Inexhaustibility of colloidal dispersions.

E.I. Kats and A.R.Muratov

L.D.Landau Institute for Theoretical Physics RAS, Moscow, Russia

Acknowledgments :

I.M.Khalatnikov who hired me to the Landau Institute.

Motivation.

Hard spheres are the fruit flies of statistical physics.

Part I. Structure factor.

Basic facts I.

- The pair correlation function is defined as $g(r) = 1 + \bar{n}h(r) = \langle n(r)n(0)\rangle/\bar{n}^2 - \bar{n}\delta(r)$, and two other correlation functions are useful to describe the scattering data : the total correlation function $h(r)$ and the direct correlation function $c(r) = -\delta^2\mathcal{F}/[T\delta n(r)\delta n(0)]$. The functions $h(r)$ and $c(r)$ enter to the exact Ornstein-Zernike equation.

$$h(\mathbf{x}) = c(\mathbf{x}) + \bar{n}\int d^3y\, h(\mathbf{y})c(\mathbf{x}-\mathbf{y})\ .$$

- $$S(q) = 1 + \frac{4\pi\bar{n}}{q}\int_0^\infty dr\, r\, sin(qr)h(r)\ .$$

  OZ equation can be rewritten in Fourier representation as

$$S(q) = 1 + \bar{n}h(q) = 1/(1 - \bar{n}c(q))\ ,$$

- PY closure equation

$$c(r) = (1 - e^{\beta V(r)})g(r)\ ,$$

  (where $V(r)$ is an interaction potential between particles and $\beta = (k_B T)^{-1}$).

Basic facts II.

- HNC closure looks like

  $$g(r) = e^{\gamma(r) - \beta V(r)} ,$$

  where $\gamma(r) = h(r) - c(r)$.
- If the form of the interparticle potential $V(r)$ is known, the closure relation allows to solve the OZ equation and then to compute $S(q)$.
- The interaction potential is very large and repulsive for small interparticle distance $r < \sigma$, (where σ stands for an effective size of the particle hard core) $V(r) = \bar{V} \gg k_B T$, and vanishes outside the interaction region $R_{int} < r$, $V(r) = 0$.
- PY and HNC closure relations imply that

  $$g(r) \propto e^{-\beta \bar{V}} , \quad r < \sigma\, ; c(r) = 0 , \quad R_{int} < r \, .$$

Experimental input.

- What is directly measured in any scattering experiment is not the static structure factor. The measured quantity is the scattering intensity $I(\mathbf{q}, \bar{n})$ (where as before $\mathbf{q}$ is the scattering wave vector, and $\bar{n}$ is the average particle concentration).
- For a very dilute dispersion, when $\bar{n} = \bar{n}_{dil}$ is small $\bar{n}_{dil}\sigma^3 \ll 1$, $I(q, \bar{n}_{dil})$ is the scattering intensity from a single particle, termed traditionally as the particle form factor.
- For molecular liquids, or for colloidal dispersions with relatively small polydispersity, the static structure factor can be determined as $S(q) = \bar{n}_{dil}\, I(q, \bar{n})/(\bar{n}\, I(q, \bar{n}_{dil}))$
- For our approach we need to know experimental $I(q)$ data for q in the vicinity of the first peak (in the spirit of weak crystallization theory).

Basic facts III.

- It is impossible to calculate accurately the correlation functions $h(r),\ c(r)$ in the r-space by the Fourier transformation of the static structure factor, because $S(q)$ decreases too slow, usually as q^{-1}. Luckily for the function $\gamma(r)$ situation is much better. It can be obtained by the Fourier transformation if the measured experimental data $I(q,\bar{n})$. The reason is that $\gamma(r)$ is a smooth function and its Fourier transform decreases fast, e.g., for the hard spheres like $1/q^3$.
- For the hard spheres it is sufficient to know the scattering intensity for $q < 10/\sigma$. Then function $\gamma(r)$ can be calculated directly from the static structure factor and the exact OZ equation (without an explicit use of any closure equation !)

$$\gamma(r) = \frac{1}{2\pi^2 r\bar{n}} \int_0^\infty dq\, q \sin(qr)(S(q) - 2 + 1/S(q)) .$$

- the PY closure reads as

$$c(r_i) = (1 + \gamma(r_i))(e^{-\beta V(r_i)} - 1) ,$$

the HNC closure is

$$c(r_i) = e^{\gamma(r_i) - \beta V(r_i)} - 1 - \gamma(r_i) .$$

Our procedure.

