

Hard and Interacting Sphere Suspensions. Theory versus Experiment: Do we need a theory? ¹

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What are colloids?

- ▶ Low limit size: when detailed knowledge of the internal degrees of freedom is not needed: 1 nm ;
- ▶ Upper limit size: particles should behave due to Brownian motion (Brownian displacement $\langle h \rangle$ in a gravity field g is \propto a particle diameter σ) :

$$\langle h \rangle \simeq \frac{T}{mg}, K_B \equiv 1; \frac{\pi g \rho \sigma^4}{6} = T$$

It gives $\sigma \simeq 1 \mu\text{m}$ (for a brick, $m = 1 \text{ kg}$, $\langle h \rangle \simeq 10^{-20} \text{ cm}$).

- ▶ In time domain, time to move \propto particle size

$$\tau \simeq \frac{\eta \sigma^3}{T}$$

yields for a $1 \mu\text{m}$ colloid in water $\tau \simeq 1 \text{ s}$ (for a brick it is about 10^7 years!).

Various colloidal suspensions:

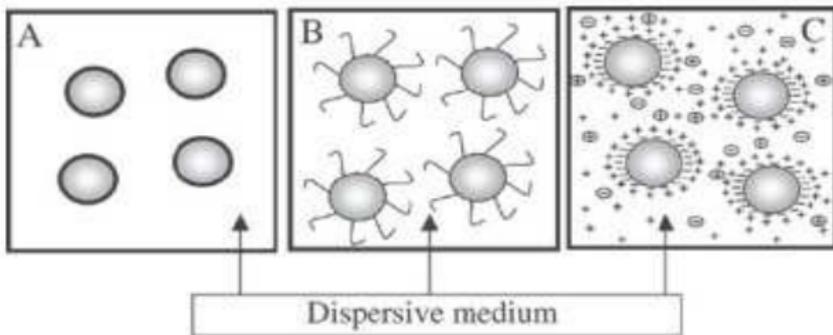


Figure: colloidal suspensions

For deionized suspensions of charged particles, the long-range order appears in extremely dilute dispersions, $\phi \simeq 0.005$, whereas for hard spheres it occurs at $\phi \simeq 0.5$.

PNIPAM shell of the Particles

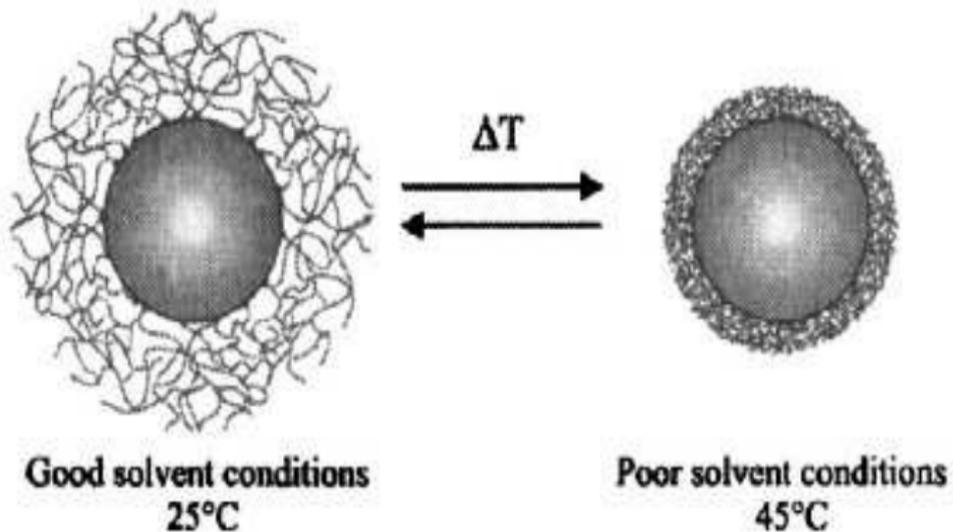


Figure: Temperature control of particle volume fraction.

PNIPAM has a volume transition in which the network in the shell expelling water. Thus the effective volume ϕ_{eff} can be adjusted through the temperature.

Phase Diagram of Hard Spheres

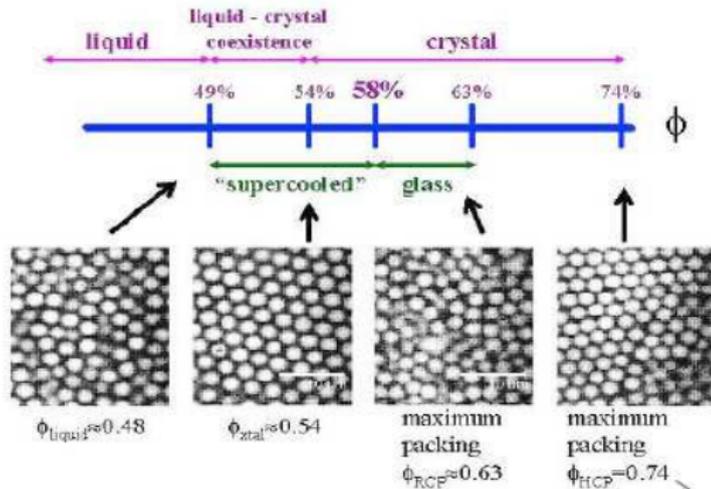


Figure: Phase Diagram of Hard Spheres.

- ▶ Other than ϕ control parameters: aspect ratio, polydispersity but not the size of the sphere.
- ▶ $\phi_{\text{HCP}} \equiv \pi/\sqrt{18}$.
- ▶ Delay prior to nucleation \propto to polydispersity.

Note of caution: ϕ_{RCP} is ill-defined:

- ▶ Experimentally and numerically ϕ_{RCP} is in a window from 0.60 to 0.68.
- ▶ Close packed implies that the spheres are in contact with one another with the highest possible coordination number on average. But increasing the degree of coordination, and thus, the bulk system density, comes at the expense of disorder. Thus, "random" and "close packed" are at odds with one another.
- ▶ Better defined notion is maximally random (or less ordered) jammed (MRJ), where a particle is jammed if it cannot be translated while fixing the positions of all of the other particles in the system (this eliminates "rattlers", particles without any contacts!).
- ▶ MRJ state to be the one that minimizes order parameter (e.g., scalar crystalline and bond orientational) among all jammed structures.

ϕ_{RCP} and average kissing number Z versus aspect ratio

Clays are important examples of non-spherical particles.

