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Binary colloidal nanoparticles with a large size ratio in analytical ultracentrifugation

Xufeng Xu,^[a, b] and Helmut Cölfen^{*[a]}

Sedimenting colloidal particles may feel a surprisingly strong buoyancy in a mixture with other particles of a considerably larger size. In this paper we investigated the buoyancy of colloidal particles in a concentrated binary suspension *in situ* in a centrifugal field. After dispersing two different fluorescence-labeled silica nanoparticles with a large size ratio (90 nm and 30 nm, size ratio = 3) in a refractive index matching solvent, we used a multi-wavelength analytical ultracentrifuge to measure the concentration gradients of both particles *in situ*. The concentration of the 90 nm silica nanoparticles was used to calculate the effective solvent density for the 30 nm silica nanoparticles. The exponential Boltzmann equation for the sedimentation-diffusion equilibrium with locally varying effective solvent density was then used to theoretically predict the concentration gradient of 30 nm silica nanoparticles, which describes the experimental results very well. This finding proves the validity of effective buoyancy in colloidal mixtures and provides a good model to study sedimenting polydisperse colloids.

Colloidal particles in a natural settling are mostly of high polydispersity as species of varied sizes are dispersed in the same suspension. These polydisperse systems are nonetheless capable of remarkable self-organization, including the formation of crystalline structures such as opals^[1] or demixing into different layers of higher monodispersity^[2–4]. In recent years, researchers have been investigating colloidal mixtures of different sizes^[5–7] to model natural polydisperse colloidal particle behavior in settling processes. It was found that by carefully tuning the size ratio colloidal mixtures of two different sizes may form a variety of binary crystalline structures^[8–10] inspired by the opal formation^[11]. Several unexpected physical phenomena^[12,13] were also observed when the colloidal particles of different sizes settled in the dispersion. The standard Archimedes principle might even become invalid as it was found that the solvent density felt by particles may change due to the presence of other particles^[14]. Due to the solvent density change, the smaller particles in the suspension may even be levitated, which is known as effective buoyancy^[15].

The effective buoyancy was theoretically investigated by P. Biesheuvel et al and R. Piazza et al^[16,17]. They studied the behavior of a sedimenting colloidal particle mixture of unequal sizes and found that the bigger particles in the mixture contributed to the effective solvent density felt by the smaller particles. As the

effective solvent density increased with the concentration of the bigger particles, it even became possible for the smaller particles to be levitated in a dispersion of concentrated bigger particles. In the sedimentation-diffusion equilibrium the total force acting on the particles was cancelled out, which was expressed in Equation (1). The osmotic pressure gradient was described as given in Equation (2) by modifying the Gibbs-Duhem (GD) equation^[18].

$$F_i^{tot} = \frac{k_B T}{\phi_i} \frac{\partial \phi_i}{\partial r} - \frac{\partial \mu_i^{exc}}{\partial r} - v_i (\rho_i - \rho_F) g = 0 \quad (1)$$