- To take $S(q)$ near its first peak from scattering experimental data $I(q)$.
- To compute $\gamma(r)$ from OZ equation (without any closure relation)

$$\gamma(r) = \frac{1}{2\pi^2 r\bar{n}} \int_0^\infty dq\, q \sin(qr)(S(q) - 2 + 1/S(q)) \, .$$

- To chose (to guess) a trial form of the interparticle potential $V(r)$.
- Using a closure relation (PY, HNC, or something else) to compute $c(r)$ and $h(r)$.
- To compute $\gamma(r) = h(r) - c(r)$, and to re-compute $S(q)$.
- To minimize the difference $S(q)_{computed} - S(q)_{experimental}$ over the variational parameters entering into $V(r)$.

Analysis of the data.

- As the first test of our approach we treat the hard sphere model data obtained by the exact solution of the OZ and PY equations as our input ”experimental” data.
- The effective interaction potential is the hard sphere potential supplemented by the correction terms

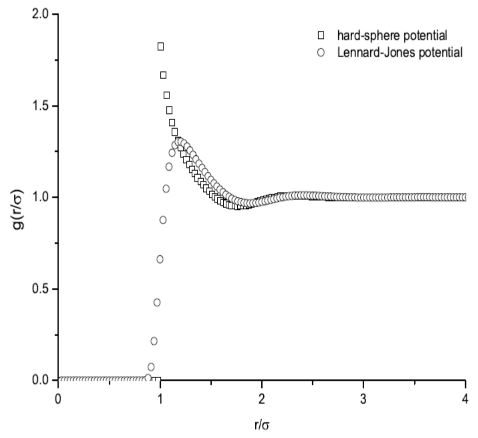
  $$\beta V(x) = (-V_a\, e^{-\kappa_a (x-1)} + V_r\, e^{-\kappa_r (x-1)})/x\ .$$

  (x here is r/σ).
- Fitting four adjustable parameters V_a, V_r, κ_a and κ_r we estimate the corrections to the hard sphere potential smaller than $\beta V(r) < 0.05$. The calculated structure factor deviates from its ”experimental” value less then 0.07% !.
- If we take the Lenard-Jones potential without the hard core part,

  $$\beta V(r) = -V_a\, r^{-6} + V_r\, r^{-12}\ ,$$

  then the fitting to the ”experimental” data (the exact OZ and PY equation solution for the hard spheres) gives $V_a = 0.4, \quad V_r = 1.26$, and the deviation of the calculated structure factor from the ”experimental” data is about 0.7%, i.e., 10 times worse.

Pair correlation function for hard-sphere and LJ potentials.



Polymethylmetacrylate (PMMA) spheres.

- Using our new methodology and depletion interaction potential induced by the polystyrene we fitted perfectly all available experimental data (besides our new procedure is simpler and faster than that used before).

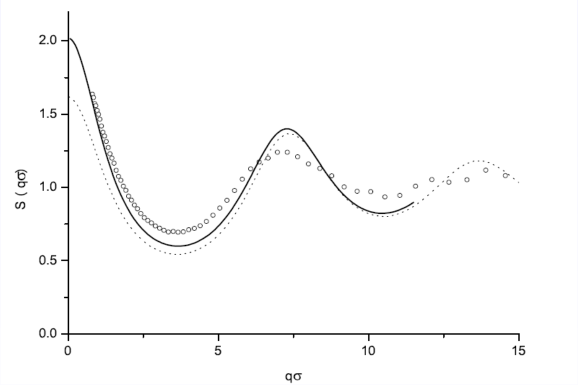


FIGURE – $S(q)$ for PMMA spheres and depletion potential. Circles - experimental data, dotted line - previous numeric simulation, solid line - our new approach. Volume fraction of PMMA particles $\phi = 0.2$, concentration of PEG $c_p = 23 mg/L$.