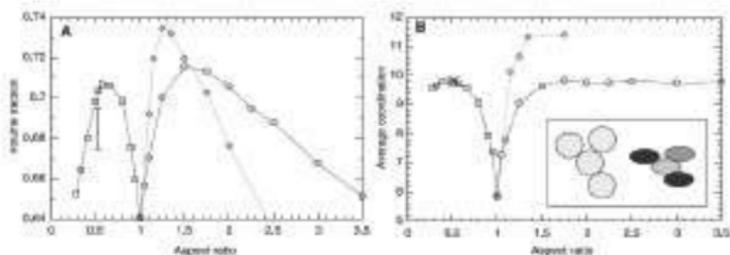


Figure: prolate (circles), oblate (squares), biaxial (diamonds) ellipsoids

Crystal close packing shows no such singular behavior and almost independent of aspect ratio for small deviations from 1. Isostatic system: $Z = 2f$ (frictionless particles) and $Z = f + 1$ (strong friction). Number degrees of freedom $f = 3$ for spheres, $f = 5$ for uniaxial ellipsoids and $f = 6$ for biaxial ellipsoids.

Why it is interesting?

Suspensions are scaled-up version of atomic systems:

- ▶ A few names: Van der Waals, Einstein, Onsager, Debye....
- ▶ Colloidal dispersion with a particle concentration of about 10^{13} cm^{-3} has elastic constants of the order of about 10 dyn/cm^2 , whereas in atomic solids with atomic density around 10^{22} cm^{-3} , the elastic constants have a value around 10^{12} dyn/cm^2 .
- ▶ Atomic or molecular systems require several Kilobars pressure for observing structural phase transitions, whereas for colloids it is about 10^{-5} bar .

- ▶ **Hard sphere colloids are genuine soft matter systems!**
- ▶ **The next step beyond the ideal gas is the hard sphere suspension with entropy driven phase transition, like in Bose gas.**
- ▶ **Liquid and crystal coexisting for volume fractions between freezing $\phi_f = 0.49$ and melting $\phi_m = 0.545$, and dynamic glass transition at $\phi_g \simeq 0.56 - 0.58$.**

A few words on dynamics

- ▶ Deborah number De (Old Testament: "The mountains flowed before the Lord"):

$$De = \frac{\tau_{in}}{\tau_{ex}}$$

- ▶ Practical criteria: viscosity larger than 10^{13} Poise, or observation time larger than 100 s. There is very little we can do with to move up or down these criteria! Even then ergodic statistical mechanics can be applied within each individual component if $\tau_{component} \ll t_{obs} \ll \tau_{system}$
- ▶ In scattering experiments

$$\tau_{ex} \propto \frac{1}{D(k)k^2}; \tau_{in} \propto \frac{\sigma^2}{D}$$

and in the range $k\sigma \gg 1$, $De \gg 1$. However, nothing is wrong and in this range one measures the short time limit of the self-diffusion coefficient D_s .

Typical time scales

- ▶ Solvent relaxation time (solvent degrees of freedom relax to an equilibrium distribution, constrained by a non-equilibrium configuration of the much slower particles):
 $10^{-13} \text{ s} - 10^{-12} \text{ s}$

- ▶ Longitudinal (sound waves) hydrodynamic time
 $\tau_s \simeq \sigma/v_s \propto 10^{-12} \text{ s} - 10^{-11} \text{ s}.$

- ▶ Shear viscous relaxation time

$$\tau_\eta = \frac{\rho_s \sigma^2}{\eta} \propto 10^{-10} \text{ s} - 10^{-8} \text{ s}$$

- ▶ Brownian relaxation time

$$\tau_B \simeq \frac{2\rho_p}{9\rho_s} \tau_\eta$$

- ▶ For $t \gg \tau_B$ the velocities have relaxed and only the particle positions remain as degrees of freedom relaxing by diffusion

$$\tau_l = \frac{\sigma^2}{D_0} \propto 10^{-3} \text{ s}$$

Equation of States for 1D Tonks - Jepsen Liquid:

N rods with a distribution of lengths $\{l_i\}$, where $1 < i < N$ in a line box of total length L .

- ▶ Rescaling of all lengths by a factor $1 + \epsilon$: $l_i \rightarrow (1 + \epsilon)l_i$, and $L \rightarrow (1 + \epsilon)L$. Because excluded volume is irrelevant in this transformation, only entropy of mixing, the reversible work δW_{tot} associated with this process $\delta W_{tot} = -\rho T \delta L$, where $\rho = N/L$, and $\delta L = \epsilon L$.

The same expansion can be done in two steps:

- ▶ (a) rod sizes are sequentially rescaled, one at a time $l_1 \rightarrow (1 + \epsilon)l_1$, then $l_2 \rightarrow (1 + \epsilon)l_2$, and so on;
- ▶ (b) the box size is expanded $L \rightarrow (1 + \epsilon)L$.
- ▶ In a step (a) any rod that is expanded behaves as a confined wall ("piston"), therefore the work needed to rescale particle i is $P\delta l_i = P\epsilon l_i$. Consequently the work needed to perform step (a) is $\delta W_a = \sum_{i=1}^N P\delta l_i \equiv P\delta L_p$, where $\delta L_p \equiv \delta L\phi$, and p stands for particles, and $\phi \equiv \sum_i l_i/L$ is particle volume fraction. Furthermore, $\langle l \rangle = \phi/\rho$.
- ▶ For a step (b) the work $\delta W_b = -P\delta L$, and the total work $\delta W_{tot} = \delta W_a + \delta W_b = P\phi\delta L - P\delta L$. From the other hand by its definition $\delta W_{tot} = -\rho T\delta L$, therefore the equation of state

$$P = \frac{\rho T}{1 - \phi}$$

3d generalization

- ▶ For $d=3$ (equal size σ hard spheres) one still has $\delta W_{tot} = \delta W_a + \delta W_b$, with $\delta W_{tot} = -\rho T \delta V$ and $\delta W_b = -P \delta V$.
- ▶ Each particle is surrounded by an excluded volume of diameter 2σ where no other particle's center of mass may be found. Thus the work needed to expand σ into $\sigma + \delta\sigma$

$$\delta W_{\sigma \rightarrow \sigma + \delta\sigma} = \rho T g(\sigma) \delta V_{sweep}$$

where $\rho T g(\sigma)$ is an entropic (kinetic) force per unit area felt by a given particle ($g(r)$ gives probability to find a particle at the distance r) and δV_{sweep} is the volume change of the excluded volume sphere

$$\delta V_{sweep} = 2^{d-1} S_d(\sigma) \frac{\delta\sigma}{2}$$

- ▶ Summing over all particles

$$\delta W_a = \sum_i \delta W_{\sigma} \rightarrow \sigma + \delta\sigma = \rho T g(\sigma) 2^{d-1} \delta V_p$$

where $\delta V_p = \phi \delta V$.