$$\frac{\partial \Pi}{\partial r} = -g (\rho_{susp} - \rho_F) \quad (2)$$

$$\rho_{susp} = \rho_F + \sum_i \phi_i (\rho_i - \rho_F) \quad (3)$$

Where F_i^{tot} is the total force acting on the particle, ϕ_i , v_i and μ_i^{exc} are the volume fraction, volume and excess chemical potential of species i , ρ_i , ρ_{susp} and ρ_F are the density of species i , suspension and pure fluid respectively, Π is the osmotic pressure, r is a radial position, g is the acceleration due to gravity. As shown in Equation (3), ρ_{susp} is the volume average density of a mixture, averaging over all the particle types and the fluid. Experimentally, R. Piazza et al used a quite simple and intuitive turbidity measurement for a very diluted dispersion of a copolymer fluid of poly-tetrafluoroethylene and gold particles to test the theory^[17]. This buoyancy of small particles in a centrifugal field was also found by M. Chen et al^[19]. She observed that after the sedimentation of a binary mixture of polystyrene nanoparticles (150 nm and 300 nm), it became difficult to spot the smaller nanoparticles at the bottom of the sediment. The reason for this might be that most of the smaller nanoparticles were lifted to the upper part of the sediment. More specifically, near the bottom the high concentration of the bigger nanoparticles increased the effective solvent density dramatically, which then induced a strong buoyancy felt by the smaller nanoparticles. Besides the theoretical and limited experimental work, there is still a lack of thorough and quantitative investigation of the buoyancy effect in a concentrated binary colloidal nanoparticle suspension. In this paper, we dispersed two different fluorescence-labeled (fluorescein isothiocyanate (FITC) and rhodamine B isothiocyanate (RITC)) silica nanoparticles (SNPs) in a refractive index matching solvent of 80 vol% glycerol and 20 vol% water so that we could measure the separate concentrations of the binary SNPs of a large size ratio (90 nm and 30 nm, size ratio = 3) at a total concentration as high as 10 vol% using a multi-wavelength (MWL) UV-Vis detector^[20–22] embedded in the analytical ultracentrifuge (AUC). A centrifugal field was applied to the binary SNPs suspension and, after the sedimentation-diffusion equilibrium^[23] (AUC-SE) was reached, the individual concentration gradients were measured for the two different nanoparticle species using a procedure described in a recent publication^[24]. It was observed that at some radial position, the buoyancy of 30 nm RITC-SNPs started to appear and proceeded. This was demonstrated by a flattening of the concentration gradient with increasing concentration of 90 nm FITC-SNPs. Quantitatively speaking, using the ‘generalized Archimedes’ principle’ (GAP) by R. Piazza^[15,17], the effective density was calculated based on the concentration of 90 nm FITC-SNPs. The calculated effective density was then plugged into the exponential concentration distribution^[25,26]. By these

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means the concentration gradient of 30 nm RITC-SNPs can be effectively buoyancy corrected. In this way the buoyancy effect was theoretically predicted and the calculated concentration gradient agreed with the experimental data. Our binary SNPs of a large size ratio in a concentrated suspension, therefore, provide a good model to study polydisperse colloidal particle behavior in a centrifugal field or in natural sedimentation.

We first analyzed the concentration gradients of the monodisperse dispersions of 90 nm FITC-SNPs and 30 nm RITC-SNPs respectively in AUC-SE experiments. For a very diluted dispersion, the dispersion behaves ideally^[27] and the resulting concentration gradient in the AUC-SE simply follows the exponential concentration distribution^[28]. At a higher concentration, the second osmotic virial coefficient A_2 needs to be included in the exponential equation to account for the non-ideality^[27]. For diluted 30 nm and 90 nm SNPs dispersions with concentrations as low as 0.5 vol%, Equation (4) was used to fit the experimental concentration profile^[28]:

$$c(r) = c(r_1) \exp\left(\frac{r^2 - r_1^2}{2L_\omega^2}\right) \quad (4)$$

$$L_\omega = \sqrt{\frac{kT}{v(\rho_p - \rho_s)\omega^2}} \quad (5)$$

where:

r is an arbitrary radial position and $c(r)$ is the corresponding nanoparticle concentration;

r_1 is a reference radial position and $c(r_1)$ is the corresponding nanoparticle concentration

L_ω is the so-called centrifugal length

ρ_p is the colloidal particle density

ρ_s is the solvent density

v is the volume of one particle

ω is the angular velocity of the ultracentrifuge

Figure 1: Experimental (black line) and fitted (red line) concentration gradients for A) 90 nm SNPs and B) 30 nm SNPs of 0.5 vol% in an AUC at 1100 rpm, 25 °C. The blue dashed lines indicate the residuals, which equal the difference of experimental and fitted data.