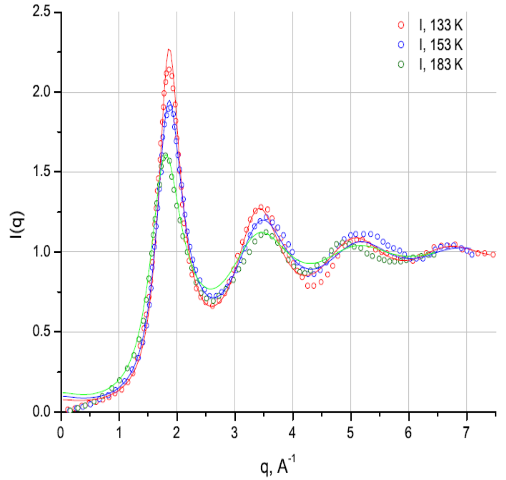
Neutron scattering data on liquid krypton.

- We perform the fit the experimental data with the LJ potential. The values of parameters determined from the same fitting

T	σ	$\bar{n}$	V_a	V_r	Coordination number
133	3.91	0.72	2.56	1.91	7.3
153	3.55	0.68	3.11	3.77	6.5
183	3.55	0.68	2.64	3.6	4.7

  Four parameters were used as adjustable : scaling factor for the wavevector σ, density $\bar{n}$ and the amplitudes of the Lenard-Jones potential V_a and V_r.
- By common wisdom for the krypton one should expect the Lenard-Jones interaction potential provides an adequate description of the system. Surprisingly enough it is not the case ! The catch is in a small q region.

Scattering intensity for liquid krypton



Something is wrong ?

- The exact thermodynamic relation

$$S(0) = k_B T \left(\frac{\partial \bar{n}}{\partial P} \right)_T \quad .$$

- We take the needed values of the parameters from the handbook and calculate the structure factor at $q = 0$ for a few temperature points along the liquid-gas coexistence line : $S(q = 0, T = 133K) \approx 0.076$, $S(q = 0, T = 153K) \approx 0.13$, $S(q = 0, T = 183K) \approx 0.459$.
- With these exact values for the $S(q = 0)$, we perform again the fitting of the scattering data in the broad range of the wave vectors. We found also the interaction potential, and all three curves can be rescaled and collapsed into a single universal (master) curve.
- As a byproduct we found that temperature dependencies of $S(q = 0)$ and correlation length (inverse width of the first peak) are the same ($\propto 1/T$).

Note on thermodynamic inconsistency : two routes to compute pressure P

- The virial route

$$P = nT - \frac{n^2}{6}\int_0^\infty r\frac{dV}{dr}4\pi r^2 dr \ .$$

- The compressibility route

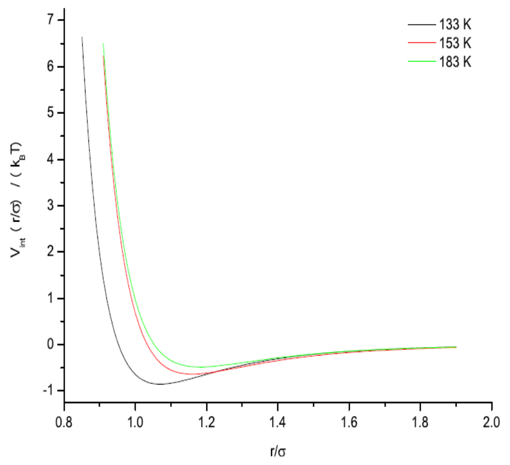
$$T\frac{dn}{dP} = 1 + n\int_0^\infty h(r)4\pi r^2 dr \ .$$