- ▶ Combining everything together the equation of state

$$\frac{P}{\rho T} = 1 + 2^{d-1} \phi g(\sigma)$$

Three byproducts:

- ▶ For 1d

$$g(l) = \frac{1}{1 - \phi}$$

- ▶ All virial coefficients for 1d Tonks and Jepsen liquid are unity.
- ▶ For 3d the equation of state coincides with that derived by Leibowitz (and he has calculated 5 virial coefficients).

Qualitative speculations

- ▶ Spherically symmetric pairwise potential

$V(r) = V_{sr}(r) + V_{lr}(r)$, where

$$V_{sr}(r) = \infty, \quad r \leq 1,$$

$$V_{sr}(r) = 0, \quad r > 1.$$

($\sigma \equiv 1$).

- ▶ The long range part V_{lr} is a generalized Kac potential (M.Kac studied a model with pure attractive long range potential)

$$V_{lr} = -\epsilon_a \gamma_a^3 \exp(-\gamma_a r) + \epsilon_r \gamma_r^3 \exp(-\gamma_r r)$$

Both the attractions and repulsions are long ranged, $\gamma_a^{-1}, \gamma_r^{-1} \gg 1$, but the repulsions are longer $\gamma_r \leq \gamma_a \ll 1$, and the both are weak, $\epsilon_r \gamma_r^3, \epsilon_a \gamma_a^3 \ll T$.

Typical potentials

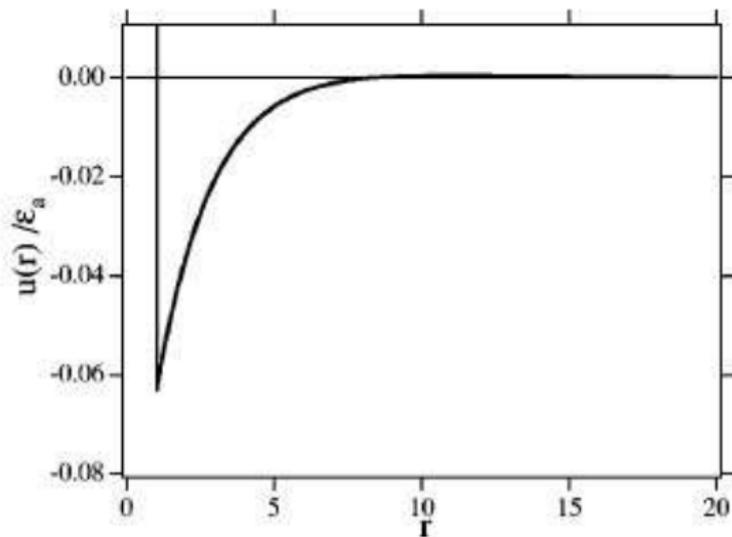


Figure: Potential $V(r)$ (supplemented by short range attraction) versus interparticle separation.

- ▶ Short range part produces rather deep minimum, while long range tails due to frustrating competition between attractions and repulsions might yield to a minimum about 100 times smaller.
- ▶ Potential determines the phase behavior through its integral over space, it is multiplied by a factor r^2 which gives for $r \simeq 10$ the same factor 100. The fact is that there are many more particles of separations between say 11 and 12 particle diameters than between 1 and 2 (**Similar to weak crystallization spirit**).

Second virial coefficient

$$B_2 = -\frac{1}{2} \int d^3r [\exp(-V(r)/T) - 1]$$

and for our potential

$$B_2 = \frac{2\pi}{3} - 4\pi \left(\frac{\epsilon_a}{T} - \frac{\epsilon_r}{T} \right)$$

under asymptotically (at $\gamma_r, \gamma_a \rightarrow 0$) exact approximations

- ▶ $\epsilon_a \gamma_a^3, \epsilon_r \gamma_r^3 \ll T$;
- ▶ region of integration of V_{lr} is extended down to $r = 0$, whereas the hard core actually cuts it off below $r = 1$.
- ▶ Introducing reduced energy $\epsilon \equiv \epsilon_a/T$ and the ratio $\alpha = \epsilon_r/\epsilon_a$

$$B_2 = \frac{2\pi}{3} - 4\pi\epsilon(1 - \alpha)$$

- ▶ When no repulsion, i.e, $\alpha = 0$ in the limit $\gamma \rightarrow 0$ the free energy is calculated exactly (Penrose, Leibowitz, Van Kampen)

$$\frac{F}{NT} = \frac{F_{HS}}{NT} - 4\pi\epsilon\rho$$

where $\rho = N/V$, and F_{HS} (hard sphere part) is a function only of density and it is convex up to fluid - solid transition.

- ▶ For $\alpha \neq 0$ similarly (but even in the limit $\gamma_a \rightarrow 0$ **approximately !**)

$$\frac{F}{NT} = \frac{F_{HS}}{NT} - 4\pi\epsilon(1 - \alpha)\rho$$

and corresponding pressure

$$\frac{P}{T} = \frac{P_{HS}}{T} - 4\pi\epsilon(1 - \alpha)\rho^2$$

- ▶ For densities below 1-st order phase transition fluid to solid (i.e., in a liquid state), P_{HS} is a smooth monotonically increasing function of density.
- ▶ If $\epsilon_a > \epsilon_r$, then $\alpha < 1$ and long range tail contribution to P is negative. When T decreases this term becomes more and more negative (via $\epsilon \propto 1/T$) until the fluid phase is unstable separating into dilute and dense fluids.
- ▶ However if $\epsilon_r > \epsilon_a$, the pressure is convex at all temperatures. Only one fluid phase! Another 1-st order phase transition (liquid - solid) can occur.

Structure factor $S(q) = 1 + \rho h(q)$, where indirect correlation function $h(r) = g(r) - 1$.

- ▶ Approximations are easier for direct correlation function $c(q)$ related to $h(q)$ by Ornstein - Zernike equation

$$h(q) = \frac{c(q)}{1 - \rho c(q)}$$

or

$$S(q) = \frac{1}{1 - \rho c(q)}$$

- ▶ $S(q)$ must be positive and finite for all q . It diverges if $1 - \rho c(q) = 0$.
- ▶ For our potential (a steep short range repulsion plus a weak tail) $c(r) = c_{sr}(r) + c_{lr}(r)$, for $r < 1$, $c(r)$ is dominated by hard sphere interaction, whereas for $r \gg 1$ it is close to $-V_{lr}/T$.

