

Phase Separation in Binary Nearly-Hard-Sphere Colloids: Evidence for the Depletion Force.

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Abstract. – A binary aqueous suspension of large (L) and small (S) nearly-hard-sphere colloidal polystyrene spheres is shown to segregate spontaneously into L-rich and S-rich regions for suitable choices of volume fraction and size ratio. This is the first observation of such purely entropic phase separation of chemically identical species in which at least one component remains fluid. Simple theoretical arguments are presented to make this effect plausible.

Can a mixture of large (L) and small (S) hard spheres, chemically identical and with no other interaction, separate spontaneously, at volume fractions typical for a fluid phase, into L-rich and S-rich regions? Surprisingly, the answer to this question appears to be YES. In this letter, we present the first unambiguous experimental evidence [1] for this effect. The system we studied was a binary aqueous suspension of polystyrene spheres (radii 4.0 μm and 0.8 μm), and our method was direct visual observation through an optical microscope. Our system is for all practical purposes in the hard-sphere limit: the Coulomb interaction has been thoroughly screened out. We comment on this near the end of the article. Our results confirm the recent liquid-theory arguments of Biben and Hansen [2,3] and of Asakura and Oosawa [4], and complement earlier experiments by Sperry [5], Vincent *et al.* [5], Gas *et al.* [6], and Bibette *et al.* [7] on chemically distinct species, and the simulations of de Kuijper *et al.* [8] on repulsive « α -exp-6» mixtures.

We describe our experimental procedure and results in detail below. First let us make plausible the idea of fluid phase separation in a system with purely repulsive interactions, in particular, hard spheres. Consider a mixture of two types of particles (colloids, polymer chains, soft spheres, ...), with effective sizes r_1 and r_2 ($r_1 > r_2$), and volume fractions ϕ_1 and ϕ_2 . If two large particles get within $2(r_1 + r_2)$ of each other, a smaller particle cannot enter

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the region in between. Part of the surface of each large particle is now off-limits to the smaller particles. The osmotic pressure of the small particles on the larger ones is thus unbalanced and drives the large particles together. Integrating (over the accessible surface of the large spheres) the component of the osmotic pressure force along the line joining the centres of the large spheres gives the effective force of attraction. The corresponding potential [4, 9] has a depth of

$$U = 1.5k_B T \phi_2 r_1 / r_2, \quad (1)$$

and width $2r_2$, where T is the temperature. We see that U can, in principle, be of order $k_B T$ for arbitrarily small volume fraction of small particles, provided the radius ratio is large enough! For $U/k_B T \approx 1$, a condensation of large particles should occur as ϕ_1 is increased to typical liquid-phase values. The above potential has been used in effective-hard-sphere calculations of phase diagrams for polymer-colloid mixtures [6] as well as for emulsion droplets suspended in a micellar solution [7], and the results compare tolerably well with experiment. Nonetheless, the approach is clearly unsatisfactory from a fundamental point of view.

An alternative and more general approach can be taken, namely that of density functionals [10, 2, 3]. Ideally, we would like to calculate $S_{\text{eff}}(q)$, the *effective* static structure factor for the large particles, by integrating out the small-particle density field, at least in the limit of $\phi_2 \ll 1$. Although we cannot do this exactly, a Gaussian approximation readily gives

$$S_{\text{eff}}(q) = [1 - \rho_{10} C_{11}(q) - \rho_{10} \rho_{20} S_{22}(q) [C_{12}(q)]^2]^{-1}, \quad (2)$$

where ρ_{10} and ρ_{20} are the mean number densities of big and small particles, $C_{ij}(q)$ ($i, j = 1$ or 2) are the partial direct pair correlation functions, and S_{22} is the partial structure factor for the small particles. We see that irrespective of the nature of the interactions in the system, the magnitude of the large-particle structure factor is *increased* by the presence of the small particles. Specifically for the case of the hard spheres of radii r_1 , r_2 ($r_1 > r_2$) with $\phi_2 \ll 1$ (so that $S_{22}(q) = 1$), a highly simplified calculation which uses excluded volume in a crucial way gives [11]

$$C_{12}(q = 0) = -\frac{4\pi}{3} r_1^3, \quad (3)$$

so that

$$S_{\text{eff}}^{-1}(q = 0) = 1 - \rho_{10} C_{11}(q = 0) - \phi_1 \phi_2 \left(\frac{r_1}{r_2} \right)^3. \quad (4)$$

While this cannot be taken seriously for large values of r_1/r_2 (since the estimated $S_{\text{eff}}(q)$ would become negative), the trend suggests that once r_1/r_2 is big enough, the resulting growth in the osmotic compressibility of the large particles will cause them to condense. We plan to develop this approach elsewhere. For now we shall content ourselves with these qualitative arguments, and go on next to describe our experiment.

We began with two commercial samples (M/s Bang Laboratories, Inc., USA) of monodisperse ($\pm 1\%$) aqueous suspensions of polystyrene spheres («polyballs») of diameters $4 \mu\text{m}$ and $0.8 \mu\text{m}$, each at 1% volume fraction. The samples contained substantial amounts of ionic impurities, which is desirable from our point of view, because they screen the Coulomb interaction between the polyballs to the point where they can be treated essentially as hard spheres. The measured ionic conductivities (σ) were $88.1 \mu\text{S cm}^{-1}$ and $27.1 \mu\text{S cm}^{-1}$ for $0.8 \mu\text{m}$ and $4 \mu\text{m}$ starting suspensions, respectively. Assuming all the small ions to be H^+ , one can estimate the ionic concentrations n (cm^{-3}) = σ (S cm^{-1})/ Λ ($\text{S cm}^2 \text{ mol}^{-1}$), where Λ is the molar conductivity (for H^+ , $\Lambda = 349.8 \text{ S cm}^2 \text{ mol}^{-1}$; for K^+ , $\Lambda = 73.5 \text{ S cm}^2 \text{ mol}^{-1}$). Using these, one