- It can be verified that B_2 and B_3 in our approach

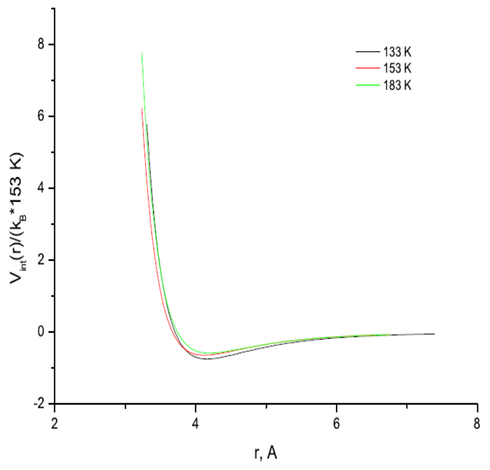
$$P = \frac{4\pi nT}{6}\left(\sigma^3\gamma(\sigma) - \int_\sigma^b dr\,(\exp(-V(r)/T) - 1)\,\partial_r(r^3\gamma(r))\right)$$

do not depend on the route.

Interaction potential for liquid krypton.



Rescaled interaction potential for liquid krypton.



At low concentration and short range potentials, $S(q)$ exhibits a very weak dependence on potential shape.

- If the total correlation function $h(r) = g(r) - 1$ is split into two parts, with $h_0(r) = -1$ for $r < \sigma$, and $h_1(r) = g(r) - 1$ for $r > \sigma$, then

  $$S(q) = 1 + \frac{4\pi\bar{n}}{q} j_1(q) + \bar{n} h_1(q)$$

  (j_1 is a spherical Bessel function, and it is exact for hard spheres).
- Isosbestic points are defined as values of the wave-vectors q for which $S(q)$ is invariant under changes of the effective attractive potential well depth (or e.g., temperature, density).
- Since $h_0(q) = 4\pi\bar{n}j_1(q)/q$ for hard spheres, the isosbestic points for short range and not too strong potentials are close to $q_m\sigma = m\pi$.
- Closure equations often produce inconsistent results that depend on the physical path taken). However for systems with short ranged potentials, our procedure (+ thermodynamic matching of $S(q = 0)$) ensures thermodynamic consistency.

One more result to the same point : Our criterion of the Fisher - Widom line.

- The decay $rh(r)$ to zero can be either exponential (monotonic) if attraction dominates repulsion, or damped oscillatory otherwise.
- The Fisher - Widom line separates the phase diagram into two regions characterized by these two different types of asymptotic decay (c.f., with the so-called Boyle point T_B in a dilute system : If pair repulsion dominates the second virial coefficient $B_2(T) > 0$ (so the pressure is larger than the ideal gas value), whereas if attraction is dominant then $B_2(T) < 0$. In the Boyle point $B_2(T_B) = 0$.
- Our criterion : the Fisher - Widom crossover occurs close to the line where the isothermic compressibility $\chi_T = (\partial p(k_B T)^{-1}/\partial\rho)^{-1}$ takes its ideal gas value $(\rho k_B T)^{-1}$.

Part II. Drying of colloidal films.

Characteristic time scales.

- Solvent relaxation time, $10^{-13} - 10^{-12}\,s$
- Hydrodynamic time $\tau_s \simeq \sigma/v_s \propto 10^{-12} - 10^{-11}\,s$
- Viscous relaxation time $\tau_\eta \simeq \rho_s\sigma^2/\eta \propto 10^{-10} - 10^{-8}\,s$
- Brownian relaxation time $\tau_B \simeq (2\rho_p/9\rho_s)\tau_\eta$
- Particle position diffusion time $\tau_d \simeq \sigma^2/D \propto 10^{-3}\,s$.