Then:

- ▶ c_{PY} which is zero for $r > 1$, and

$$c_{lr}(q) = \frac{8\pi\epsilon}{[1 + (q/\gamma_a)^2]^2} - \frac{8\pi\epsilon\alpha}{[1 + (q/\gamma_r)^2]^2}$$

and

$$S(q) = \frac{1}{1 - \rho(c_{PY}(q) + c_{lr}(q))}$$

Bounded and positive definite interactions

- ▶ Potentials do not diverge at the origin and no attractions at all: $V(r) \equiv \epsilon f(r/\sigma)$, where V varies from ϵ at $r = 0$ to zero at $r \rightarrow \infty$. $f(x)$ does not have to be analytic!
- ▶ Dimensionless temperature $t \equiv T/\epsilon$, and density $\phi = \pi\rho\sigma^3/6 = \pi\bar{\rho}/6$.
- ▶ The key idea is that at high density $\rho\sigma^3 \gg 1$ the average interparticle distance $a \simeq \rho^{-1/3}$ becomes vanishingly small ($\ll \sigma$), i.e., the potential is extremely long range.
- ▶ In this limit and without short range excluded volume interaction $c(r) = -V(r)/T$ (since $c(r) \propto \delta^2 F/\delta\rho^2$).
- ▶ Thus

$$S(q) = \frac{1}{1 + \bar{\rho}t^{-1}f(q)}$$

Since $f(x)$ decays monotonically from unity at $x = 0$ to zero at $x \rightarrow \infty$ for its Fourier transform $f(q)$ there are two possibilities

- ▶ It has a monotonic decay from the value $f(q = 0)$ to zero at $q \rightarrow \infty$ (M -potentials);
- ▶ It has oscillating behavior at $q \rightarrow \infty$, attaining necessary negative values for certain range of q (O potentials).
- ▶ Let q^* is the value of q at which $f(q)$ attains its minimum negative value. It implies a maximum of $S(q)$ at q^* and this maximum becomes a singularity at the spinodal line

$$\bar{\rho}t^{-1}|f(q^*)| = 1$$

System must reach a crystalline state. If the Fourier transform $f(x)$ has negative component, then an increase in temperature can be compensated by an increase in density. Thus $S(q^*)$ will have a divergence at all T .

Systems with O potentials freeze at all temperatures!

Systems with M potentials:

- ▶ $S(q)$ is a monotonic function of q at high densities, and one can always find a temperature high enough, so that mean field assumptions are granted and freezing is impossible at such temperatures.
- ▶ That does not imply that such systems do not freeze at all. One merely has to go to low enough temperature and density, where interaction is much larger than T . Then the system will display a hard sphere type of freezing.
- ▶ An upper freezing temperature t_u must exist for M potentials, implying that system must remelt at $t < t_u$ upon increasing of the density.

PY exact solution

- ▶ In real space the OZ equation

$$h(x) = c(x) + \int d^3y h(y)c(x-y)$$

The direct correlation unction tends to zero with increasing x much more rapidly than the indirect correlation function.

- ▶ The PY closure equation

$$c(x) = (1 - \exp(V(x)/T)) g(x)$$

For the PY closure $c(x)$ vanishes exactly outside the range of $V(x)$.

- ▶ Qualitative basis is in representation of multi-particle distribution function n_s as one-particle density $n(y)$ under the imposition of suitable external potential

$$\frac{n_s(y, x_1, \dots, x_{s-1})}{n_{s-1}(x_1, \dots, x_{s-1})} = n(y|U)$$

where $U(x) = V(x, x_1) + \dots + V(x_1, x_{s-1})$

PY - continuation:

- ▶ To derive it we consider $n(y|U) \exp(U(y)/T)$ as a functional of $n(y|U)$ as U is changed from 0 to its final value. Performing Taylor expansion, taking $U(y) = V(y, x)$, and truncating the expansion at first order, after some algebra, we end up with the PY closure relation:



$$c(x) = (1 - \exp(V(x)/T)) g(x)$$

- ▶ In words: spatial correlations in ρ in two volume elements have a direct and an indirect component. In the direct component only ρ fluctuations in the two volume elements are considered, whereas the fluctuations in all the surrounding volume elements are kept fixed. The indirect contribution is added when the fixation is released:

$$g_{total} = c + g_{indirect}$$

For auxiliary function $\tau(x) \equiv g(x) - c(x)$ for hard spheres

$$\tau(r) = 1 + n \int_{r < \sigma} \tau(r') d^3 r' - n \int_{r' < \sigma; |r-r'| > \sigma} \tau(r') \tau(r-r') d^3 r'$$

Wertheim, Baxter found $\tau(r)$ at $r < \sigma$ (where it coincides with $c(r)$), and then $g(r)$ at $r > \sigma$, where it coincides with $\tau(r)$.

► Wertheim, Baxter solution:

$$-c(x) = \alpha + \beta x + \gamma x^2 + \delta x^3$$

►

$$\alpha = \frac{(1 + 2\phi)^2}{(1 - \phi)^4}; \beta = -\frac{6\phi(1 + 0.5\phi^2)}{(1 - \phi)^4}$$

$$\gamma = 0; \delta = \frac{\phi(1 + 2\phi)^2}{2(1 - \phi)^4}$$

Similar strategy for interacting hard spheres:

$$V(r) = \begin{cases} \infty, & r < \sigma \\ V_a(r) + V_r(r), & \sigma < r < b \\ 0, & r > b \end{cases}$$

- ▶ To find $\tau(r)$ at $r < \sigma$, i.e., to solve Ornstein-Zernike equation with the PY closure relation:

$$\tau(\mathbf{x}) = 1 + n \int d^3\mathbf{y} (e^{-\beta V(\mathbf{y})} - 1) \tau(\mathbf{y}) (e^{-\beta V(\mathbf{x}-\mathbf{y})} \tau(\mathbf{x}-\mathbf{y}) - 1),$$

- ▶ To find $g(r)$ at $r > b$;
- ▶ To interpolate $\tau(r)$ from σ to b .

