Excluded Volume Interactions

Reference text:

The Structure and Rheology of Complex Fluids, Ronald G. Larson

Statistical Mechanics, Donald A. McQuarrie

Soft Matter Physics, M. Doi

Slides from Complex Fluids and Soft Matter, Ronald G. Larson

Macroscopic Thermodynamics

For systems whose natural variables are T and V (volume),

Internal energy

Helmholtz free energy: $A \equiv U - TS$ ← entropy

$$(dA \equiv dU - SdT - TdS)$$

First Law of Thermodynamics: $dU = TdS - pdV$

heat flow   work

These two imply: $dA = -SdT - pdV$

multi-component system: $G \equiv$ Gibbs free energy

$$\mu_j \equiv \left(\frac{\partial G}{\partial N_i}\right)_{T,p,N_k,k \neq j}$$

$$dA = -SdT - pdV + \sum_j \mu_j dN_j \qquad \mu_j = \text{chemical potential of j}$$

Gibbs free energy: $G \equiv H - TS$ \qquad enthalpy: $H \equiv U + pV$

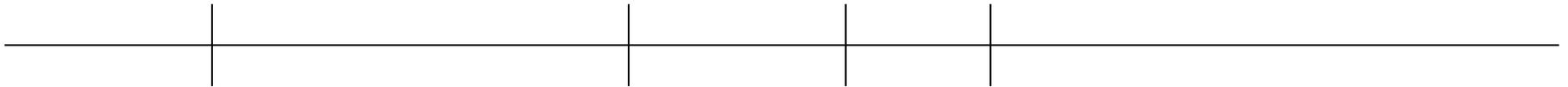$$G \equiv U - TS + pV = A + pV$$

More detail: McQuarrie: Statistical Mechanics, Doi: Soft Matter Physics"

Microscopic Thermodynamics

Boltzmann distribution: $p_j \propto \exp(-\frac{E_j}{k_B T})$ $\qquad p_j \equiv prob.\,of\,state\,j$

Boltzmann distribution is a special case of a *Poisson distribution*

example: randomly divide a long line into a huge number of segments

In the limit of large number of cuts, the distribution of line segment lengths is

$$p(L) \propto \exp(-\frac{L}{<L>})$$ normalization constant

$$\sum_j p_j = 1$$

$$p_j = \exp(-\frac{E_j}{k_B T})/ \sum_j \exp\left(\frac{-E_j}{k_B T}\right) = \exp(-\frac{E_j}{k_B T})/Q$$

Q = partition function, $Q \equiv \sum_j \exp(\frac{-E_j}{k_B T})$ sum is over all states, including ones with same energy (i.e., degenerate states)

connection to macroscopic thermodynamics: $A = -k_B T\, lnQ$

Application: Metropolis Monte Carlo Simulation

We wish to obtain thermodynamic averages of properties of a system, such as a molecular system, with a great many microstates, too many to average over all of them. So, we need to *sample* these microstates *fairly*, i.e., weighted by their contribution to free energy.

So, we pick a starting state, S_1, and choose a possible re-arrangement of this state to slightly different State S_2 randomly out of a total of N possible re-arrangements.

$$E_i = \text{energy of State } S_i \; ; \; i = 1, 2$$

If $E_2 < E_1$ transition to state S_2 from S_1, with probability unity,

if $E_2 > E_1$ transition to state S_2 from S_1, with probability exp $[-(E_2 - E_1)/k_B T]$ where we use a random number to decide if to transition. If we do not transition, the system is kept in State 1 for that step of the simulation.
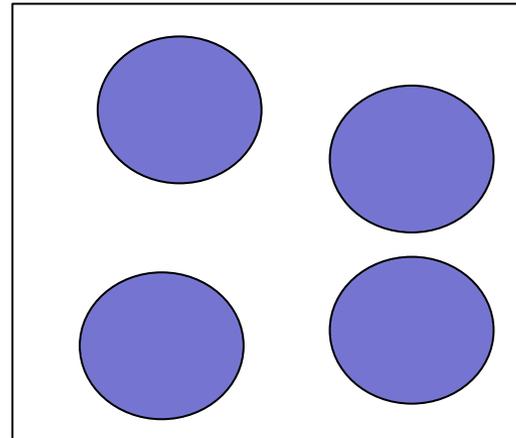
We then draw randomly a new State S_2 out of the N possibilities and repeat.

Application: Metropolis Monte Carlo Simulation

reject
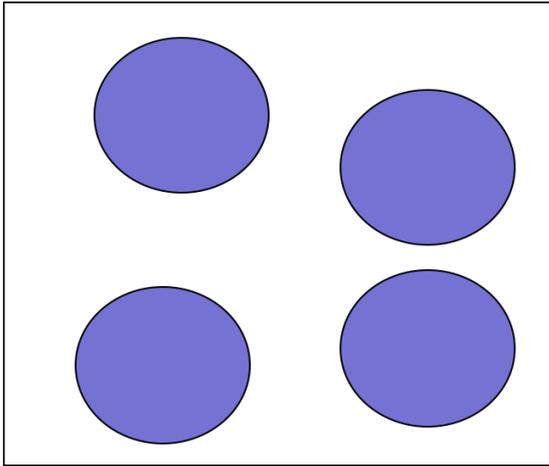
accept

If for any State i, there are always the same number N possible new states that can be sampled, then in a long run, any state i will be sampled with frequency equal to its Boltzmann weight:
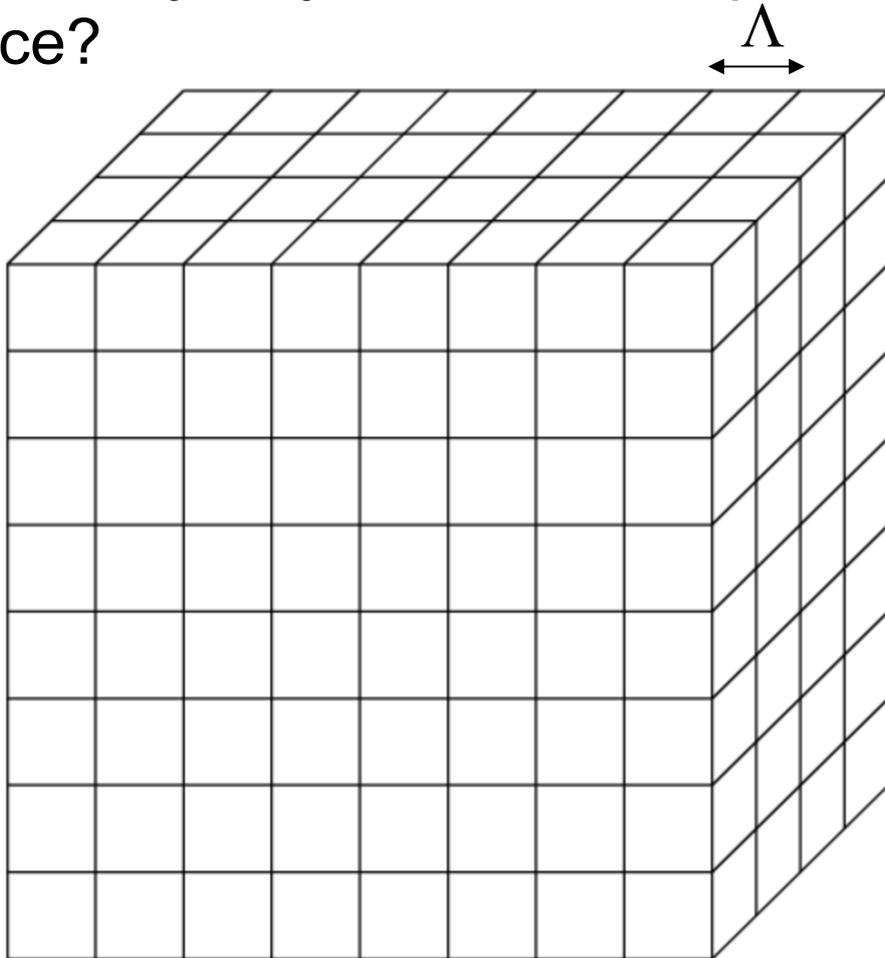
$$p_i = \exp(-\frac{E_i}{k_B T})/ \sum_j \exp\left(\frac{-E_j}{k_B T}\right)$$

This is the proper thermodynamic weight that this state should receive in the thermodynamic ensemble. Thus, any property averaged over the sampled states will converge to its thermodynamic average. E.g., $\bar{E} = \sum_j p_j \ E_j$

Non-Interacting Particles

$E_j = 0$, for every state j $$Q \equiv \sum_{j=1}^{N} \exp\left(\frac{-E_j}{k_B T}\right) = N = No. of\ states$$

How many ways are there of placing a single particle in 3D space?

Λ

Λ = lattice spacing (or "deBroglie wavelength")

There are V/Λ^3 places to put a single particle

V^N/Λ^{3N}

ordered ways of placing N particles, allowing overlap

number of ways of ordering the N particles: $N!$

Particle-Wave Dualism

Prof. Louis De Broglie   1923

$$\lambda_{dB} = h/p$$

All particles are waves!

λ_{dB} = de Broglie wavelength

h = Planck's Constant
  6.63×10^{-34} Joule·second

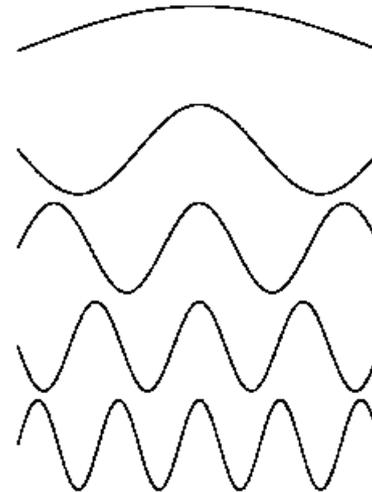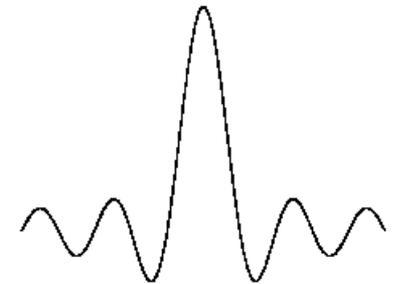p = momentum of particle
= mass × velocity

$E = p^2/2m$

m – particle mass

$E = (h/\lambda)^2/2m$

adding these ...   results in this

Non-Interacting Particles

Helmholtz free energy of purely entropic system: $A = -TS$

$$A = -k_B T \, lnQ \qquad Q = \text{partition function}$$

overlapping (phantom) particles: $\quad E_j = 0$, for every state j

$$Q = total\ number\ of\ unique\ states = \frac{V^N}{N!\Lambda^{3N}}$$

V = system volume, Λ = lattice spacing (or "deBroglie wavelength)"

V/Λ^3 = number of positions at which a particle can be placed

$$A/k_B T = -lnQ \quad = -NlnV + \ln(N!) + const \quad \text{(const. involves } \Lambda \text{)}$$