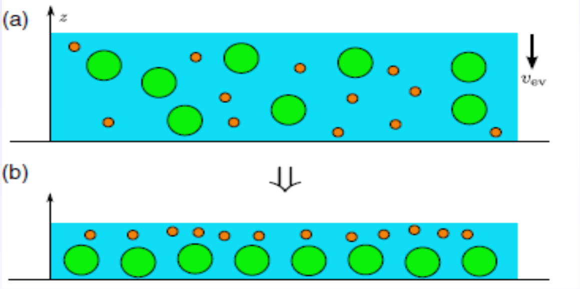
Why drying colloidal films are interesting?.

- Solid thin films on surfaces are often made by spreading a thin liquid film containing solid colloidal particles onto the surface, and then allowing the liquid to evaporate (paints, cosmetics and so on).
- If there is only one species of colloidal particle with a diffusion constant D, the time scale for diffusion across the height of the film h^2/D.
- The evaporation time scale is h/v_{ev}, and the competition with diffusion is quantified by Peclet number $Pe = v_{ev}h/D$. The drying film is near equilibrium if $Pe < 1$. If $Pe > 1$ particles accumulate near the descending interface at the top of the film.
- For a mixture of colloidal particles there is a generic tendency to segregate. This type of stratification is highly desirable because it allows the independent control of the properties of the top and the bottom.

Naive picture.

- If *Pe* < 1 the concentration gradient created by evaporation is quickly flattened by diffusion. Thus the film remains uniform.
- If *Pe* > 1 - the concentration gradient increases and colloidal particles accumulate near the top of the film.
- If there are two types of colloidal particles of different sizes the larger colloidal particles (with smaller *D* and larger *Pe*) naive arguments predict that the larger particles accumulate near the surface. However, experiments show that it is not always the case ! ?

Drying of binary colloidal films.



Definitions and Notations.

- Colloidal film

$$h(t) = h_0 - v_{ev} t$$

- Colloidal particles are hard spheres r_1 and r_2 with $r_2 = \alpha r_1$ and $\alpha > 1$ (the particles volumes $\nu_2 = \alpha^3 \nu_1$).
- The particle volume fractions $\phi_i(z, t)$ and initially the film is uniform $\phi_i(z, 0) = \phi_i^{(0)}$.
- For a dilute mixture

$$f(\phi_1, \phi_2) = \sum_i \frac{1}{\nu_i} \phi_i \ln(\phi_i) + \sum_{i,j} \frac{1}{\nu_i \nu_j} a_{ij} \phi_i \phi_j$$

  where $a_{ij} \equiv (2\pi/3)(r_i + r_j)^3$ is the second virial coefficient.
- $v_i(z)$

$$v_i(z) = -\frac{D_i}{k_B T} \frac{\partial \mu_i}{\partial z}$$

  and

$$\mu_i = \ln(\phi_i) + 1 + 2 \sum_j \frac{a_{ij} \phi_j}{\nu_j}$$

Equations to solve. I

- $$\frac{\partial \phi_i}{\partial t} = -\frac{\partial}{\partial z}\left(\phi_i v_i\right)$$

  (particle conservation law) and

  $$\frac{\partial \phi_i}{\partial t} = -\frac{\partial}{\partial z}\left(\frac{\phi_i D_i}{k_B T}\frac{\partial \mu_i}{\partial z}\right)$$

- We find

  $$v_1 = -D_1\left[\left(\frac{1}{\phi_1}+8\right)\frac{\partial \phi_1}{\partial z} + \left(1+\frac{1}{\alpha}\right)^3\frac{\partial \phi_2}{\partial z}\right]$$

  and

  $$v_2 = -D_2\left[\left((1+\alpha)^3\right)\frac{\partial \phi_1}{\partial z} + \left(\frac{1}{\phi_2}+8\right)\frac{\partial \phi_2}{\partial z}\right]$$