Interaction potentials:

- ▶ Depletion: $V_a(r) \equiv 0$, for $r > b_a$ and for $r \leq b_a$:

$$V_a(r) = V_a^0 \frac{(b_a - r)^2(2b_a + r)}{(b_a - \sigma)^2(2b_a + \sigma)}$$

- ▶ Yukawa (attraction or repulsion):

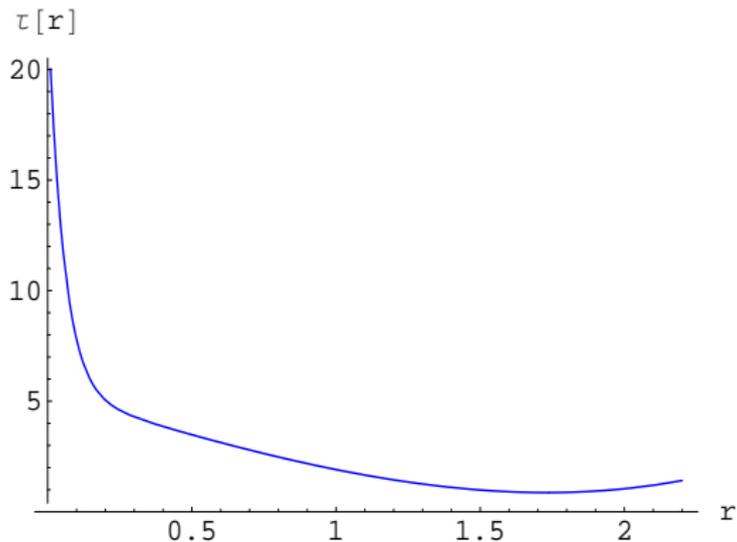
$$V_r = \pm V_r^0 \frac{\exp \kappa(\sigma - r)}{r}$$

where

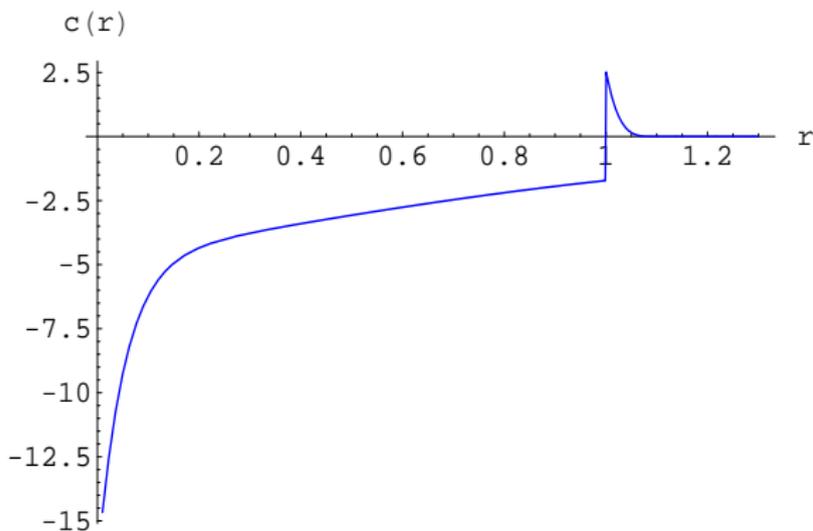
$$V_r^0 = \frac{Q}{\epsilon(1 + \kappa\sigma)^2}$$

Nature is on our side:

The function $\tau(r)$ is a smooth function for $r < b$, and approaches 0 at large r



Unlike $c(r)$



In Fourier space a jump at $x \equiv (r/\sigma) = 1$ corresponds to $1/q$ behavior at $q \rightarrow \infty$:

$$c(q) = \frac{4\pi}{q} \int dx x \sin(qx) c(x)$$

To get better convergence for $b < x$

$$\begin{aligned}\tau(x) - 1 &= \frac{4\pi}{8\pi^3 x} \int dq q \sin(qx) h(q) = \\ &= \frac{1}{2\pi^2 x} \int dq q \sin(qx) \frac{c(q)}{1 - nc(q)} = \\ &= \frac{1}{2\pi^2 x} \int dq q \sin(qx) \left(c(q) + \frac{nc^2(q)}{1 - nc(q)} \right) = \\ &= c(x) + \frac{1}{2\pi^2 x} \int dq q \sin(qx) \frac{nc^2(q)}{1 - nc(q)} = \\ &= \frac{n}{2\pi^2 x} \int dq q \sin(qx) \frac{c^2(q)}{1 - nc(q)}.\end{aligned}$$

- ▶ With this $c(q)$ one can find $\tau(x)$ (or what is the same $g(x)$) for $x > b$

$$\tau(x) = \frac{\rho}{2\pi^2 x} \int dq q \sin(qx) \frac{c^2(q)}{1 - \rho c(q)}$$

- ▶ Pressure

$$P = \frac{4\pi\rho T}{6} \left(\sigma^3 \tau(\sigma) - \int_{\sigma}^b dr (\exp(-V(r)/T) - 1) \partial_r (r^3 \tau(r)) \right)$$

- ▶ Coordination number

$$N = 4\pi \int_{\sigma}^b dr r^2 g(r)$$

Note of caution: Two "routes" connecting P and $g(r)$

- ▶ The virial route

$$P = \rho T - \frac{\rho^2}{6} \int_0^\infty r \frac{dV}{dr} g(r) 4\pi r^2 dr$$

- ▶ The compressibility route

$$T \frac{d\rho}{dP} = 1 + \rho \int_0^\infty h(r) 4\pi r^2 dr$$

- ▶ It can be verified that B_2 and B_3 in the PY theory do not depend on the route.
- ▶ VdW pressure holds at low densities

$$P = \frac{T}{(1/\rho) - \sigma}$$

How to find $\tau(r)$?

- ▶ For a weak potential ($V < T$), $\tau(r)$ has almost the same polynomial form as for HS. For a relatively short ranged (but not small!) $V > T$, the modification of the HS ansatz is essential only for relatively small $r \simeq b - \sigma$.
- ▶ This suggests the ansatz

$$\tau(r) = c_0 + c_1 r + c_3 r^3 + \tau_s(r)$$

with $\tau_s = c_4 / (x + c_5)^2$ growing at $x \rightarrow 0$.

- ▶ Then the PY closure allows to calculate $c(r)$, then $g(r)$ for $r > b$, and eventually the $\tau(r)$ is well defined for all r .