Stirling's approx: $\quad \ln(N!) \approx NlnN - N \quad \approx NlnN \quad$ *(N large)*

$$A/k_B T \; = -S/k_B \; = Nln\left(\frac{N}{V}\right) = Nln(v) + const$$

$v = N/V =$ number density

$$A/(Vk_B T) \approx vln(v) + const$$

Pressure $P = vk_B T$

Non-Interacting Particles
(Generalization 1: non-uniform concentration)

$$A/k_B T = -S/k_B \; = Nln(v) + const \qquad v = N/V =$$

number density

$$A(\boldsymbol{x})/(Vk_B T) \approx \; v(\boldsymbol{x})\ln[v(\boldsymbol{x})] \; + const \; = v(\boldsymbol{x})\ln[\frac{v(\boldsymbol{x})}{v_0}]$$

$$\boldsymbol{x} = \text{position vector}$$

$v_0 = $ reference concentration; A is then
free energy relative to reference state

example: consider the reference state to be one of uniform
concentration v_0. Relative to this, a non-uniform
concentration has free energy:

$$\frac{A}{k_B T} = \frac{-S}{k_B} = \int_V vln(v/v_0)dV$$

The integral is
over physical
space

Non-Interacting Particles
(Generalization 2: multiple species)

$$A/k_B T = -S/k_B = N ln\left(\frac{N}{V}\right) = N ln(v) + const$$

$v = N/V =$ number density

generalize:

$$A/(k_B T) = \sum_i N_i \, ln(v_i) + const$$

(uniform concentration)

consider the reference state to be one in which each particle type is separated from the others at a uniform concentration $v_0 = \sum_i v_i$ Relative to this, free energy is:

$$\frac{A}{k_B T} = \sum_i N_i \, ln(v_i) - \sum_i N_i \, ln(v_0) = \sum_i N_i \, ln(v_i/v_0)$$

$$\frac{A}{V k_B T} = \frac{-S}{V k_B} = \sum_i v_i \, ln(x_i)$$
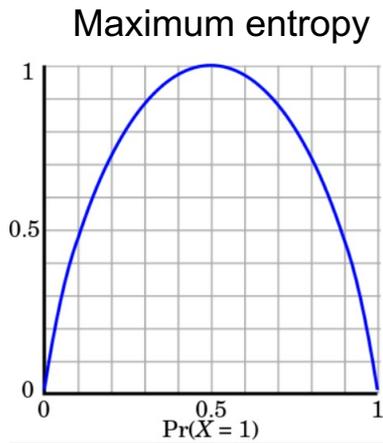
$x_i = v_i / \sum_i v_i$ = mole fraction of i

"Ideal mixing" entropy

Non-Interacting Particles
(Generalization 3: non-uniform *probability* distribution)

$$A/k_B T = -S/k_B = \sum_i N_i \, ln(P_i)$$

N_i =number of particles in state i

P_i =probability (or fraction of times) that particle is in state i = N_i/N

$$= N \sum_i P_i \, ln(P_i)$$

N = total number of particles

(equal *a priori* probability of each state)

Maximum entropy

$$-\sum_i P_i \, ln(P_i)$$

= *Shannon entropy (per particle)* from information theory

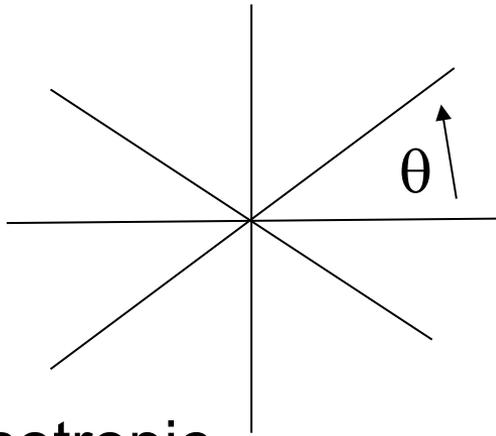high Shannon entropy means low information content, and vice versa

Claude Shannon, Univ. of Mich. grad, born in Petoskey, MI

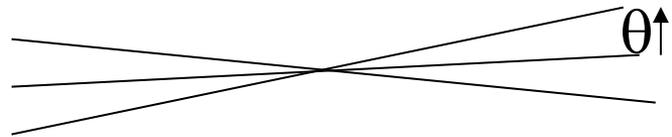"Information content of the known universe:" $10^{10^{123}}$

Non-Interacting Particles
(Generalization 4: non-uniform distribution in orientation space)

θ

θ

anisotropic distribution, $\psi(\theta)$

isotropic

3D isotropic $\psi_0(\Omega) = \psi_0(\theta, \phi) = \dfrac{1}{4\pi}$

In 3D space, $\psi(\theta, \phi)\mathrm{d}\theta d\phi$ = probability orientation angles are between θ and θ+dθ and between ϕ and ϕ+dϕ

$$\frac{A}{k_B T} = \frac{-S}{k_B} = \int_0^{2\pi} \int_0^{\pi} \psi ln(\psi/\psi_0) \underline{sin\ \theta d\theta d\phi} = \int_\Omega \psi ln(\psi/\psi_0) d\Omega$$

$$d\Omega = du^2$$

reference state: uniform orientation distribution

(Generalization 5: densely concentrated particles & extension to Flory-Huggins theory)

Helmholtz free energy of purely entropic system: $A = -TS$

$$A = -k_B T \, lnQ \qquad Q = \text{partition function}$$

Interacting particles: $Q = \dfrac{\prod V^{N_i}}{\prod(\Lambda^{3N_i}N_i!)} \int ... \int \exp[-\dfrac{U_n}{k_B T}]$

Integral is over reduced coordinates that each vary from 0 to 1

$\prod(V^{N_i}/N_i!)$ gives the interaction-independent contribution to entropy:

$$S/k_B = \ln[\prod(V^{N_i}/(\Lambda^{3N_i}N_i!))]$$

(Generalization 5: densely concentrated particles & extension to Flory-Huggins theory)

$$S/k_B = \ln[\prod(V^{N_i}/(\Lambda^{3N_i}N_i!))]$$

Now consider *non-interacting; i.e., overlapping,* particles with N_1 particles in a volume V_1 and N_2 particles in a volume V_2 and mixing them in a volume $V = V_1 + V_2$. Take $\phi_i \equiv V_i/V$. The resulting *change* in entropy is given by

$$\frac{-\Delta S}{k_B} = N_1 \ln\phi_1 + N_2 \ln\phi_2$$

"ideal translational (aka Flory-Huggins) entropy" Try deriving!

This mixing entropy is the same as that derived for *non-overlapping* particles on a lattice, where the volumes $V_1 = v_1 N_1$ and $V_2 = v_2 N_2$ are the volumes of densely packed particles each particle with volumes v_1 and v_2 and the mixture has volume $V = V_1 + V_2$. The contributions to entropy S from the overlaps in the mixture is cancelled out by the contributions from overlaps to S in the volumes V_1 and V_2 so that $-\Delta S$ is unchanged. (Lazaridis and Paulaitis, JPC 96:3847, 1992)

$$\frac{-\Delta S}{k_B} = N_1 \ln x_1 + N_2 \ln x_2 \quad \text{*"ideal mixing* entropy"}$$

Colloidal forces

- The structure of matter at the length scales greater than the atomic is governed by **electromagnetic forces**.

- At the temperatures of interest to us, around 200-500 K, **molecules** composed of covalently bonded atoms can be regarded as **indivisible units**, and the electromagnetic forces that we need consider are those that the molecules exert on one another.

Colloidal forces

- The force F between two such molecules is often described using a **potential function W (r)**, which for spherical molecules separated by a distance r is given by

$$F = -\frac{dW}{dr}$$

- A potential function can also be used to describe the force between a pair of colloidal particles. The electromagnetic forces that contribute to **W (r)** can be grouped into several categories, namely **excluded volume (or steric)**, **van der Waals**, **electrostatic**, **hydrogen bonding**, and **hydrophobic**.
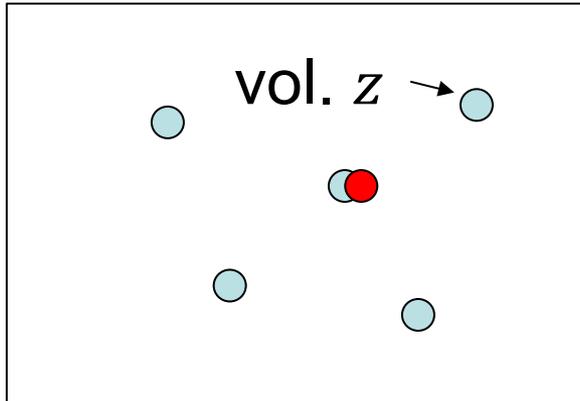
Excluded-volume interactions

- When molecules or atoms are brought closer and closer together, their **electron clouds** eventually overlap, producing a very strong repulsion that increases so steeply with decreasing intermolecular distance that it easily overpowers all other forces.

- This **excluded-volume force** is largely responsible for determining the **short-range structure of liquids** and the crystallographic order of solids composed of small molecules, or of **densely packed hard colloidal particles**.

- Consider the **excluded-volume forces** for the simplest cases, **hard spherical particles** and **hard nonspherical particles**

Excluded Volume Effects

z = excluded volume parameter

consider *dilute* particles

add a particle

probability that *a particular particle* overlaps another: $vz = \phi$, volume fraction

for N particles, number of configurations:

vol. V

$$\Omega \approx \frac{[V(1 - vz/2)]^N}{N! \, \Lambda^{3N}}$$

factor of 2 avoids double counting

$$N = vV$$

$$S = k_B ln\Omega = -k_B N ln[v(1 - vz/2)] \quad \text{(ignore *const.*)}$$

vol. z

Recall for Non-Interacting Particles

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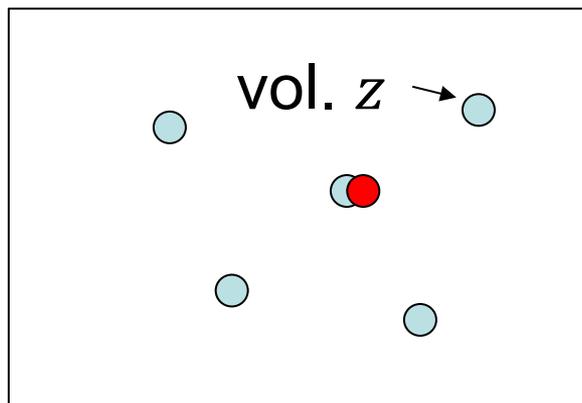Stirling's approx: $\quad \ln(N!) \approx NlnN - N \quad \approx NlnN \quad$ *(N large)*

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probability that *a particular particle*
overlaps another: $vz = \phi$, volume fraction
for N particles, number of configurations:

vol. z

vol. V

$$\Omega \approx \frac{[V(1 - vz/2)]^N}{N!\,\Lambda^{3N}}$$

factor of 2
avoids double
counting

$$N = vV$$

$$S = k_B ln\Omega = -k_B N ln[v(1 - vz/2)] \quad \text{(ignore } const.\text{)}$$

$$\approx \ - k_B\, V[vlnv + vln\left(1 - \frac{vz}{2}\right)]$$

Recall for Non-Interacting Particles

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Pressure $P = vk_B T$

Excluded Volume Effects

z = excluded volume parameter

consider *dilute* particles

add a particle

probability that *a particular particle* overlaps another: vz = ϕ, volume fraction for N particles, number of configurations:

$$\Omega \approx \frac{[V(1 - vz/2)]^N}{N!\,\Lambda^{3N}}$$

vol. z

vol. V

$N = vV$

factor of 2 avoids double counting

$$S = k_B ln\Omega = -k_B N ln[v(1 - vz/2)] \quad \text{(ignore } const.\text{)}$$

$$\approx -k_B V[vlnv + \boxed{vln\left(1 - \frac{vz}{2}\right)}]$$

change of entropy per unit volume: $k_B vln\left(1 - \frac{vz}{2}\right)] \approx -\frac{1}{2}k_B zv^2$