Equations to solve. II

- The time evolution equations

$$\frac{\partial \phi_1}{\partial t} = D_1 \frac{\partial}{\partial z}\left[(1+8\phi_1)\frac{\partial \phi_1}{\partial z} + \left(1+\frac{1}{\alpha}\right)^3 \phi_1 \frac{\partial \phi_2}{\partial z}\right]$$

  and

$$\frac{\partial \phi_2}{\partial t} = D_2 \frac{\partial}{\partial z}\left[(1+\alpha)^3 \phi_2 \frac{\partial \phi_1}{\partial z} + (1+8\phi_2)\frac{\partial \phi_2}{\partial z}\right]$$

- Boundary conditions $v_1 = v_2 = 0$ - substrate ($z = 0$) and $v_1 = v_2 = -v_{ev}$ - free surface ($z = h$). and

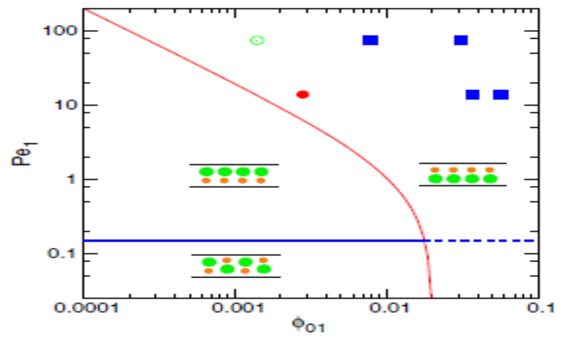
$$Pe_1 = \frac{v_{ev} h_0}{D_1}\,;\; Pe_2 = \alpha Pe_1$$

Approximate solutions to the equations (I cannot solve the equations by other means)

- Merely looking at the equations, we conclude that the cross interaction term affects the large colloidal particles stronger than the small ones (factor $(1+\alpha)^3$).
- In the derived equations, the terms $8\partial\phi_i/\partial z$ come from self-interaction terms a_{ii}, while $(1+(1/\alpha))^3\partial\phi_2/\partial z$ and $(1+\alpha)^3\partial\phi_1/\partial z$ come come from cross-interaction terms $a_{12}=a_{21}$.
- If $\alpha \gg 1$ and we have a strong concentration gradient for small colloidal particles, the larger colloidal particles will be driven to substrate. The condition

$$(1+\alpha)^3\,\frac{\partial\phi_1}{\partial z} \gg \frac{1}{\phi_2}\frac{\partial\phi_2}{\partial z}$$

Phase diagram



When both Peclet numbers are less than 1, the perturbation due to evaporation is small. When both Peclet numbers are greater than 1, initially both colloids accumulated at the free surface, but at later times, the concentration gradient of the smaller colloid becomes large and eventually drives the big colloids to the bottom.

Optional slides.

Another strategy for short range potentials.

- $V(r)$ includes hard sphere ($V(r) = \infty$ for $r < \sigma$), short range attraction and repulsion ($V = V_a + V_r$ for $\sigma < r < b$), and cutoff b ($V(r) = 0$ for $r > b$.
- To compute $\gamma(r)$ from OZ equation with PY closure relation

$$\gamma(r) = 1 + \bar{n} \int d^3y(\exp(-\beta V(y)) - 1)\gamma(y)(\exp(-\beta V(r-y))\gamma(r-y) - 1)$$

- To find $g(r)$ at $r = b$ and to interpolate $\gamma(r)$ from σ to b.

Shear viscosity

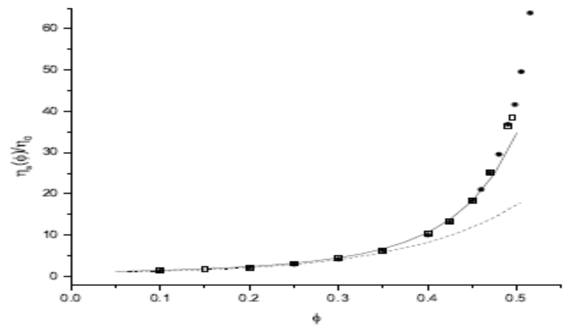


FIGURE – Open squares and solid circles - numeric simulations, dashed line - Enskog expression, solid line - contribution from soft short-wavelength density mode.