gets $\kappa \times \text{diameter} \sim 30$ (or $\kappa a_s = 117$) for the $0.8 \mu\text{m}$ suspension and ~ 85 (or $\kappa a_s = 315$) for the $4 \mu\text{m}$ suspension, where $a_s = (\text{particle concentration})^{-1/3}$ is the nearest-neighbour distance, showing that the width of the Debye layer κ^{-1} is much smaller than both the diameters and the separation between the spheres. Hence the particles can be regarded as nearly hard spheres. We then prepared three samples by mixing a volume V_b of the large-particle suspension with a volume V_s of the small-particle suspension, with $V_b:V_s = 80:20$ in one sample, $50:50$ in another, and $20:80$ in the third. In all three cases, when the samples were stored at room temperature ($\approx 295 \text{ K}$) in sealed containers for 2-3 days we observed flocculation of the large particles, clearly seen in an optical microscope at $285 \times$ magnification (fig. 1a)). We claim that this is phase separation of large hard spheres caused by the depletion mechanism described above, and we now justify this claim.

First, the attentive reader may have noted that at the nominal volume fraction of 1%, with $r_1/r_2 = 5$, the depth of the «depletion well» should be $\approx 0.075k_B T$ from eq. (1), and hence no phase separation should be seen. This is in principle correct but it happens that polystyrene spheres (density $\approx 1.05 \text{ gm cm}^{-3}$) are heavier than water, and will therefore sediment given enough time. In the sediment (consisting of small *and* large particles) the volume fraction of both species is much higher, typically of order 0.5. It is only in the sediment that the phase separation should occur and, sure enough, that is the only place where we see it.

Secondly, we studied single-component samples from the same stock solution, which also undergo sedimentation. *No* evidence of flocculation was found in these, even after several days. This is important for the following reasons. Our suspensions, although *effectively* hard spheres, are actually charge stabilized. The Yukawa potential which stabilizes them has a very short screening length, so that it decays to zero very close to the surface of the particles. This means that we are justified in treating the particles as hard spheres, *provided* that the very narrow primary minimum in the combined hard-core, Yukawa and London-van der Waals potential [12] occurring within $(5 \div 10) \text{ \AA}$ of the surface can be neglected. The fact that one-component samples do not flocculate assures us that we can indeed neglect this primary minimum. It follows also that the flocculation seen in the two-component case is *not* due to the residual van der Waals attraction. We are left with no other explanation but the depletion force.

Thirdly, we suppressed the sedimentation completely, by raising the solvent density to match that of the polyballs. This was done by adding a calculated amount of pure D_2O (density $\approx 1.1 \text{ gm cm}^{-3}$) to the water. In these samples no sedimentation was seen, *and* no flocculation was seen either (fig. 1b)).

One might wonder whether our particles have truly additive effective hard-sphere potentials. For example, if the effective hard-repulsion distances d_{ij} between particles of type i and

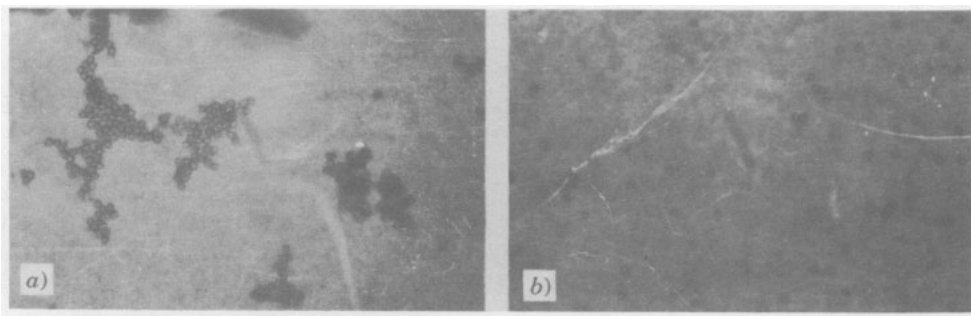


Fig. 1. - a) Flocculation of the $4 \mu\text{m}$ polyballs in the sedimented region of a 1:1 mixture of $4 \mu\text{m}$ and $0.8 \mu\text{m}$ diameter polystyrene almost hard spheres suspended in H_2O . b) Clear absence of flocculation when the same mixture as in fig. 1a) is suspended in a density-matched $\text{D}_2\text{O} + \text{H}_2\text{O}$ solvent.

j do not satisfy $d_{ij} = d_{ii} + d_{jj}$, then phase separation might still result, but not strictly because of depletion. We see no reason for this in our case, especially since the screening lengths κ^{-1} are so much smaller than the particle sizes and since the *effective* particle size should be simply the original particle size plus a species-independent screening length. Further justification can only come from a detailed comparison of experiment with the predictions of a strictly additive binary hard-sphere model.

We should point out that the condensate of large particles (fig. 1a)) seems to be in the solid phase, while the small particles (which, although visible in the microscope, do not show up in the photograph) are in a fluid phase. This is consistent with the arguments of Hall and Stell [13] which suggest that a fluid-fluid transition should be seen only if $r_1/r_2 < 3$.

Despite our limited data, we believe the experiment we have described and the checks we have applied give the first conclusive evidence for the condensation of large hard spheres from a mixture of chemically identical large and small hard spheres.

Further experimental and theoretical studies of the phase diagram over a range of radius ratios and volume fractions are in progress, and will greatly increase our understanding of this remarkable phenomenon. In particular, it will be interesting to see whether a gas-liquid phase boundary can be found for some range of radius ratios.

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