Illustrations how it works:

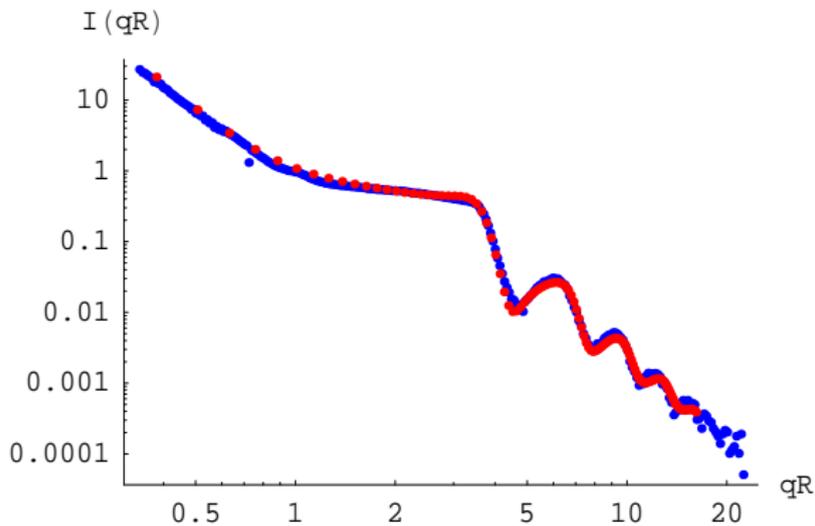
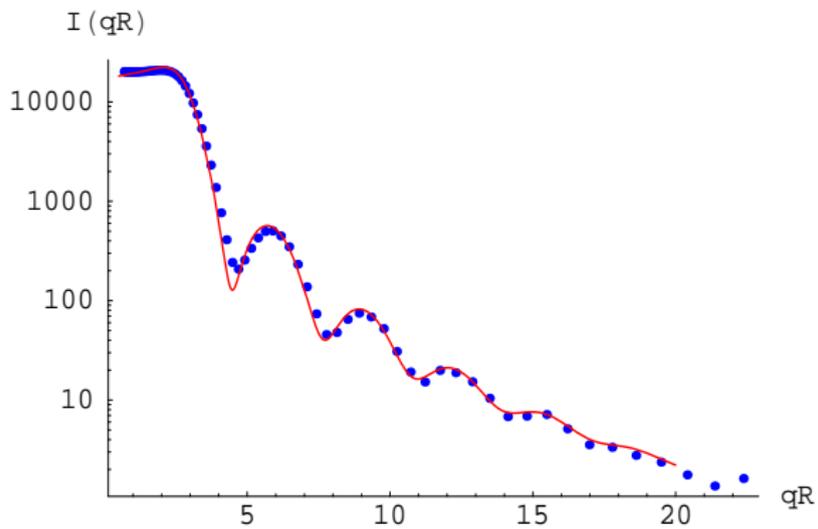
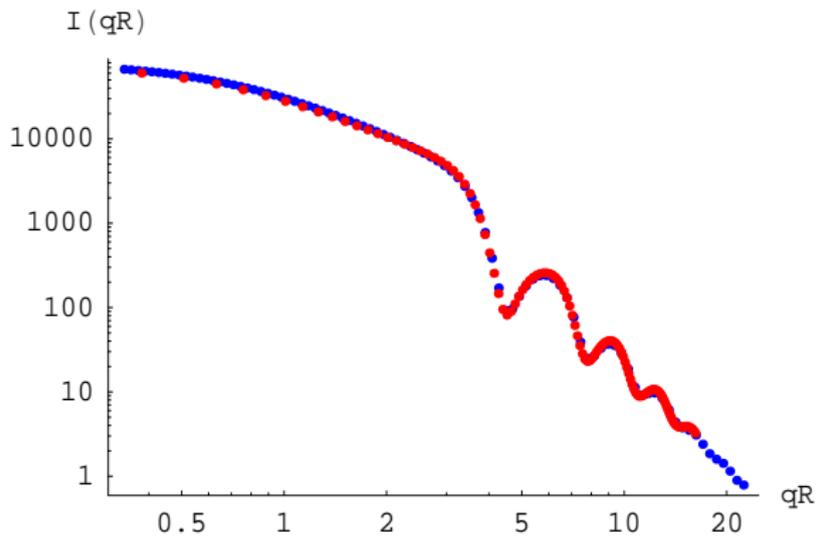