Isosbestic points

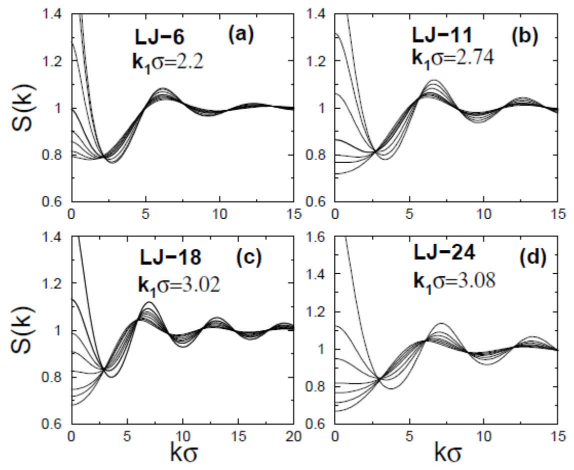


FIGURE – $S(k)$ calculated for different kinds of LJ potentials and different temperatures.

Colloidal particle (blue) immersed in a solution of polymer (red) of radius *R*, in a solvent of smaller molecules (green).

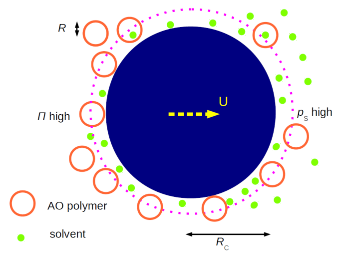


FIGURE – The particle excludes the polymer from layer of width R (indicated by a dotted line). Along the *x* axis, there are gradients of both the polymer contribution to the pressure, and the solvent contribution.

Flat wall (blue) in contact with polymer (red) in a solvent of smaller molecules (green).

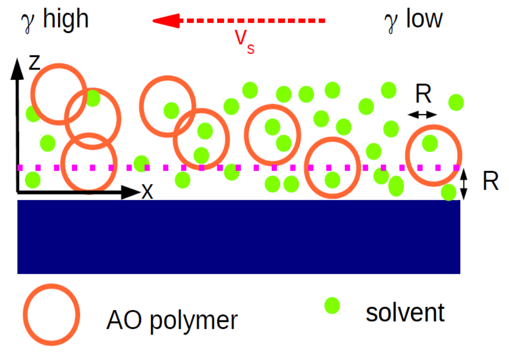


FIGURE – The wall excludes the polymer from layer of width *R*. There are gradients of both the polymer and solvent concentrations. The wall is assumed stationary, and then the fluid flows to the left.

Basic notions of diffusio-phoresis.

- The slip velocity results in flow away from low concentrations of the polymer and towards higher concentrations. This motion can be understood as a wall-bounded Marangoni effect. It reduces the total wall/solution surface free energy as the region of low polymer concentration expands

$$v_s = \frac{R^2 k_B T}{2\eta} \nabla_x \rho_p$$

- The equation rests on the fact that the hydrostatic pressure is uniform (fast relaxation via solvent flow). Then a gradient of the osmotic pressure Π is balanced by a counter-gradient in the solvent contribution into the pressure (it relaxes much slower via diffusion motion of the polymer).
- For a colloidal particle $R_c \gg R$ the drift velocity

$$U = -v_s = \Gamma \nabla \ln \phi_p\,;\, \Gamma = -\frac{\phi_p k_B T}{2\eta R} \simeq -\phi_p D_p$$

where $\phi_p = \rho_p R^3$ and $D_p \propto k_B T/(\eta R)$

Estimations.