(due to excluded volume)

for small v

Hard Sphere Phase Diagram

Figure 2.1 The hard-sphere phase diagram. Below volume fraction $\phi < \phi_1 = 0.494$, the suspension is a disordered fluid. Between $\phi_1 = 0.494$ and $\phi_2 = 0.545$, there is coexistence of this disordered phase with a colloidal crystalline phase with FCC (or HCP) order; the colloidal crystalline phase is the equilibrium one up to the maximum close-packing limit of $\phi_{cp} = 0.74$. Nonequilibrium colloidal "glassy" behavior can also occur between $\phi_g = 0.58$ and the limit of random close packing at $\phi_{rcp} = 0.64$. (From Poon and Pusey, fig. 5, with kind permission of Kluwer Academic Publishers, Copyright 1995.)
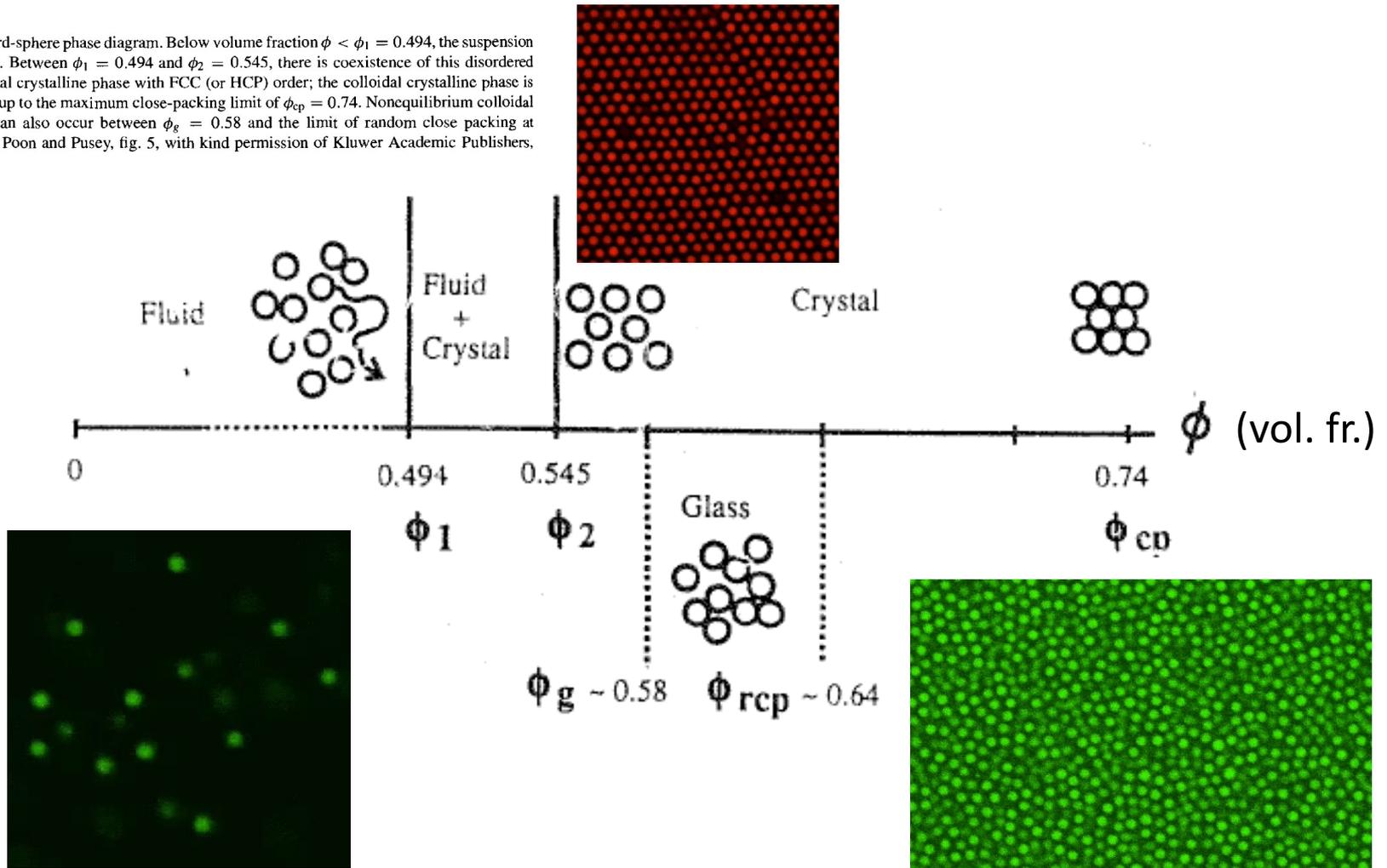

videos from Solomon group

Hard Sphere Phase Diagram

- Amazingly, the hard-sphere crystallization transition is driven by entropy! At high packing densities, the ordering of the spheres onto a regular lattice gives each sphere greater room for positional fluctuations than would be the case for random packing at the same density, thus more than compensating for the entropic cost of the ordering.

# Packing – Configurational vs. Translational Entropy
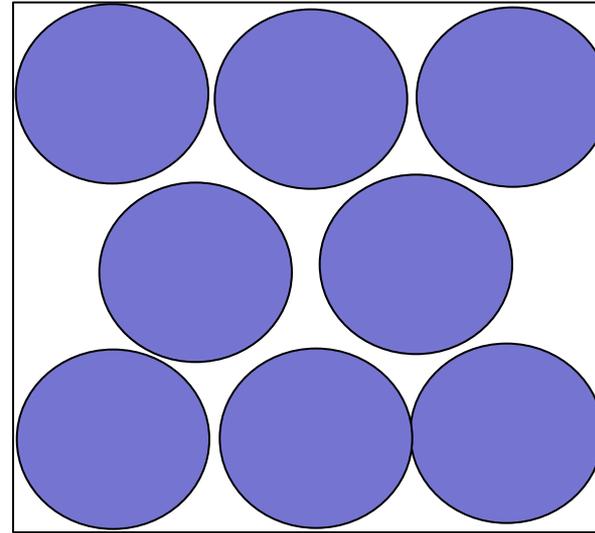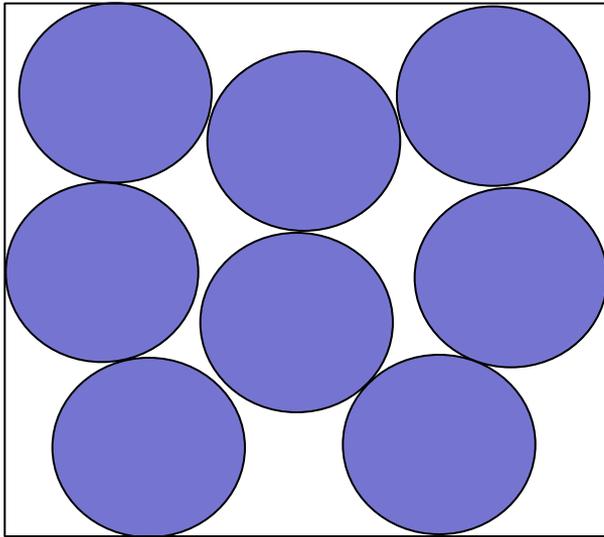
Which one looks more crowded?

Hard Sphere Phase Diagram
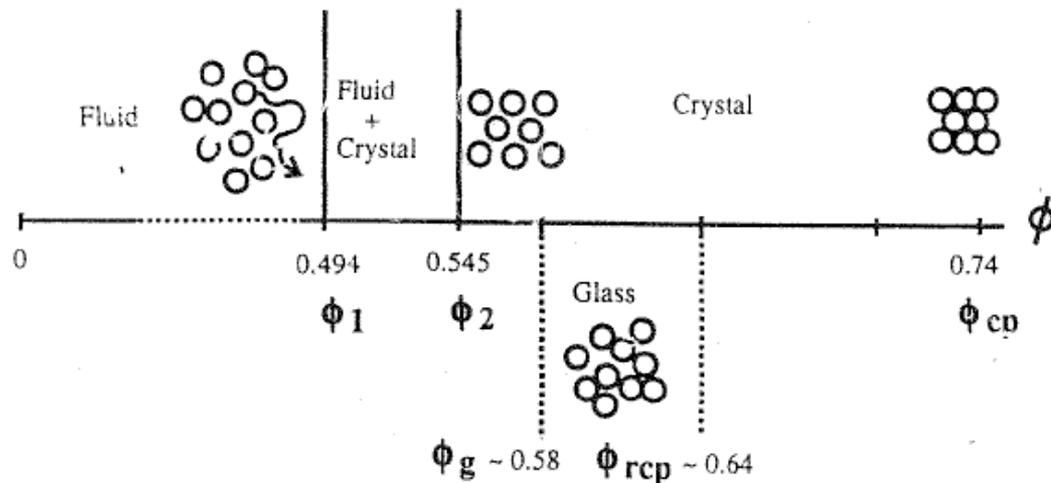
- In the volume-fraction range 0.494 = φ1 < φ <φ2 = 0.545, the disordered phase and the colloidal crystalline phase coexist. The colloidal crystalline phase can theoretically persist from 2 up to the concentration at the HCP limit, cp = 0.7405; this is the highest volume fraction that respects the hard-core diameter of the spheres.

Hard Sphere Phase Diagram
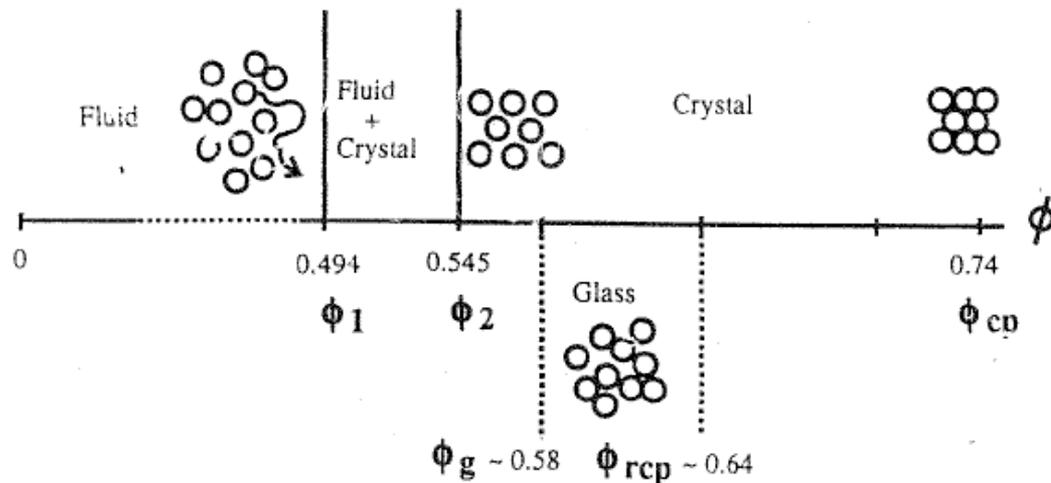
- In addition to these equilibrium phases, there is a metastable glassy disordered state that can exist at volume fractions above about 0.56. This phase exists because at such high densities the long-range Brownian motions of the spheres are suppressed by the crowding or "caging" effect of neighboring spheres, and critical nuclei needed to induce crystallization cannot form. Thus, if the concentration of spheres can be increased quickly enough (say, by centrifugation) so that the concentration regime where crystallization occurs is bypassed, one obtains a colloidal glass.

Hard Sphere Phase Diagram
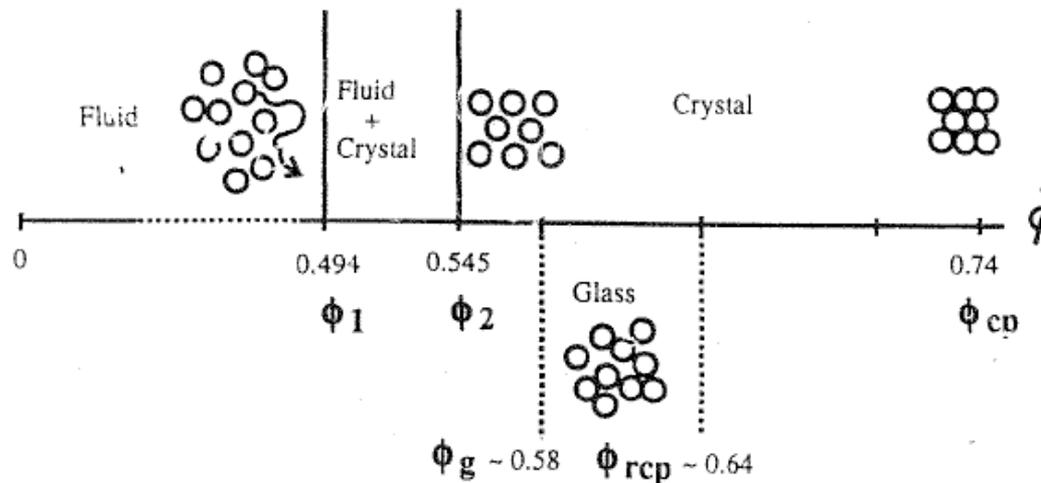
- The most densely packed state of a glassy suspension of hard spheres is "random close packing," for which φ = 0.64. This concentration is 86% that of ordered close packing.