In **Figure 1A** the data was fitted using Equation (4) and $L_\omega = 0.153$ cm was converted to the particle diameter $d = 87.6$ nm by using Equation (5). The particle diameter independently measured by scanning electron microscopy (SEM) in **Figure S1** was 84.0 ± 7.7 nm. The size distribution from the two independent measurements agreed with the relative deviation of ca. 4%. In **Figure 1B**, the fitted particle diameter $d = 33.7$ nm deviated ca. 10% from the size ($= 30$ nm) measured by the sedimentation velocity experiment (AUC-SV) in our previous publication^[24]. The concentration gradient of a SNPs dispersion of a concentration as high as up to 30 vol% could be fitted with non-ideality including exponential Boltzmann distribution^[29]. This is how it was possible to obtain the knowledge about the second virial coefficient A_2 ^[24]. Overall, the exponential Boltzmann distribution worked well when using the constant solvent density (1.2 g/cm³ for the glycerol and water mixture) for the monodisperse dispersions of 90 nm and 30 nm SNPs.

Proceeding to the binary suspension of 30 nm and 90 nm SNPs at a high concentration (1 vol% and 9 vol% separately and 10 vol% in total), the solvent density could not be considered constant anymore because under these conditions the effective buoyancy needed to be taken into account. Before the effective buoyancy was applied, its limits of validity were examined^[17]: 1)

30 nm SNPs could be treated as nearly hard spheres^[24] and at concentrations as low as 1 vol% the self-interaction could be totally neglected; 2) The centrifugal length of 90 nm SNPs ($L_\omega = 0.153$ cm) was much larger than both the radius of 30 nm and 90 nm SNPs; 3) Transport processes are totally avoided in an AUC-SE experiment. When these three constraints are satisfied, the GAP theory^[17] can be applied.

The fitting procedure consisted of the following two steps: Step 1 was the calculation of the effective density (ρ^*) using the Generalized Archimedes' principle (GAP). Since the binary suspension satisfied the three constraints of the GAP and the size ratio was relatively high, Equations^[17] (6), (7), and (8) were applied:

$$\rho^* - \rho = q^3 f(\varphi_2) m_2' n_2 \quad (6)$$

$$f(\varphi_2) = (1 - \varphi_2)^3 / (2(4 - \varphi_2)\varphi_2 + (1 - \varphi_2)^4) \quad (7)$$

$$m_2' = (\rho_2 - \rho) v_2 \quad (8)$$

Where:

ρ is the solvent density

ρ_2 is the silica nanoparticle density^[28]

q is the size ratio

φ_2 is the volume fraction of 90 nm SNPs

v_2 is the particle volume

n_2 is the number density of 90 nm SNPs

By these means, the effective density ρ^* was calculated from the volume fraction of 90 nm SNPs (φ_2) in **Figure S2**. In **Figure 2** the effective (solvent) density and the constant solvent density were compared. The constant solvent density remained unchanged irrespective of the presence of multiple particles while the effective density was calculated based on the concentration of 90 nm SNPs.

Figure 2: The calculated effective solvent density (solid line) and the constant solvent density (dashed line).

In Step 2, the effective density (ρ^*) modified exponential Boltzmann distribution was used:

$$c_r = c_0 * \exp\left(M \frac{\omega^2(r^2 - r_0^2)}{2RT}\right) \quad (9)$$

$$M = M_p (1 - \rho v_{\text{bar}}) \quad (10)$$

Where:

r is an arbitrary radial position and c_r is the corresponding nanoparticle concentration

r_0 is a reference radial position and c_0 is the corresponding nanoparticle concentration