Figure: HS with depletive attraction

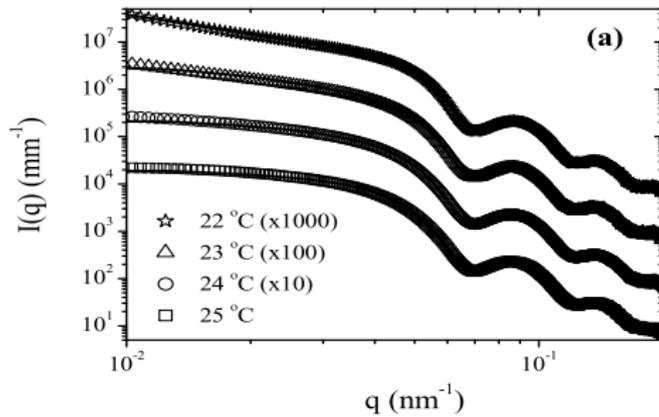
Sticky HS



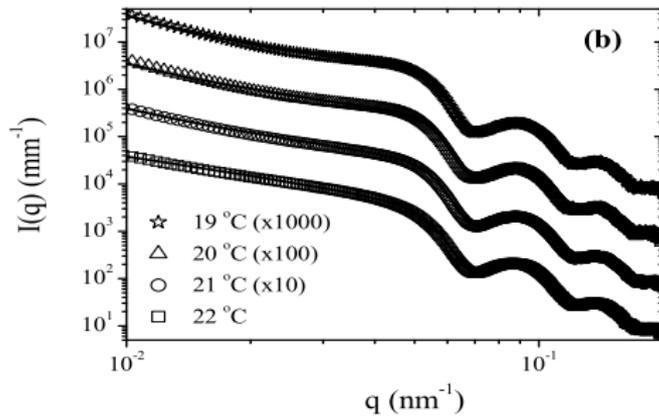
HS with depletive attraction



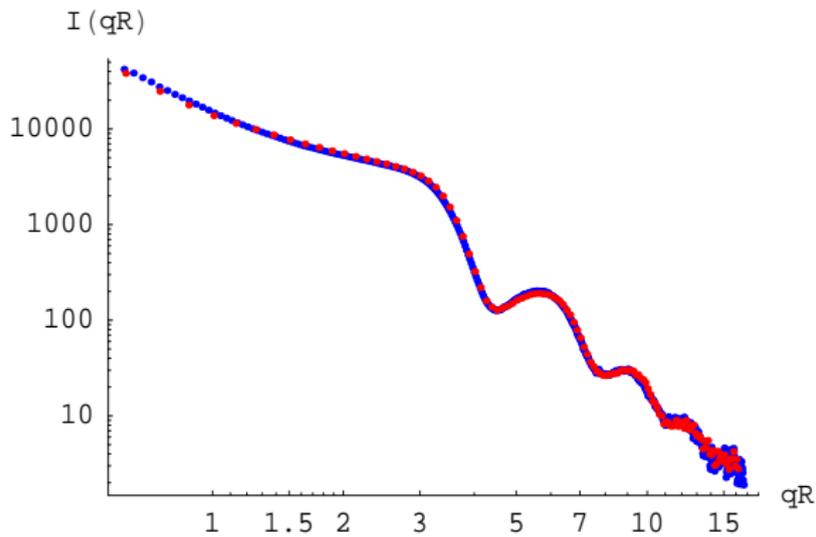
Sticky HS



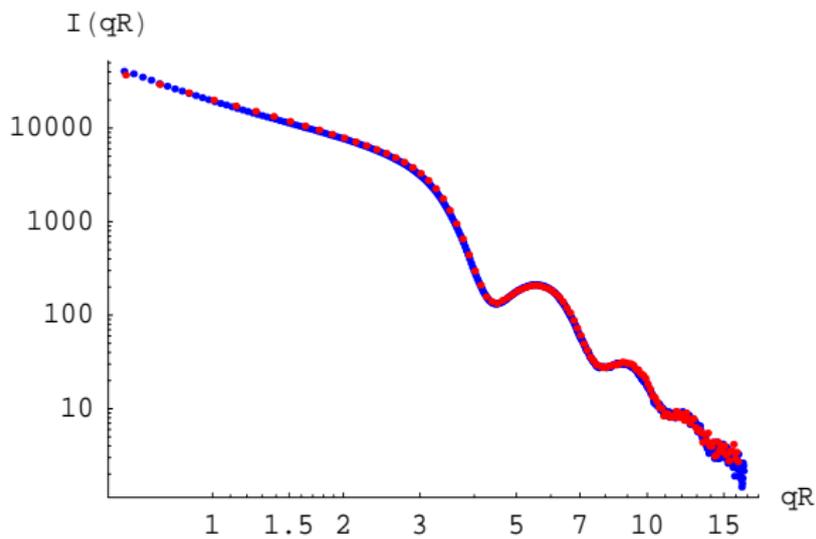
Sticky HS



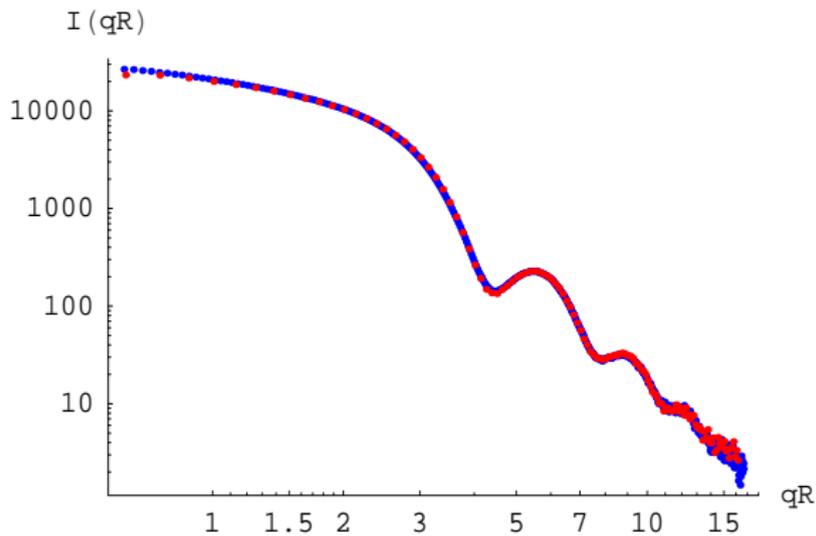
Sticky HS



Sticky HS



Square well potential



Not everything is so unclouded!

- ▶ Increasing polymer concentration (e.g., up to 46 *mg/ml*) we increase depletion potential up to $V_{a0} \simeq 6T$;
- ▶ However, already for $V_{a0} \simeq 3.7T$, $S(q \rightarrow 0)$ becomes very large, $g(\sigma) \simeq 32$ and $N \simeq 3.55$;
- ▶ This means that there are strong fluctuations as a precursor of the two phase state, consisting of liquids with different density;
- ▶ OZ equation with PY closure cannot describe this situation;
- ▶ It can be done by adding Debye-Bueche function

$$I(q) \rightarrow F(q) \left(S(q) + \frac{Dl^3}{(1 + (ql)^2)^2} \right)$$

where l is a characteristic cluster size, D describes the normalized contribution from the clusters to the scattering intensity, and volume fraction ϕ in the aggregates is larger than in the bulk liquid.

Aggregations:

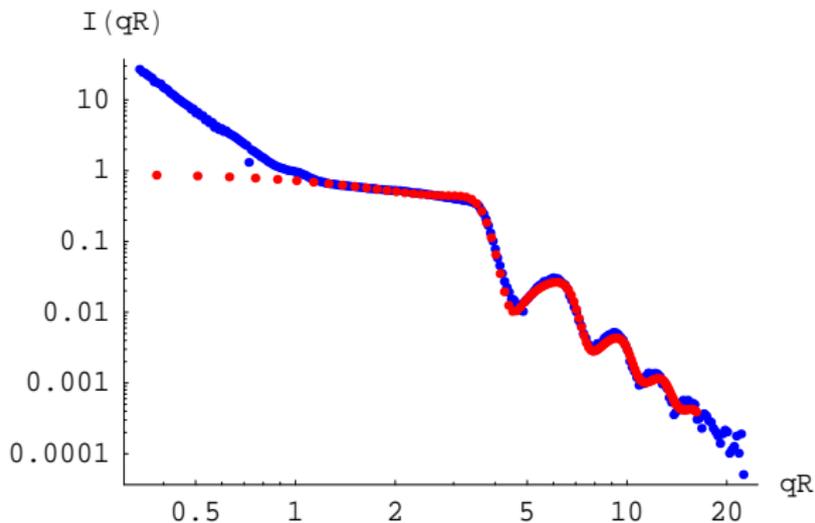
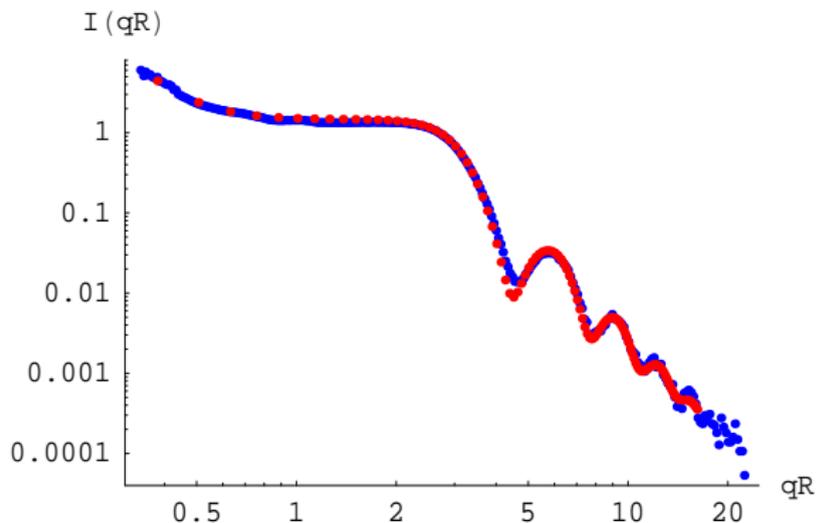
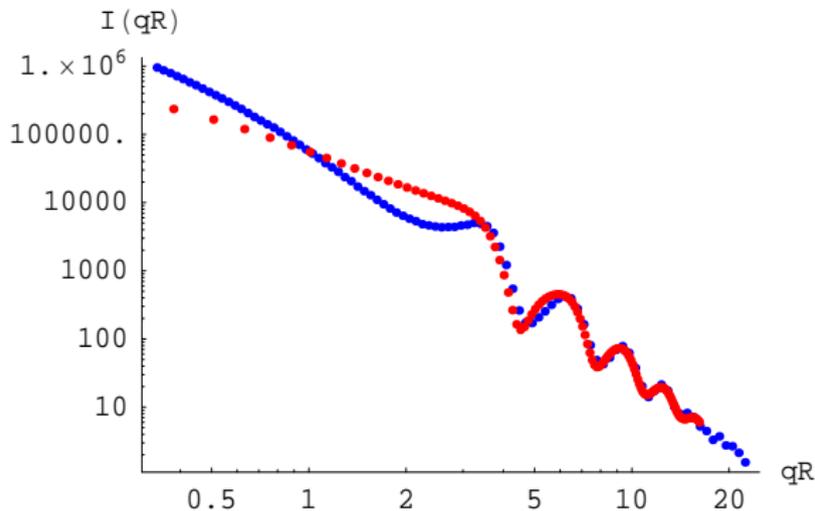


Figure: Without Debye correction.

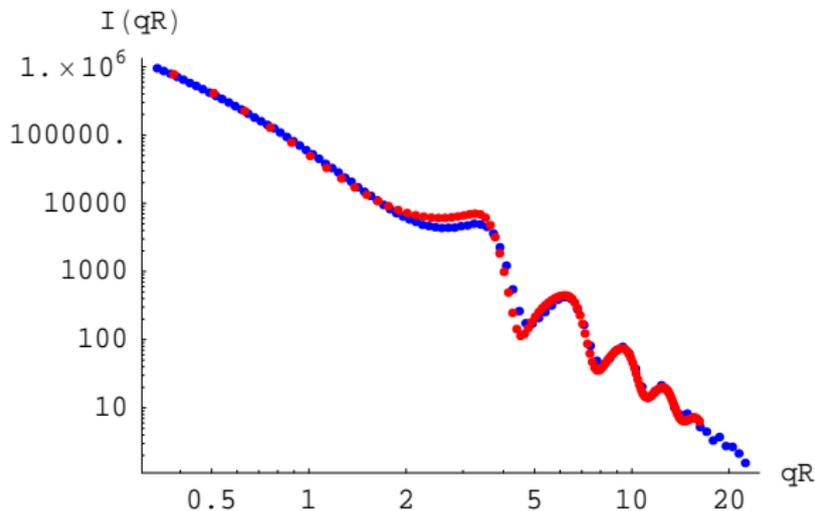
The same but with Debye corrections included



Without Debye contribution from the clusters



The same but with Debye corrections included



Spinodal line

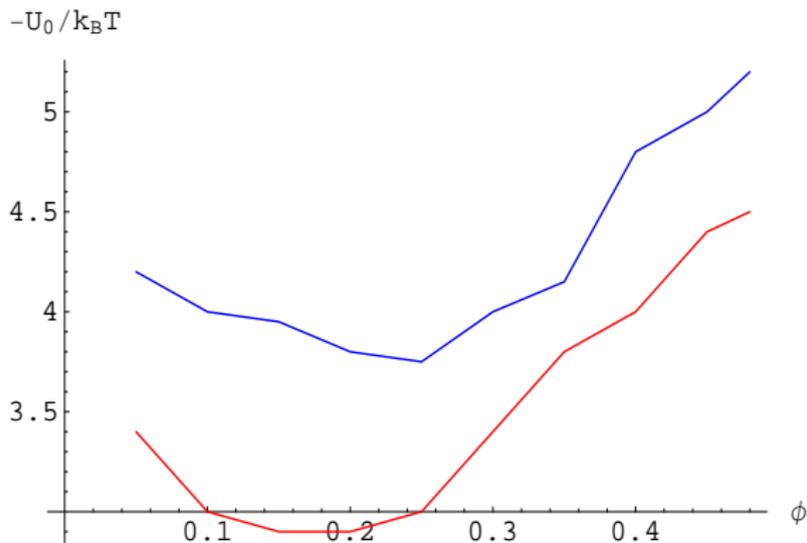


Figure: Line of limiting stability of liquid phase: blue - $b = 1.13$, red - $b = 1.25$

Optional slide: Where to go further on:

- ▶ Close to the freezing transition liquids are more complex than suggested by the pair correlation function!
- ▶ Structural shape factor $\zeta = C^2/4pS$, relied on a Voronoi analysis, C is the circumference, and S is the surface area of the Voronoi cell of each particle (Voronoi cell of a particle a consists of all points closer to a than to any other sites).
- ▶ ζ reflects the structural changes close to freezing in more detail than the changes in $g(r)$.