- This difference in maximum packing between the ordered and disordered states shows that the ordered state has more "free volume" than the disordered one, and it is the difference in entropy associated with this free volume that drives the ordering transition.

Hard Sphere Phase Diagram
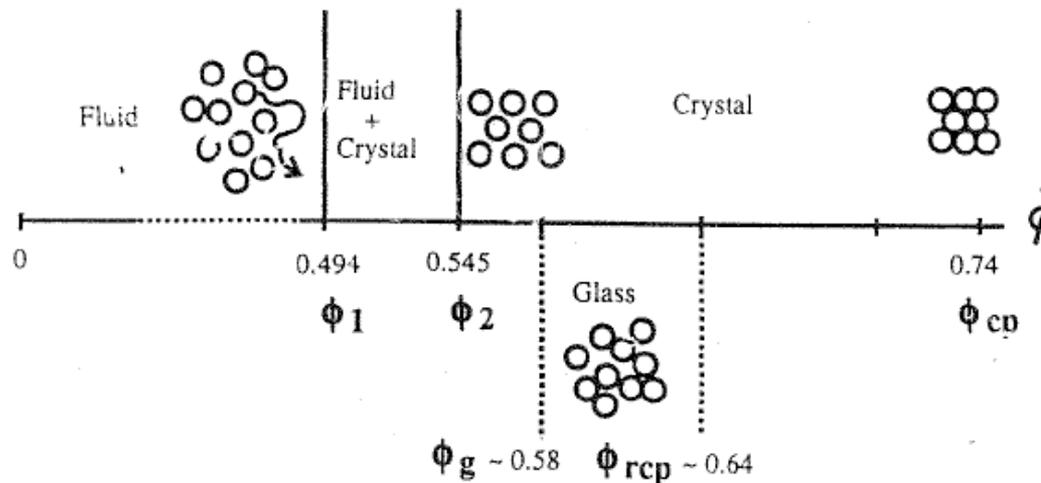
- The most densely packed state of a glassy suspension of hard spheres is "random close packing," for which φ = 0.64. This concentration is 86% that of ordered close packing.

- Interestingly, the density of liquids composed of spherical molecules or atoms at their melting point is also typically about 86% as high as the density of the crystal at 0 K.

Hard Sphere Phase Diagram

- Even in the liquid state, with $\phi < \phi_1 = 0.49$, local order is not entirely absent. Liquid-state packing of hard spherical objects leads to correlations in molecular positions. For example, a hard spherical molecule in the liquid state is surrounded by, and is in near contact with, on average about nine nearest neighbors.

- The positional correlations that exist between pairs of molecules are described by the radial distribution function, g(r).

- g(r) is proportional to the probability of finding the center of mass of a second molecule a distance r away from the center of mass of a given central molecule.

https://en.wikipedia.org/wiki/Radial_distribution_function
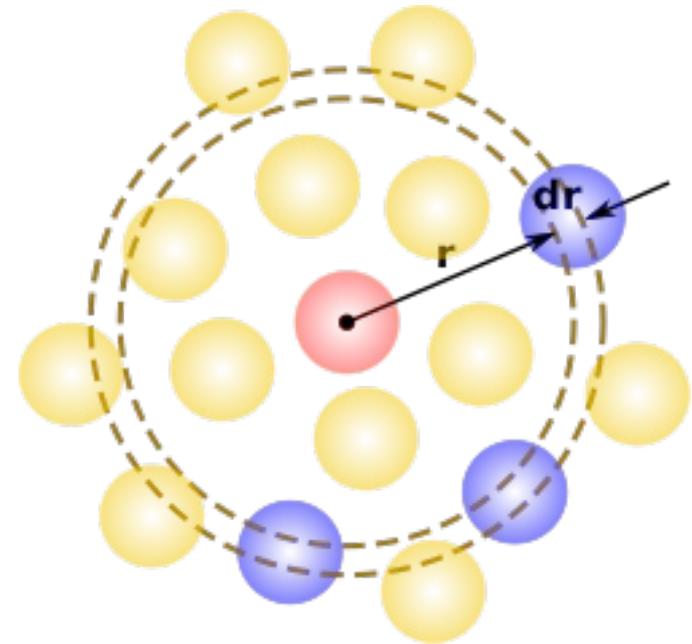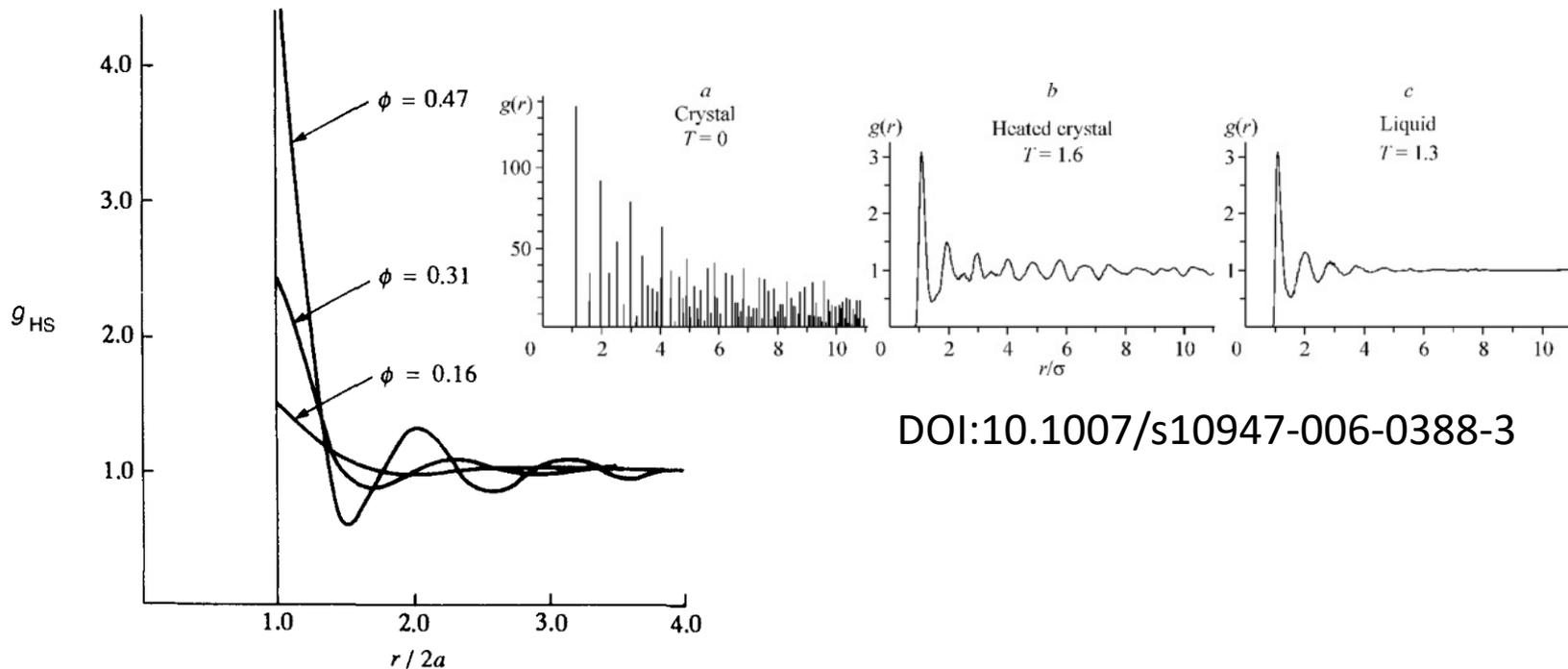
Figure 2.3. Radial distribution function $g_{HS}(r)$ for suspensions of hard spheres in the disordered state at various volume fractions ϕ, calculated from the Percus–Yevick equation. (From Russel et al. 1989, with permission of Cambridge University Press.)

- The normalization is chosen so that g(r) = 1 for molecules with no positional correlation.

- Note that the largest peak is at nearest-neighbor contact, where r/2a = 1. At high concentrations (ϕ >= 0.4), there are smaller peaks at next-neighbor packing "shells" located roughly at r/2a ≈ 2, 3, and so on. In the colloidal crystal state (> 0.545), these peaks become infinitely sharp and repeat out to infinite distances.

Structure factor

- In the general case in which the phase might (or might not) have positional order, one can define an anisotropic pair correlation function, g(**x**), where **x** is a position vector relative to a given molecule. The Fourier transform of the pair correlation function, namely,

$$S(\mathbf{k}) \equiv \int g(\mathbf{x}) \exp(i\mathbf{k} \cdot \mathbf{x})\, d\mathbf{x} \equiv \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} g(\mathbf{x}) \exp(i\mathbf{k} \cdot \mathbf{x})\, dx_1\, dx_2\, dx_3$$

- is called the structure factor with **k** the wave vector.
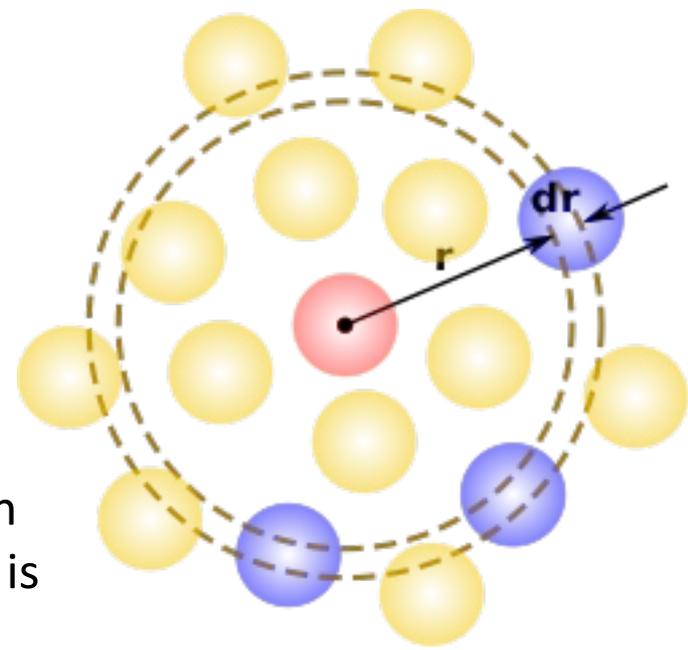
https://en.wikipedia.org/wiki/Radial_distribution_function

Osmotic pressure is the minimum pressure which needs to be applied to a solution to prevent the inward flow of its pure solvent across a semipermeable membrane.