ω is the angular velocity of the ultracentrifuge

M is the buoyant molar mass

M_p is the particle mass

v_{bar} is the partial specific volume of the SNPs

Finally, the two concentration gradients, using the constant density and effective density separately, were plotted in **Figure 3**. In **Figure 3A**, when the fixed solvent density ($= 1.2$ g/cm³) was applied, we found that the fitted concentration gradients agreed with the experimental profile trend in the meniscus region. However, it predicted an exponential increase which deviated severely from the flatter experimental gradient in regions closer to the bottom. In comparison, when the effective density was used, the resulting flattened concentration gradient yielded a good fit near the bottom part of the cell, but a small discrepancy between the fitted profile and experimental data was found in the meniscus region. This might result from a dramatically increasing concentration of 90 nm SNPs in this region and the associated strong hard sphere repulsion with 30 nm SNPs (**Figure S2**). **Figure 3B** was plotted to demonstrate that when using the fixed solvent density, $\ln(\text{concentration})$ followed a straight line with $r^2 - r_0^2$, while after taking into account the effective density a much flattened gradient was predicted for the bottom of the cell which agreed better with the experiment as compared to the one for constant density. Another binary suspension with different concentrations in a centrifugal field with a different angular velocity is shown in **Figure S3**. The flattened part near the bottom also agreed well with experimental data by considering the effective buoyancy. The disagreement of theory and experiment in the meniscus region was also reduced when the concentration of 90 nm SNPs was lowered to 3 vol%, suppressing the hard sphere repulsion between 30 nm and 90 nm SNPs. Therefore, these two examples demonstrated that by calculating the effective density using the concentration of 90 nm SNPs and replacing the constant solvent density with the varying effective value in the Boltzmann distribution, the effective buoyancy can be considered in the binary colloidal system of 30 nm and 90 nm SNPs. Overall, the unusually flattened concentration gradient of 30 nm SNPs compared to the expected one was well fitted by employing this method. However, the effective buoyancy could not be applied to 90 nm SNPs due to their relatively high concentration and accordingly significant interparticle interaction. Moreover, the effective density felt by 90 nm SNPs was insignificant due to the low concentration of 30 nm SNPs. When using Equation (11)^[17], the effective density (ρ^*) nearly equaled the pure solvent density (ρ), considering $q = 1/3$ and φ_2 was as low as only 0.01.

$$\rho^* - \rho = (1 + q)^3 (\rho_2 - \rho) \varphi_2 \quad (11)$$

Figure 3: Experimental concentration profile (black line) for 30 nm SNPs in the binary suspension of 30 nm (1 vol%) and 90 nm (9 vol%) SNPs in an AUC at 2800 rpm, 25 °C. The fitted profiles for 30 nm SNPs using the constant solvent density (blue line) and the effective density (red line). A was plotted as volume fraction vs $r_{\text{bottom}} - r$ and B was plotted as $\ln(\text{concentration})$ vs $r^2 - r_0^2$ where $r_{\text{bottom}} - r$ is the distance from the cell bottom, r_0 is the meniscus' radial position.

In summary, a binary mixture of fluorescence-labeled 30 nm and 90 nm SNPs was dispersed in a refractive index matching solvent of 80 vol% glycerol and 20 vol% water at a high total particle concentration (10 vol%) so that the concentrations of both particles could be obtained individually by measuring the absorbance spectra in an MWL UV-vis optics embedded AUC. By applying the principle of effective buoyancy^[30], the constant solvent density was replaced by a locally varying density which depended on the local concentration of 90 nm SNPs. The calculated effective density was then plugged into the exponential Boltzmann distribution and the locally density-corrected concentration gradients of 30 nm SNPs were calculated. The theoretically calculated profile was a good fit for the experimental concentration profile. The good quality of the fitted result was demonstrated by plotting $\ln(\text{concentration})$ vs $r^2 - r_0^2$. When considering a fixed density, the plot was linear which clearly deviated from the experimental data, while using the effective density the flattened experimental gradient was predicted well, especially for the bottom part of the cell. These findings proved the validity of the effective buoyancy in a binary colloidal nanoparticle dispersion, especially of a large size ratio and at a high concentration. For settling colloidal dispersions in practical

cases^[31,32], the size polydispersity and the concentration are normally both high. Thus, the effective density needs to be considered for the colloidal particle behavior. In Conclusion, our investigated system and the results provide a good model to study sedimenting polydisperse colloidal particles in natural and industrial cases.

