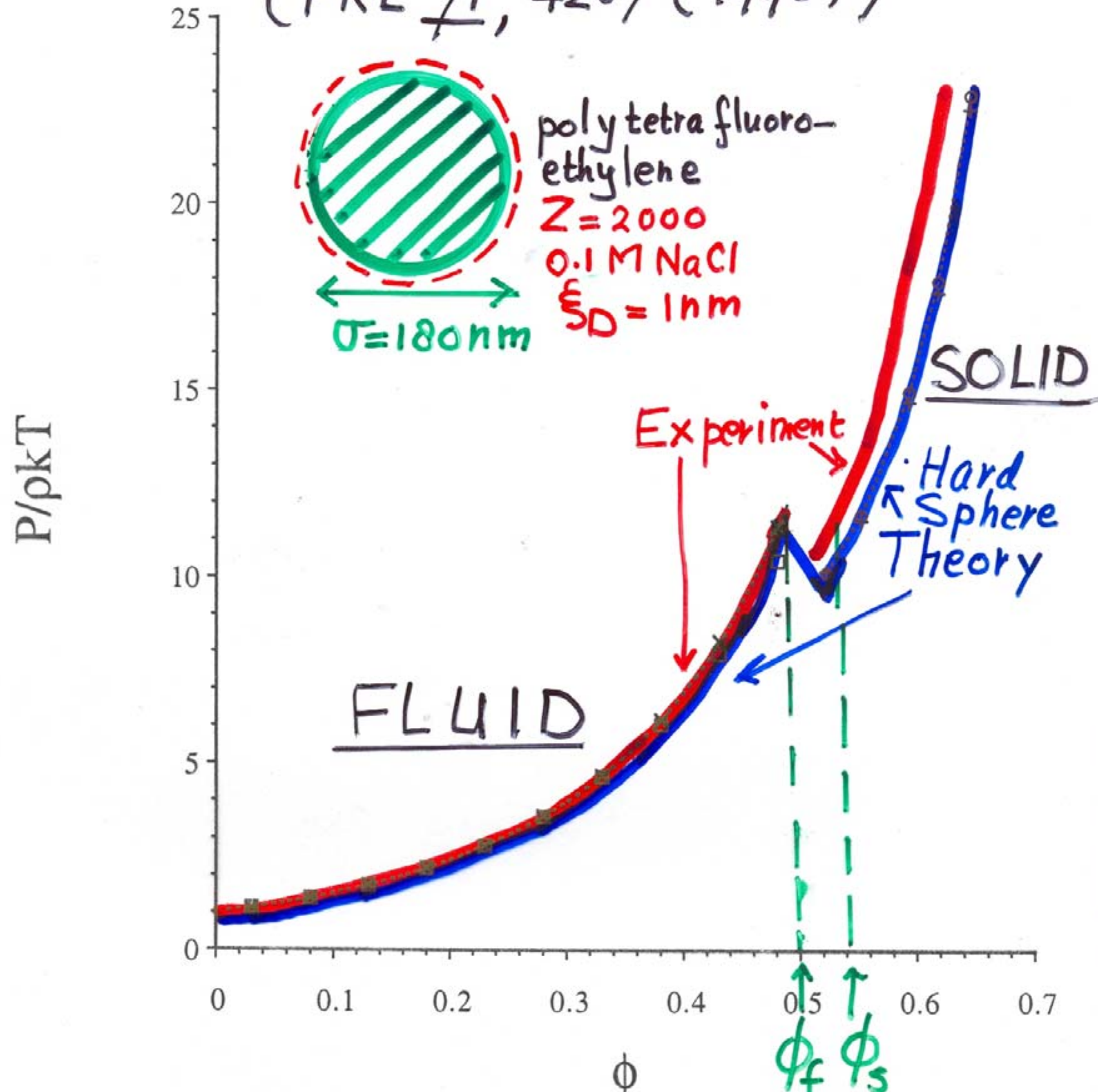
$$m^* = V\left(d_{particle} - d_{medium}\right)$$

$$\frac{1}{kT}\Pi(z) = \frac{1}{\xi_g}\int_z^h \rho(z')\,dz'$$

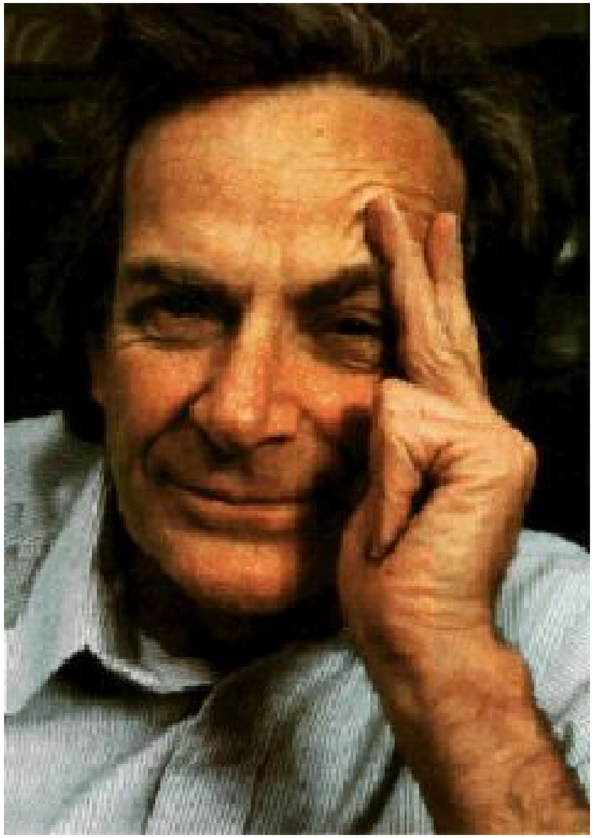
R. Piazza, T. Bellini, V. Degiorgio

# An Experimental Test of the Hard Sphere Equation of State

(PRL 71, 4267 (1993))