Osmotic Pressure

Membrane allows water, but not particles, to pass through

Let A_{tot} be the total free energy, consisting of solution with volume V and pure solvent of volume $V_{tot} - V$

Remember: $dA = -SdT - pdV$
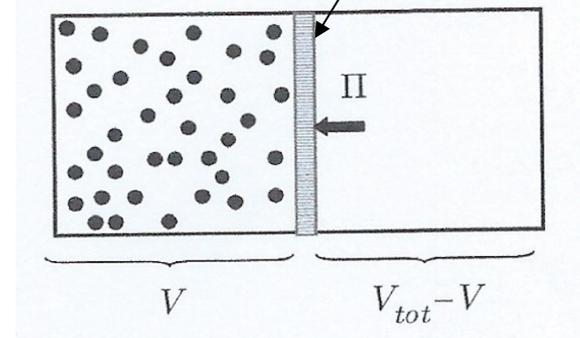
Doi, Soft Matter Physics, 2013

Recall Macroscopic Thermodynamics

For systems whose natural variables are T and V (volume),

Internal energy

Helmholtz free energy: $A \equiv U - TS$ ← entropy

$$(dA \equiv dU - SdT - TdS)$$

First Law of Thermodynamics: $dU = TdS - pdV$

heat flow   work

These two imply: $dA = -SdT - pdV$

multi-component system: $G \equiv$ Gibbs free energy

$$\mu_j \equiv \left(\frac{\partial G}{\partial N_i}\right)_{T,p,N_k,k \neq j}$$

$$dA = -SdT - pdV + \sum_j \mu_j dN_j \qquad \mu_j = \text{chemical potential of j}$$

Gibbs free energy: $G \equiv H - TS$ enthalpy: $H \equiv U + pV$

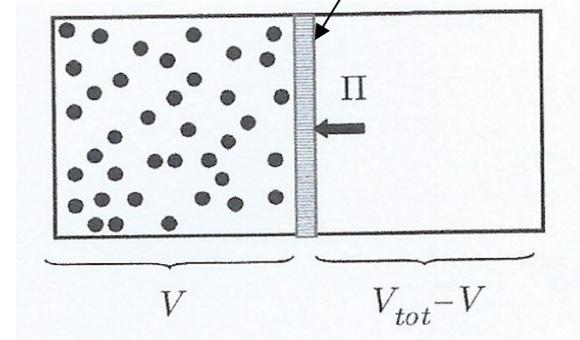$$G \equiv U - TS + pV = A + pV$$

More detail: McQuarrie: Statistical Mechanics, Doi: Soft Matter Physics"

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Doi, Soft Matter Physics, 2013

The work done by semi-permeable membrane is $-\Pi dV$

This must be equal to change in free energy dA_{tot}

Thus, $\Pi = -\dfrac{\partial A_{tot}(V)}{\partial V}$

$f(\phi) \equiv \dfrac{free\ energy}{vol}$ of uniform soln w/ vol. fraction ϕ

$A_{tot} = Vf(\phi) + (V_{tot} - V)f(0)$

Note that $\phi = \dfrac{V_{solute}}{V} = \dfrac{Nz}{V}$

So that $\dfrac{\partial f(\frac{V_{solute}}{V})}{\partial V} = -f' \dfrac{V_{solute}}{V^2} = -f' \dfrac{\phi}{V}$

So $\boxed{\Pi = -f(\phi) + \phi f'(\phi) + f(0)}$ Chain rule

Dilute Solution Expansion

lowest order term: $\quad \Pi = \dfrac{N k_B T}{V} = v k_B T = \dfrac{\phi k_B T}{z}$

N = number of particles in V

(van't Hoff's law, analogous to ideal gas law)

z = vol. of solute

$\phi = \dfrac{V_{solute}}{V} = \dfrac{Nz}{V}$

Osmotic pressure is the minimum pressure which needs to be applied to a solution to prevent the inward flow of its pure solvent across a semipermeable membrane.

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Doi, Soft Matter Physics, 2013

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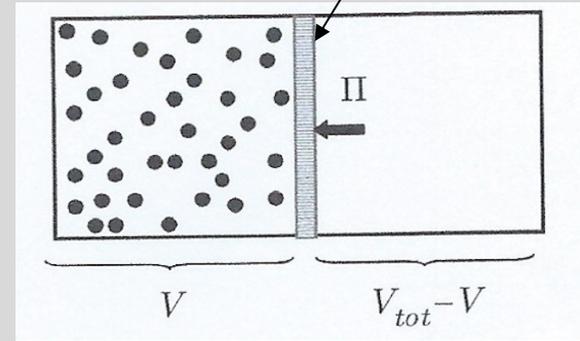
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So $\boxed{\Pi = -f(\phi) + \phi f'(\phi) + f(0)}$ Chain rule

Recall for Non-Interacting Particles

Helmholtz free energy of purely entropic system: $A = -TS$

$$A = -k_B T \, lnQ \qquad Q = \text{partition function}$$

overlapping (phantom) particles: $\qquad E_j = 0$, for every state j

$$Q = total \; number \; of \; unique \; states = \frac{V^N}{N! \Lambda^{3N}}$$

V = system volume, Λ = lattice spacing (or "deBroglie wavelength)"

V/Λ^3 = number of positions at which a particle can be placed

$$A/k_B T = -lnQ \qquad = -NlnV + \ln(N!) + const \quad \text{(const. involves } \Lambda \text{)}$$

Stirling's approx: $\quad \ln(N!) \approx NlnN - N \quad \approx NlnN \quad$ *(N* large)

$$A/k_B T \;\; = -S/k_B \; = Nln\left(\frac{N}{V}\right) = Nln(v) + const$$

$v = N/V =$ number density

$$A/(Vk_B T) \approx vln(v) + const$$

Pressure $P = vk_B T$

Dilute Solution Expansion

lowest order term: $\Pi = \dfrac{N k_B T}{V} = v k_B T = \dfrac{\phi k_B T}{z}$

N = number of particles in V
(van't Hoff's law, analogous to ideal gas law)

z = vol. of solute

$\phi = \dfrac{V_{solute}}{V} = \dfrac{Nz}{V}$

Derivation:

$$A/k_B T \approx N ln\left(\dfrac{N}{V}\right)$$

$$A \approx N k_B T ln\left(\dfrac{N}{V}\right)$$

$$\Pi = -\dfrac{\partial A_{tot}(V)}{\partial V} \approx -\dfrac{\partial A(V)}{\partial V} + f(0) \approx N k_B T \dfrac{1}{V} + 0 = v k_B T$$

Dilute Solution Expansion

lowest order term: $\quad \Pi = \dfrac{N k_B T}{V} = v k_B T = \dfrac{\phi k_B T}{z}$

N = number of particles in V

(van't Hoff's law, analogous to ideal gas law)

z = vol. of solute

$\phi = \dfrac{V_{solute}}{V} = \dfrac{Nz}{V}$

higher order
expansion: $\quad \Pi = \dfrac{\phi k_B T}{z} + A_2 \phi^2 + A_3 \phi^3 + \ldots.$

A_2, A_3 = 2nd and 3rd *virial coefficients*

Derivation:

$$A/k_B T \approx N ln\left(\dfrac{N}{V}\right)$$

$$A \approx N k_B T ln\left(\dfrac{N}{V}\right)$$

$$\Pi = -\dfrac{\partial A_{tot}(V)}{\partial V} \approx -\dfrac{\partial A(V)}{\partial V} + f(0) \approx N k_B T \dfrac{1}{V} + 0 = v k_B T$$
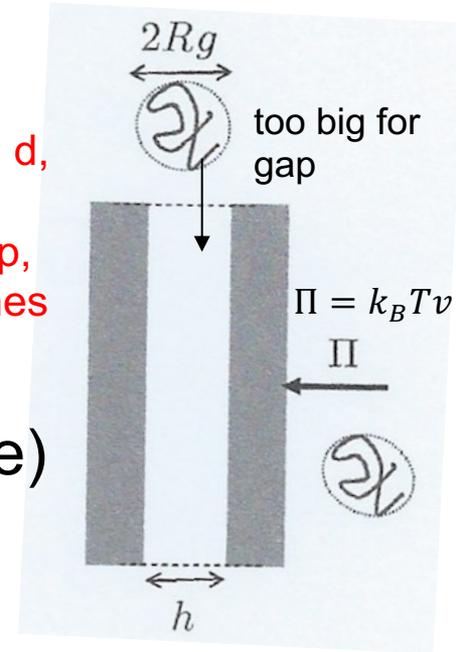
Depletion Potential

$$A/k_BT = -lnQ \quad = -NlnV + \ln(N!) + const$$

d $= 2R_g =$ depletant diameter

when h> d, particles enter gap, Π vanishes

$Area$
(of plate)

2Rg

too big for gap

$\Pi = k_BTv$

Π

h

Recall for Non-Interacting Particles

Helmholtz free energy of purely entropic system: $A = -TS$

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$$A/k_B T \;= -S/k_B = Nln\left(\frac{N}{V}\right) = Nln(v) + const \qquad v = N/V =$$
number density

$$A/(Vk_B T) \approx vln(v) + const$$

Pressure $P = vk_B T$

Depletion Potential

$d = 2R_g =$ depletant diameter

$$A/k_BT = -lnQ = -NlnV + \ln(N!) + const$$

if the number N of small depletant particles is fixed, but the volume V available to them is changed because of re-arrangement of the two surfaces, this will produce a force F given by
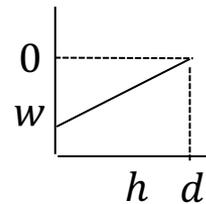
when h> d, particles enter gap, Π vanishes

too big for gap

$\Pi = k_BTv$

Π

Area (of plate)

$$N = vV \qquad F = -\partial A/\partial h = -k_BTN\frac{\partial(lnV)}{\partial h}$$

$$= -k_BTvV\frac{1}{V}\frac{\partial(V)}{\partial h} = -k_BTv\frac{\partial V}{\partial h} = \Pi\frac{\partial V}{\partial h}$$

Doi, Soft Matter Physics, 2013

Π = osmotic pressure for dilute particles

potential/area for flat plate:

$$k_BTv(Area)$$

$$Note: \frac{\partial V}{\partial h} = Area$$

$$w(h) = -\frac{1}{Area}\int_h^d F(x)dx$$

$$w(h) = vk_BT(h-d), \text{for } h < d,$$
$$= 0, \text{ for } h > d$$

Curved surfaces & Thin Gaps: Derjaguin Approximation
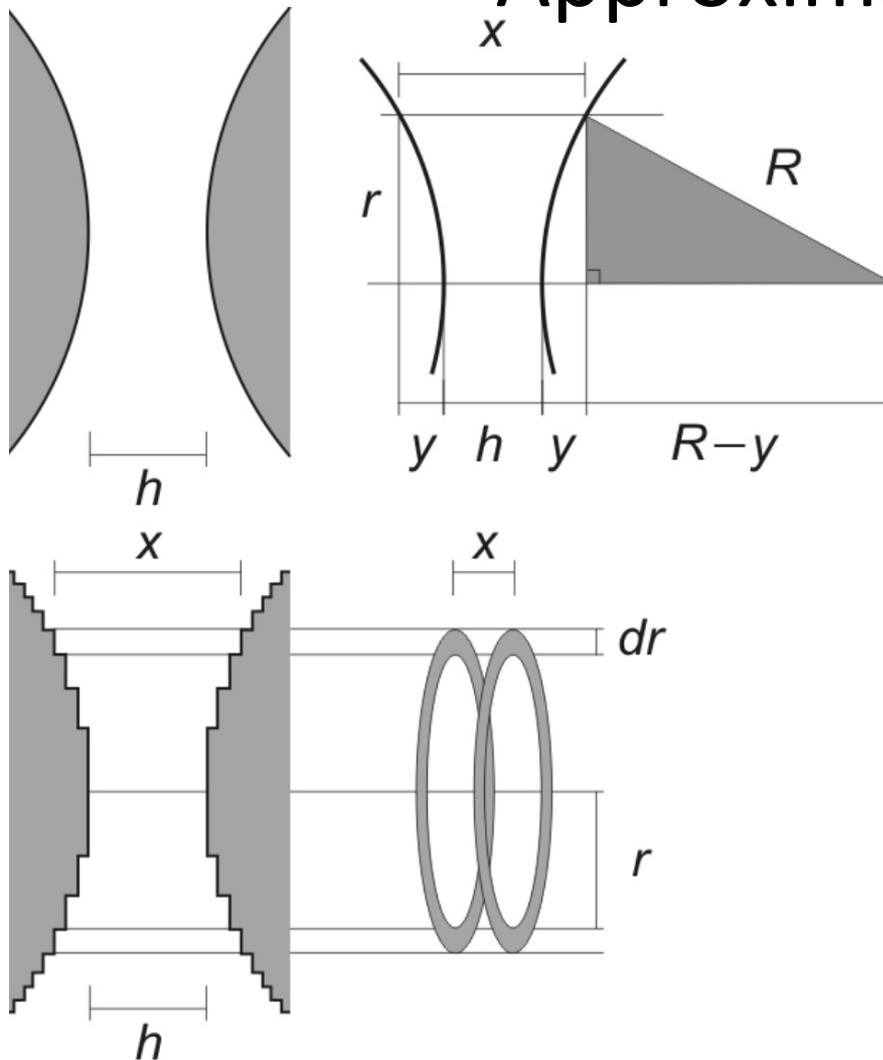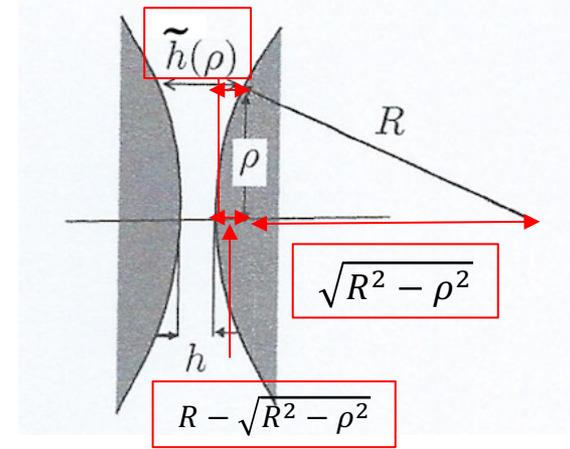