Experimental Section

Synthesis of 30 nm and 90 nm fluorescence-labeled silica nanoparticles (SNPs): The reaction vessels were cleaned and dried in an oven for further use. Rhodamine isothiocyanate (RITC) and APS (aminopropyltriethoxysilane) conjugate was prepared in the clean vessel by reacting the fluorescence and a two-fold amount of APS in dehydrated ethanol under an inert argon environment with continuous stirring for more than 17 hours. In a clean 50 ml three necked flask, 17 ml of water and 17.4 mg of arginine were mixed with the RITC/APS conjugate and then 1.11 ml of tetraethyl orthosilicate (TEOS) were added slowly beneath the solution surface by a syringe. The reaction proceeded at 70 °C for 24 hours^[24]. 30 nm RITC-labeled SNPs were synthesized. 90 nm fluorescein isothiocyanate (FITC) labeled SNPs were synthesized by the further growth of the 30 nm seed particles. In detail, 80 mg arginine, 22.5 ml water, 90 ml ethanol, 1.8 ml 30 nm SNPs dispersion and 0.55 g tetraethyl orthosilicate (TEOS) were added to a clean 250 ml glass reaction vessel. The reaction proceeded at 70 °C for 5 hours with continuous stirring. Thereafter, 0.55 g more TEOS was added and the reaction proceeded overnight, resulting in 90 nm FITC-labeled SNPs.

In a typical sedimentation-diffusion equilibrium (AUC-SE) experiment, a 3 μ l sample and reference were separately injected into the two channels of an AUC cell of 1.5 mm path length. The AUC cell was then placed into a custom-made^[21,33] Multi-Wavelength Analytical Ultracentrifuge (MWL-AUC). The measurement settings: Temperature 25 °C; wavelength range 350 – 700 nm. After a time scale of up to one week, the sedimentation-diffusion equilibrium was reached^[24].

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Keywords: Analytical ultracentrifugation • Binary colloidal nanoparticles • Effective buoyancy • Generalized Archimedes' principle • High concentration

- [1] J. V. Sanders, M. J. Murray, *Nature*. **1978**, 275, 201-203.
- [2] F. Rietz, R. Stannarius, *Phys Rev Lett*. **2008**, 100, 078002.
- [3] J. B. Knight, E. E. Ehrichs, V. Y. Kuperman, J. K. Flint, H. M. Jaeger, S. R. Nagel, *Phys Rev E Stat Phys Plasmas Fluids Relat Interdiscip Topics*. **1996**, 54, 5726-5738.
- [4] A. P. Breu, H.-M. Ensner, C. A. Kruelle, I. Rehberg, *Physical review letters*. **2003**, 90, 014302.
- [5] Y. Xia, T. D. Nguyen, M. Yang, B. Lee, A. Santos, P. Podsiadlo, Z. Tang, S. C. Glotzer, N. A. Kotov, *Nat Nanotechnol*. **2011**, 6, 580-587.
- [6] S. Belli, A. Patti, M. Dijkstra, R. van Roij, *Physical Review Letters*. **2011**, 107, 148303.