- $\Gamma \simeq -200\,\mu m^2 s^{-1}$, and if the length scale for the concentration gradient $\lambda_G \simeq 100\,\mu m$.
- The Peclet number compares diffusion to diffusio-phoresis motions

$$Pe = \frac{U\lambda_G}{D_c} \simeq \frac{\phi_p D_p}{D_c}$$

- For large colloidal particles $D_c \ll D_p$ and diffusio-phoretic motion is much faster. Namely, the osmotic pressure difference across the particle diameter is $R_c \nabla(\rho k_B T)$, and it gives the force $F \propto -R_c^3 \nabla(\rho k_B T)$ and

$$U = \frac{F}{6\pi\eta R_c} \propto -\left(\frac{R_c}{R}\right)^2 \frac{\phi_p k_B T}{\eta R} \nabla \ln \rho_p$$

- The estimation (a few $\mu m/s$) is wrong ($(R_c/R)^2$ larger) because it neglects solvent backflow.

Refined estimations and minimal model.

- For the drying film the needed Peclet number is

  $$Pe_{film} = \frac{v_{ev} h_0}{D_p}$$

  if $Pe_{film} < 1$ drying is slower than diffusion, and the concentration gradient will be smoothed out. For $Pe_{film} > 1$ accumulation of polymer particles below the descending interface maintains the concentration gradient and diffusio-phoresis.
- Zero step approach is diffusion of ideal gas in front of a moving impermeable wall

  $$\frac{\partial \phi_p}{\partial t} = D_p \frac{\partial^2 \phi_p}{\partial z^2}$$

  The bottom wall is fixed at $z = 0$, the top wall is the solvent/air interface $z_{int}(t) = h_0 - v_{ev} t \equiv (1 - t^*) h_0$ ($t^* = v_{ev} t / h_0$).
- In the limit $Pe_{film} \gg 1$ (in the regime $h_0 \to \infty$)

  $$U(z, t) = -v_{ev} Pe_{film} \phi_0 t^* \exp[-|z - z_{int}|/(D_p/v_{ev})]$$

  (ϕ_0 is initial, $t = 0$ uniform packing fraction, and BCs : zero flux at $z = 0$ and v_{ev} at $z = z_{int}$).

$Pe_{film} - \phi_0$ phase diagram.

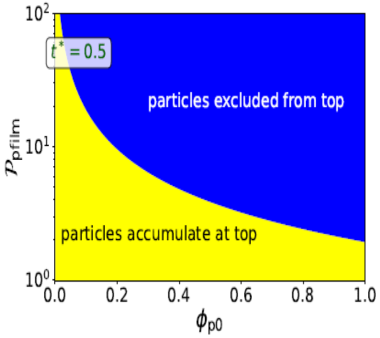


FIGURE – The region where the large particles accumulate at the descending interface at the top of the drying film (yellow), and the region where the large particles are excluded from the region at the top of drying film just below the interface (blue).

Qualitative estimations of the colloidal particles speed.

- The speed of a particle of diameter d depends on the balance between the force $f(d)$ and the drag $\xi(d)$. Let a majority species of diameter d_m dominates the osmotic pressure P.
- In the presence of a pressure gradient dP/dz the difference in pressure between the top and the bottom of a particle is $d(dP/dz)$, so the net downward force on the particle $f(d) \simeq d^3 dP/dz$.
- The friction coefficient is $\xi(\phi, d) = K(\phi, d)\xi_0$, where $\xi_0 = 3\pi d\nu$, ν is water viscosity, ϕ is particle volume fraction, $K(\phi, d)$ is the sedimentation coefficient.
- At any point, the majority species will be pushed away from the interface at the speed $v(d_m) = f(d_m)/\xi(d_m)$.
- Segregation of the other particles is determined by their velocity relative to that of of the dominant species. At low density (when $K \simeq 1$: $\Delta v(d_t) = v(d_t) - v(d_m) \simeq v(d_m)[(d_t^2/d_m^2) - 1]$.
- Species larger than d_m move down faster, and smaller size species move down slower (i.e., segregation with larger particles at the bottom and smaller particles accumulating at the top).