Treat a thin region of variable gap as a series of small regions with parallel flat surfaces, with each region having a different gap

Derjaguin Approximation for Two Spheres

$$\tilde{h}(\rho) = h + 2\left(R - \sqrt{R^2 - \rho^2}\right) \approx h + \frac{\rho^2}{R}$$

$$\sqrt{R^2 - \rho^2} = R\sqrt{1 - \rho^2/R^2} \approx R(1 + \rho^2/2R^2)$$

At position ρ, take a ring of width $d\rho$, with area $2\pi\rho d\rho$

If we have a potential *per unit area w(h)* between flat surfaces, then the potential *U(h)* between spheres is

$$U(h) = \int_0^R w(\tilde{h})2\pi\rho d\rho \qquad \text{new variable:} \quad x \equiv h + \frac{\rho^2}{R} = \tilde{h}$$

$$dx = 2\rho d\rho/R$$

$$U(h) \approx \pi R \int_h^\infty w(x)dx \qquad F(h) = -\frac{\partial U(h)}{\partial h} = \pi R w(h)$$
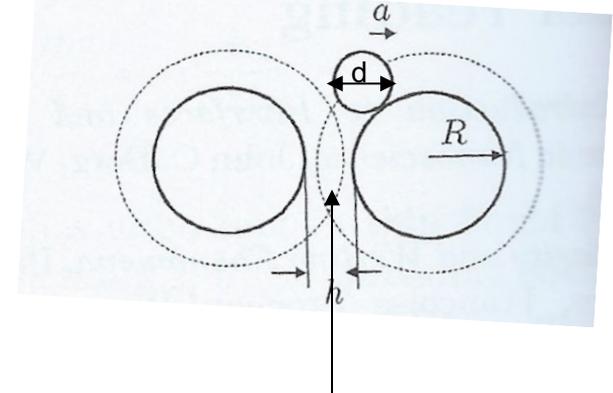
Note: if spheres have unequal radii:
$$U(h) = 2\pi\frac{R_1 R_2}{R_1 + R_2}\int_h^\infty w(x)dx$$

Depletion Potential for spheres

$v = concentration\ of\ depletant$

for flat plate: $w(h) = v k_B T(h - d), \text{for } h < d,$
$$= 0, \ \text{for } h > d$$

Doi, Soft Matter Physics, 2013

for spheres, replace h with $\tilde{h}(x)$

$$w(h) = v k_B T\big(\tilde{h}(x) - d\big), \text{for } \tilde{h}(x) < d,$$
$$= 0, \ \text{for } \tilde{h}(x) > d$$

overlapping
depletion region

for two spheres: $U(h) = \pi R \displaystyle\int_h^\infty w(x)\,dx$
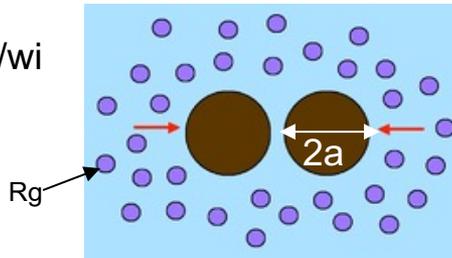
remember, $x \equiv h + \dfrac{\rho^2}{R} = \tilde{h}$

$$U(h) = v k_B T \pi R \underbrace{\int_h^d (x - d)\, dx}_{} \qquad = -\frac{1}{2} v k_B T \pi R (d - h)^2$$

volume of overlapping
depletion regions

Equilibrium phase behaviour of *isotropic* spheres
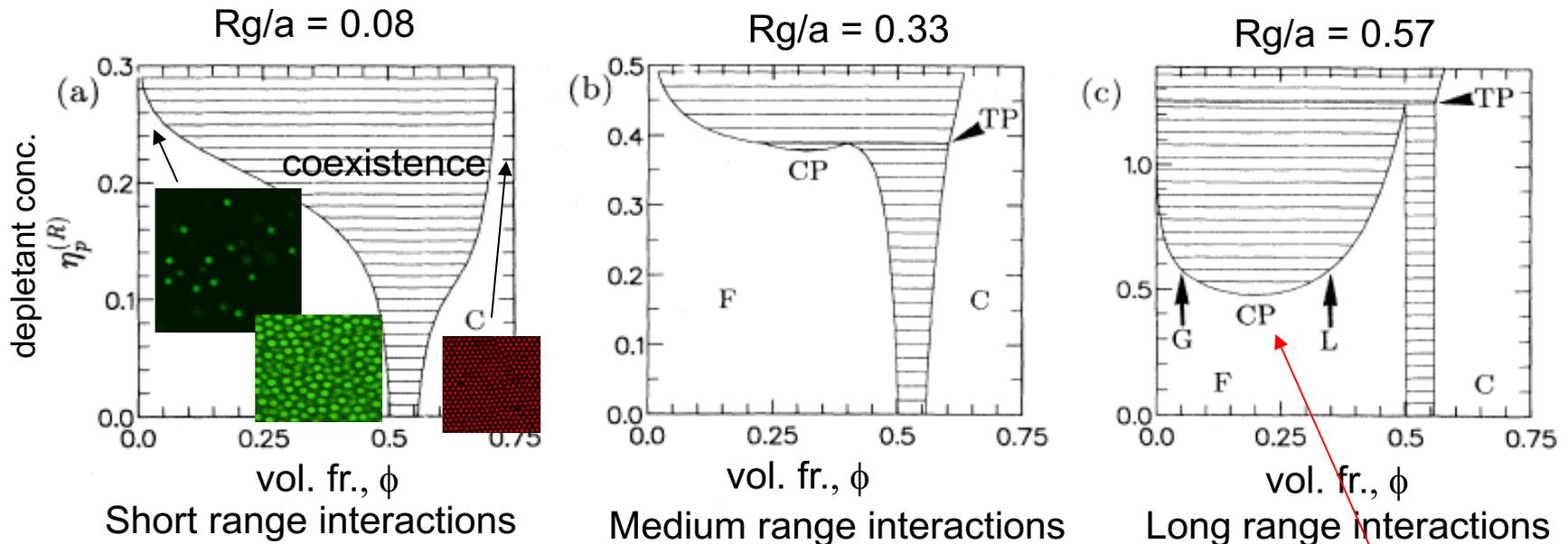
http://en.wikipedia.org/wiki/Depletion_force

Increasing attraction
(increasing depletant concentration)

Rg

2a

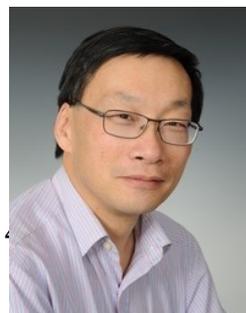Depletion interaction;
a = radius of large sphere
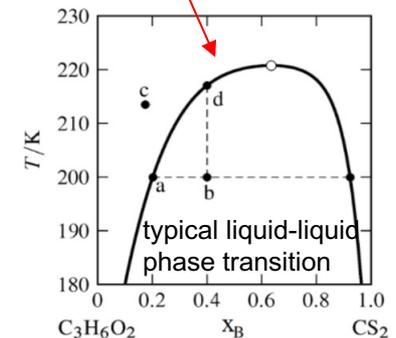Rg = radius of small sphere or polymer *depletant*

1346   S. M. ILETT, A. ORROCK, W. C. K. POON, AND P. N. PUSEY

Rg/a = 0.08

(a)

coexistence

depletant conc. $\eta_p^{(R)}$

vol. fr., ϕ
Short range interactions

Rg/a = 0.33

(b)   TP

CP

F   C

vol. fr., ϕ
Medium range interactions

Rg/a = 0.57

(c)   TP

G   CP   L

F   C

vol. fr., ϕ
Long range interactions

Illet, Orrock, Poon, and Pusey, Phys Rev E 51:1344 (1995)

depletant conc. acts as inverse temp.

typical liquid-liquid phase transition

T/K

$C_3H_6O_2$ x_B CS_2

Review on liquid-liquid phase transition

IMF = intermolecular forces

Liquid-Liquid Mixtures

$$\Delta_{mix}G_m = x_ART\ln x_A + x_BRT\ln x_B + \xi RT x_A x_B$$

- If the IMF's are net repulsive between A and B, ξ will increase.

- Once ξ is greater than 2, then two minima will emerge.

- As a result, two contaminated phases will form.
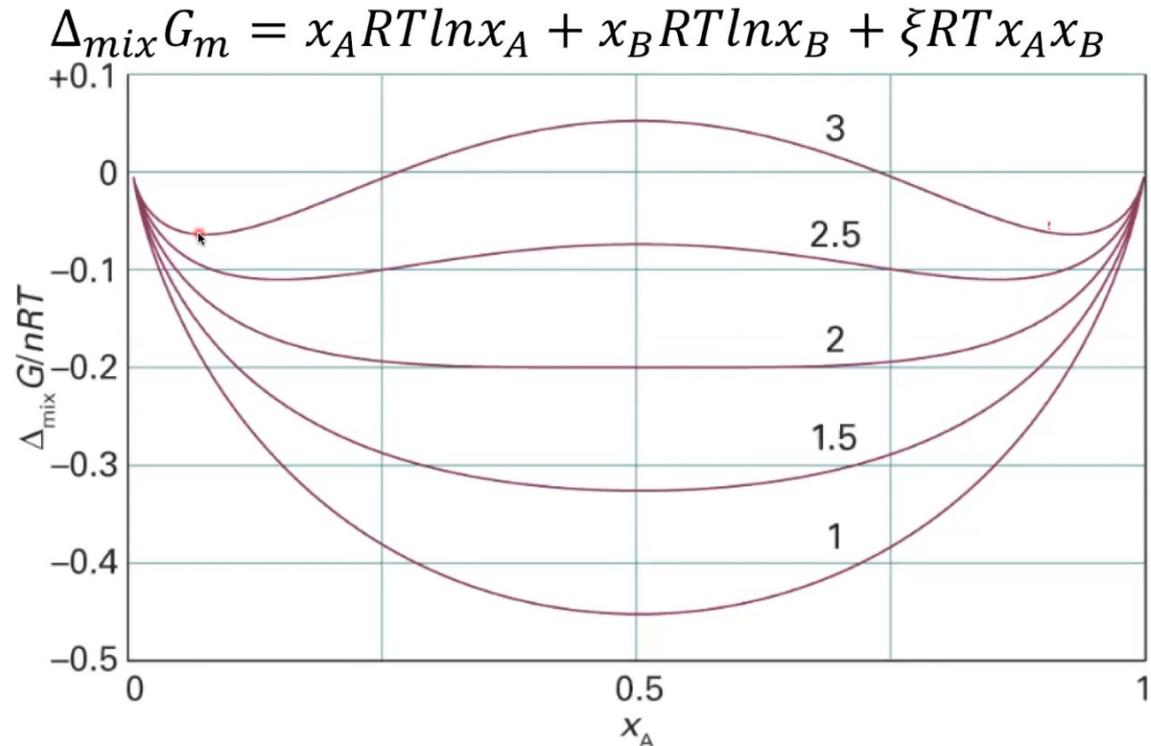
Review on liquid-liquid phase transition

Liquid-Liquid Phase Diagrams

- Using $\Delta_{mix}G_m$, a liquid-liquid phase diagram can be generated.