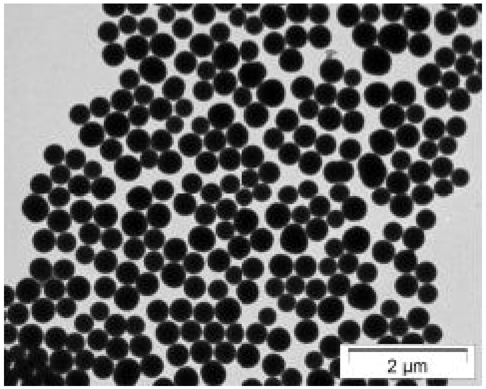


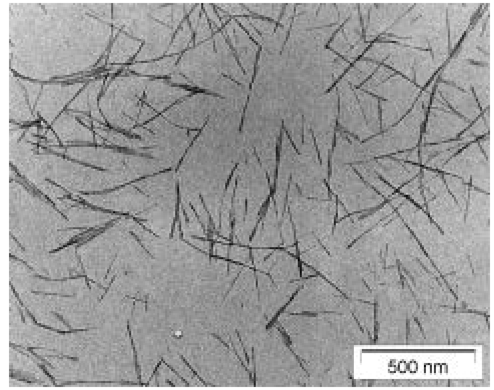
*"The same equations have the same solutions."*
Richard Feynman (1918-1988)

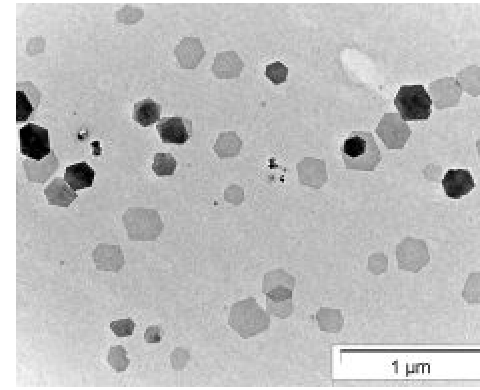


**…so what is new?**

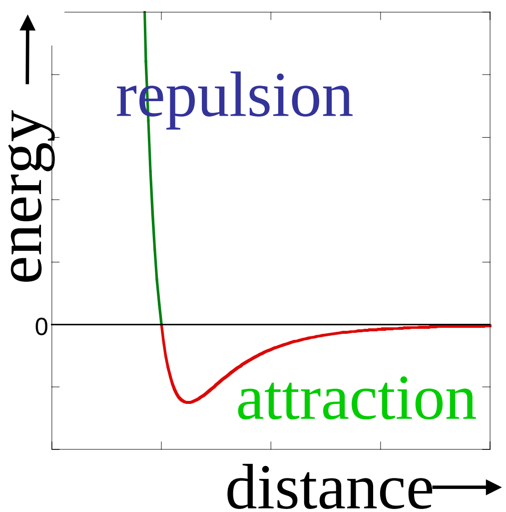
- Colloids: variable shape

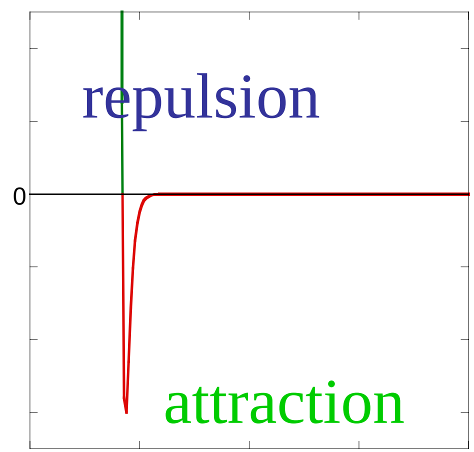


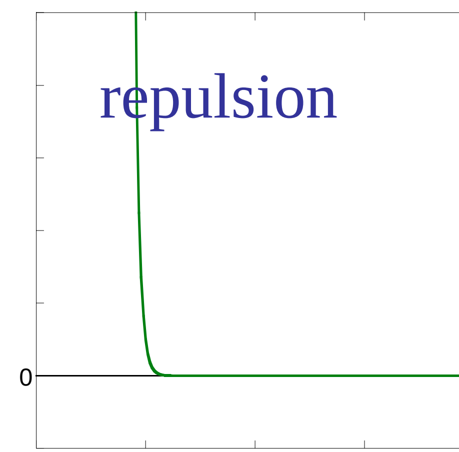




- Colloids: variable interactions




**new** and **fascinating** behaviour!

The end of lecture 2