- [7] B. Cabane, J. Li, F. Artzner, R. Botet, C. Labbez, G. Bareigts, M. Sztucki, L. Goehring, *Physical Review Letters*. **2016**, 116, 208001.
- [8] P. Bartlett, R. H. Ottewill, P. N. Pusey, *Physical Review Letters*. **1992**, 68, 3801-3804.
- [9] M. Eldridge, P. Madden, P. Pusey, P. Bartlett, *Molecular Physics*. **1995**, 84, 395-420.
- [10] E. V. Shevchenko, D. V. Talapin, N. A. Kotov, S. O'Brien, C. B. Murray, *Nature*. **2006**, 439, 55-59.
- [11] P. C. Ohara, D. V. Leff, J. R. Heath, W. M. Gelbart, *Phys Rev Lett*. **1995**, 75, 3466-3469.
- [12] A. P. Philipse, G. H. Koenderink, *Advances in Colloid and Interface Science*. **2003**, 100-102, 613-639.
- [13] C. G. Serrano, J. J. McDermott, D. Velegol, *Nature materials*. **2011**, 10, 716-721.
- [14] M. Ruzicka, *Chemical engineering science*. **2006**, 61, 2437-2446.
- [15] R. Piazza, *Reports on Progress in Physics*. **2014**, 77, 056602.
- [16] P. Biesheuvel, J. Lyklema, *Journal of Physics: Condensed Matter*. **2005**, 17, 6337-6352.
- [17] R. Piazza, S. Buzzaccaro, E. Secchi, A. Parola, *Physical biology*. **2013**, 10, 045005.
- [18] E. Spruijt, P. M. Biesheuvel, *Journal of Physics: Condensed Matter*. **2014**, 26, 075101.
- [19] M. Chen, H. Cölfen, S. Polarz, *ACS nano*. **2015**, 9, 6944-6950.
- [20] E. Karabudak, H. Cölfen in *The Multiwavelength UV/Vis Detector: New Possibilities with an Added Spectral Dimension*, Vol. 5 (Eds.: S. Uchiyama, F. Arisaka, W. F. Stafford, T. Laue), Springer Japan, Tokyo, **2016**, pp.63-80.
- [21] J. Pearson, J. Walter, W. Peukert, H. Cölfen, *Analytical chemistry*. **2018**, 90, 1280-1291.
- [22] J. Walter, K. Löhr, E. Karabudak, W. Reis, J. Mikhael, W. Peukert, W. Wohleben, H. Cölfen, *ACS nano*. **2014**, 8, 8871-8886.
- [23] H. Zhao, C. A. Brautigam, R. Ghirlando, P. Schuck, *Current protocols in protein science*. **2013**, 20.12, 21-20.12, 49.
- [24] X. Xu, T. Franke, K. Schilling, N. Sommerdijk, H. Cölfen, *Nano Lett*. **2019**, 19, 1136-1142.
- [25] K. L. Planken, H. Cölfen, *Nanoscale*. **2010**, 2, 1849-1869.
- [26] O. Lamm, *Zeitschrift für Physikalische Chemie*. **1929**, 143, 177-190.
- [27] J. L. Cole, J. J. Correia, W. F. Stafford, *Biophysical Chemistry*. **2011**, 159, 120-128.
- [28] M. Rasa, B. Ern, B. Zoetekouw, R. van Roij, A. Philipse, *Journal of Physics: Condensed Matter*. **2005**, 17, 2293-2314.
- [29] H. Cölfen in *Analytical ultracentrifugation of colloids*, Vol. 23 (Ed. D. J. SCOTT, ed. and others), Cambridge: Royal Society of Chemistry, UK, **2005**, pp.501-583.
- [30] R. Piazza, S. Buzzaccaro, E. Secchi, A. Parola, *Soft Matter*. **2012**, 8, 7112-7115.
- [31] W. W.-F. Leung, *Industrial centrifugation technology*, McGraw-Hill New York, **1998**.
- [32] P. Y. Julien, *Erosion and sedimentation*, Cambridge University Press, **2010**.
- [33] J. Pearson, M. Hofstetter, T. Dekorsy, M. Totzeck, H. Cölfen, *Analyst*. **2018**, 143, 4040-4050.

COMMUNICATION

Effective buoyancy: Sedimenting colloidal particles may feel surprisingly strong buoyancy in a mixture with other particles of a considerably larger size. We use a multi-wavelength analytical ultracentrifuge to measure and fit the effective buoyancy effect in the sedimentation-diffusion equilibrium for the binary suspension of 30 nm and 90 nm silica nanoparticles at a high concentration.

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