- This diagram will tell you below which temps the solution will separate(T_{UC}).

- It can also tell you the composition of the resulting phases.
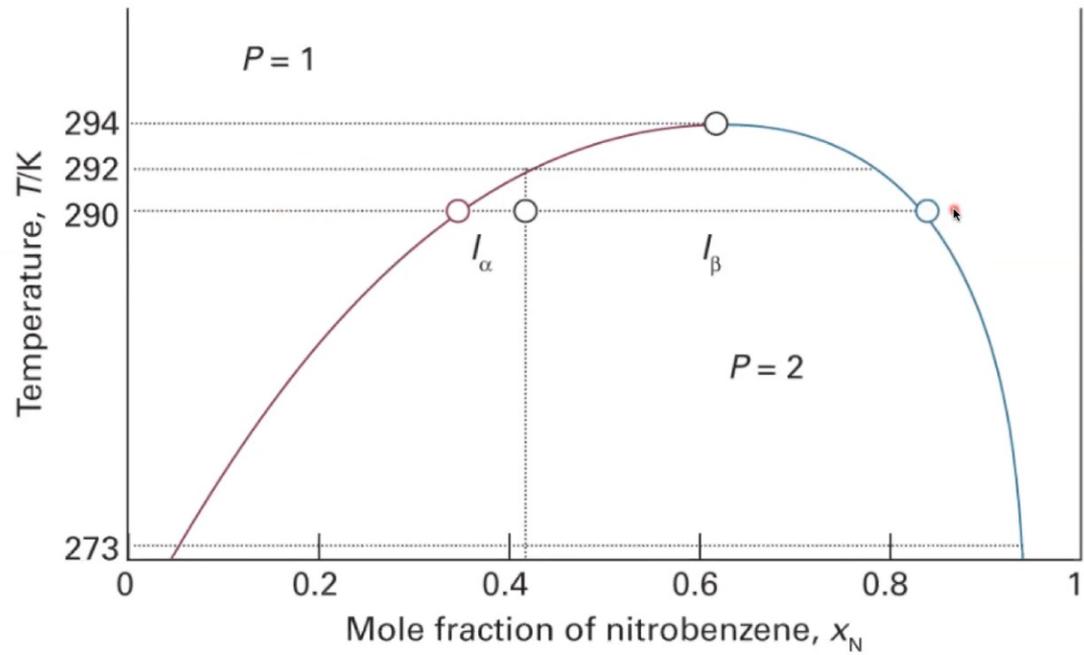
Review on liquid-liquid phase transition

Liquid-Liquid Phase Minima

For a regular solution, the phase separation can be predicted using:

$$\Delta G_{mix} = nRT(x_A \ln x_A + x_B \ln x_B + \xi x_A x_B)$$

As system will phase separate if there are more than one minimum value for ΔG_{mix}
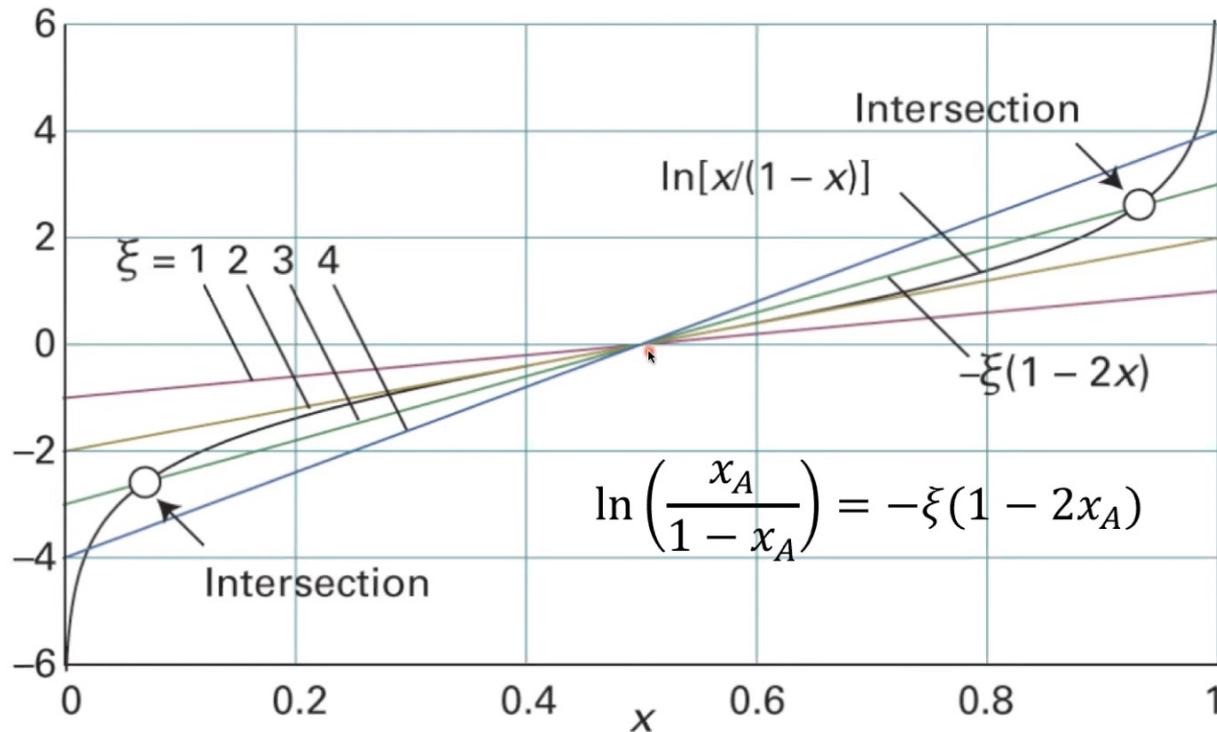
These minima can be predicted by setting: $\dfrac{\partial \Delta G_{mix}}{\partial x_A} = 0$

These yield an equation of:

$$\ln\left(\frac{x_A}{1 - x_A}\right) = -\xi(1 - 2x_A)$$
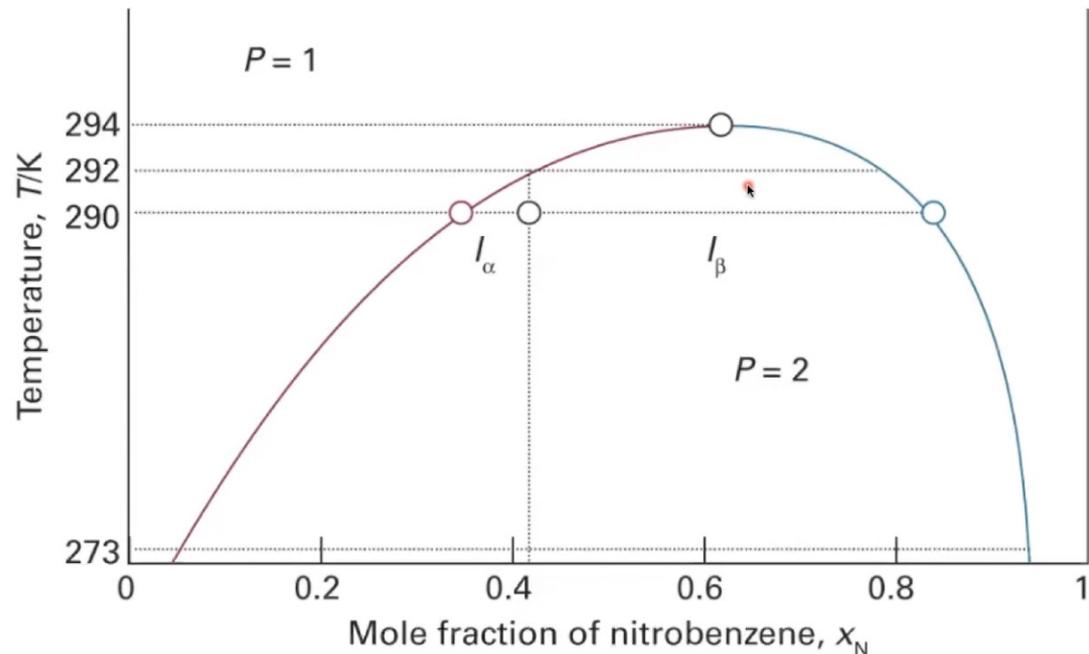
Graphical solution

Liquid-Liquid Phase Minima

$$\ln\left(\frac{x_A}{1-x_A}\right) = -\xi(1-2x_A)$$

Review on liquid-liquid phase transition
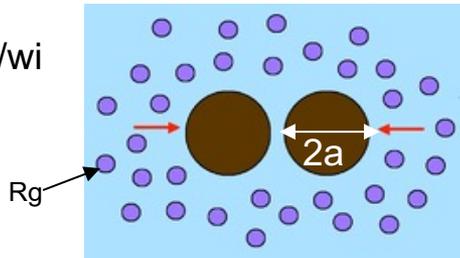
Liquid-Liquid Phase Diagrams

- The nature of ξ will change with temperature.

- Many liquid mixtures possess an upper critical temperature (T_{UC}), below which the IMF's between the components are significantly dissimilar.

Equilibrium phase behaviour of *isotropic* spheres

http://en.wikipedia.org/wiki/Depletion_force

Increasing attraction
(increasing depletant concentration)

Depletion interaction;
a = radius of large sphere
Rg = radius of small sphere or polymer *depletant*

Rg/a = 0.08   Rg/a = 0.33   Rg/a = 0.57

depletant conc. $\eta_p^{(R)}$

coexistence

vol. fr., ϕ
Short range interactions

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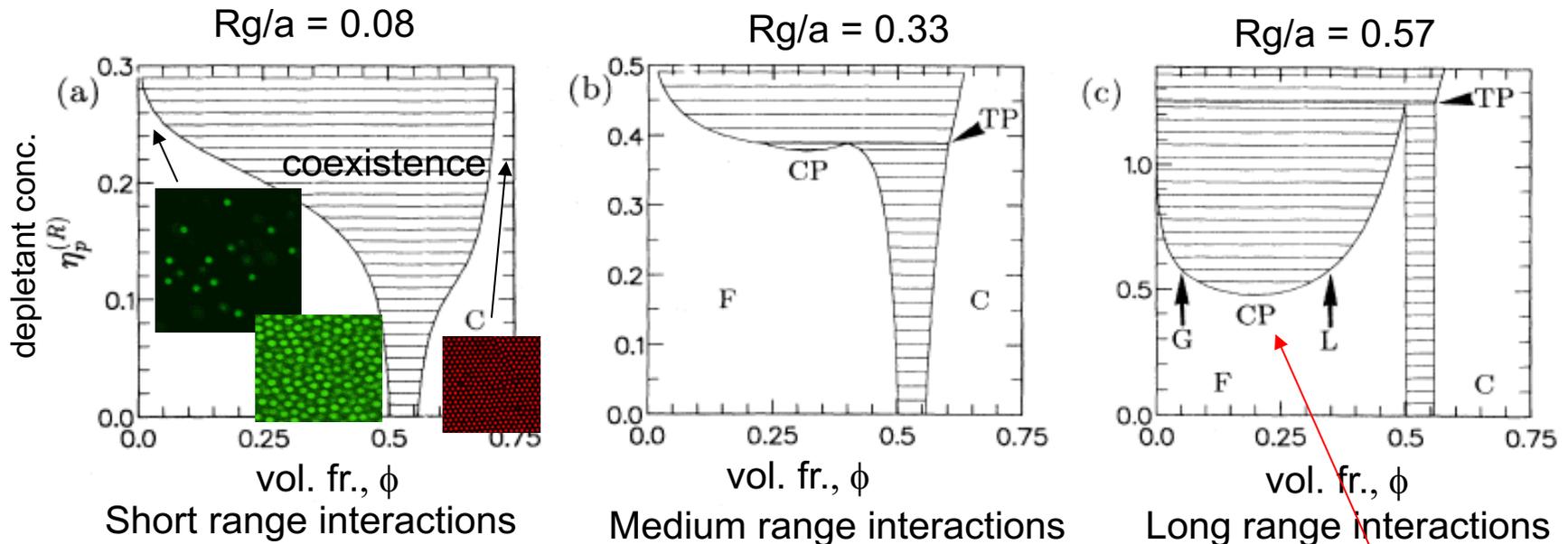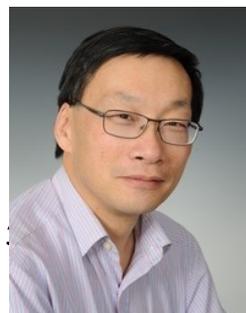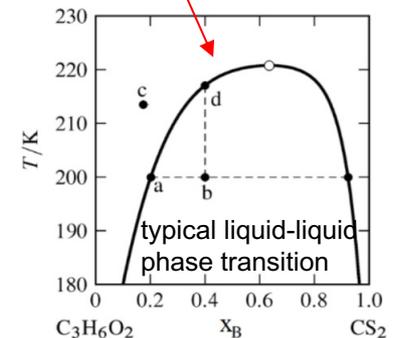
Rigid Nonspherical Particles: The Nematic Phase

- For molecules that are not spherical, packing and ordering transitions can occur that are more complex than those for spherical molecules.

- the simplest nonspherical shape is a stiff, long cylinder
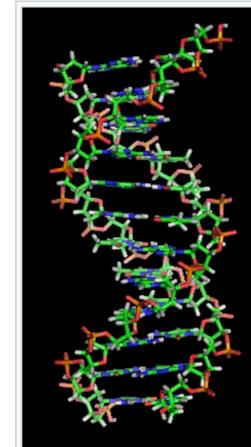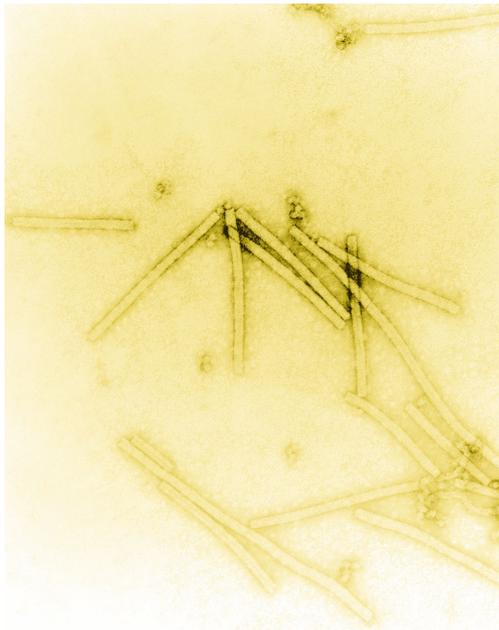
Transmission electron micrograph of TMV particles negative stained to enhance visibility at 160,000× magnification

Rod-Like Objects

tobacco mosaic virus

L= 300 nm long, d=18 nm wide

Diffusivity:

$$D = \frac{k_B T}{3\pi \mu_B L}\left(\ln\left(\frac{L}{d}\right) + 0.3\right)$$

Lecture 5 Poll: Cylinder Packing

Consider only excluded volume effects, how should we expect the closest packing of cylindrical rods be compared to the HCP limit (~0.74) of hard spheres?

- A. higher
- B. the same
- C. lower

Long URL   https://forms.gle/y4xy3HsbFV6npW956

Short URL   https://shorturl.at/gkGR7

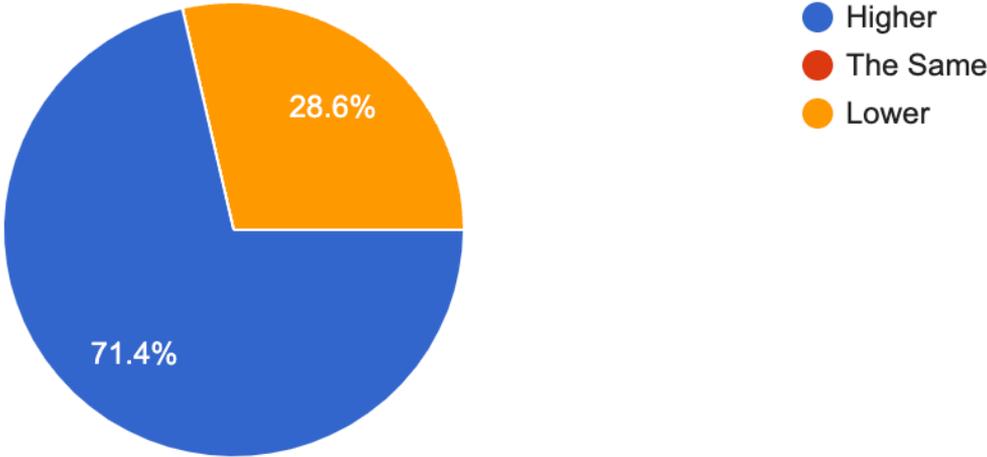Consider only excluded volume effects, how should we expect the closest packing of cylindrical rods be compared to the HCP limit (~0.74) of hard spheres?

14 responses

Higher
The Same
Lower

28.6%

71.4%

In the two-dimensional Euclidean plane, Joseph Louis Lagrange proved in 1773 that the highest-density lattice packing of circles is the hexagonal packing arrangement,[1] in which the centres of the circles are arranged in a hexagonal lattice (staggered rows, like a honeycomb), and each circle is surrounded by six other circles. For circles of diameter D and hexagons of side length D, the hexagon area and the circle area are, respectively:

$$A_{\text{H}} = \frac{3\sqrt{3}}{2} D^2$$

$$A_{\text{C}} = \frac{\pi}{4} D^2$$

The area covered within each hexagon by circles is:

$$A_{\text{HC}} = 3 A_{\text{C}} = \frac{3\pi}{4} D^2$$

Finally, the packing density is:

$$\eta = \frac{A_{\text{HC}}}{A_{\text{H}}} = \frac{\frac{3\pi}{4} D^2}{\frac{3\sqrt{3}}{2} D^2}$$

$$= \frac{\pi}{2\sqrt{3}} \approx 0.9069$$
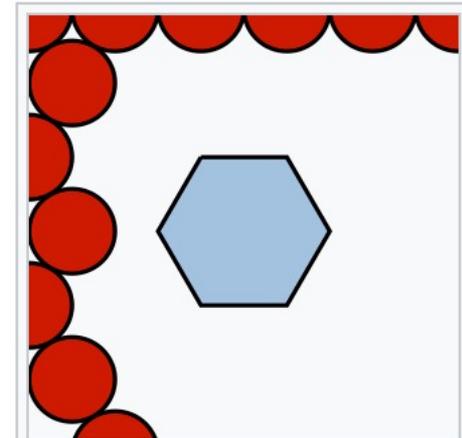
Identical circles in a *hexagonal packing* arrangement, the densest packing possible

Hexagonal packing through natural arrangement of equal circles with transitions to an irregular arrangement of unequal circles

Packing of Cylinders

- The closest packing of cylindrical rods occurs when they are parallel to each other and packed hexagonally in the plane orthogonal to their axes; in this case, $\phi = 0.9069$.

- If the density of long ordered rods is decreased, a melting transition will occur in which the in-plane hexagonal order is lost, but the orientational order of the rod axes is partially preserved.

- This partially ordered state is called a nematic. States with partial order, including the nematic state, are common for stiff molecules of high aspect ratio.

Literature presentations for Lecture 5

Soft matter*

P. G. de Gennes

Ecole Supérieure de Physique et de Chimie Industrielles de la Ville de Paris, 10 rue Vauquelin, 75231 Paris Cedex 05, France

What do we mean by soft matter? Americans prefer to call it "complex fluids," and this does indeed bring in two of the major features:

(1) Complexity. We may, in a certain primitive sense, say that modern biology has proceeded from studies on

tive sites at both ends of the space was: what is the minimum length o It turns out that the answer is r (de Gennes, 1969). The magic num Below 14 units, you will not usua the desired conformation. Above 1

Anisotropy of building blocks and their assembly into complex structures

A revolution in novel nanoparticles and colloidal building blocks has been enabled by recent breakthroughs in particle synthesis. These new particles are poised to become the 'atoms' and 'molecules' of tomorrow's materials if they can be successfully assembled into useful structures. Here, we discuss the recent progress made in the synthesis of nanocrystals and colloidal particles and draw analogies between these new particulate building blocks and better-studied molecules and supramolecular objects. We argue for a conceptual framework for these new building blocks based on anisotropy attributes and discuss the prognosis for future progress in exploiting anisotropy for materials design and assembly.

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AND MICHAEL J. SOLOMON[1]*
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[2]Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109-2136, USA
*e-mail: sglotzer@umich.edu; mjsolo@umich.edu

and deposition[9–12]. Physical methods developed include electrified jetting, microcontact printing, emulsion drying, selective deposition, surface templating, direct writing and lithography[13–20]. Biologically inspired methods include the use of plant extracts[21], fungi[22] and viruses[23] to synthesize metal nanoparticles of various shapes. These methods draw from the diverse fields of chemistry, physics, biology, engineering and materials science, and, in combination, provide a powerful arsenal for the fabrication of new

RESEARCH

REVIEW SUMMARY

NANOPARTICLES

Nonadditivity of nanoparticle interactions

Carlos A. Silvera Batista, Ronald G. Larson,* Nicholas A. Kotov*

Perspective

Beyond molecules: Self-assembly of mesoscopic and macroscopic components

George M. Whitesides* and Mila Boncheva

Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138

Self-assembly is a process in which components, either separate or linked, spontaneously form ordered aggregates. Self-assembly can occur with components having sizes from the molecular to the macroscopic, provided that appropriate conditions are met. Although much of the work in self-assembly has focused on molecular components, many of the most interesting applications of self-assembling processes can be found at larger sizes (nanometers to micrometers). These larger systems also offer a level of control over the characteristics of the components and over the interactions among them that makes fundamental investigations especially tractable.

Literature and youtube presentations for Lecture 5

- Random group assignments
- https://docs.google.com/spreadsheets/d/1EWhNBhl2nLaJGBrVEoSe4y0x5w41fPwD1HhYuJGUd9Y/edit#gid=267969935

Student	2/6	2/13	2/20	3/5	3/12	3/19	3/26	4/2	4/9	4/16
	A	A	A	D	A	A	B	C	D	A
Mitchell Godek	D	C	D	B	D	B	A	C	C	B
Jen Bradley	D	A	A	D	B	D	D	A	A	D
	B	D	D	C	B	A	C	D	D	C
Charlotte Zhao	D	D	B	B	A	C	A	B	A	A
	B	B	B	B	D	C	C	A	D	C
William Morgan	A	C	A	B	C	A	D	B	C	B
	B	C	C	C	B	B	B	D	A	D
Henry Thurber	A	D	C	A	D	D	A	B	C	A
	C	A	C	B	A	C	D	A	D	D
	C	D	B	A	C	A	B	D	A	B
Gabrielle Grey	A	A	D	C	B	D	A	D	D	C
Weiyuan Fan	D	B	D	D	C	B	B	B	B	D
Aham Lee	C	B	A	C	A	B	D	A	B	A
	C	C	B	D	C	D	C	C	C	C
Nathan Bryant	C	D	A	A	D	B	A	C	C	B
Nhayeon Lee	B	B	C	C	C	C	D	C	B	C
Nathan Irgang	B	C	B	A	A	C	B	D	B	D
Muchen Wang	A	B	C	A	D	D	C	A	A	A
Anna Klinger	D	A	D	D	B	A	C	B	B	B

Key
Video Presentation
First Paper Presentation
Second Paper Presentation

Week 3	
Group	**Paper Title**
A	P4_tetrahedral_diffusion_PNAS_15
B	P3_Weeks_Science
C	P1_Transition_Brownian_Motion_Nature_Physics
D	P2_Han_et_al_Science_Brownian_ellipsoid