

Transfer of colloidal particles between two non-miscible liquid phases

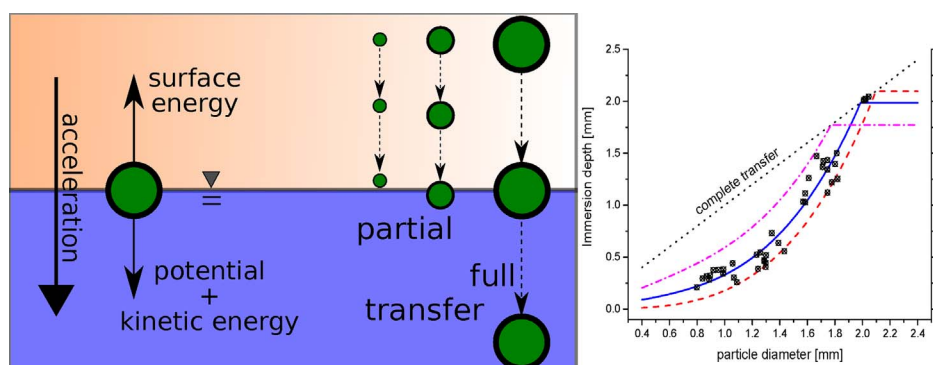


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GRAPHICAL ABSTRACT



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ABSTRACT

This work investigates a direct transfer of dispersed particles into another dispersion medium. The transfer is realized by layering the suspension above a second, non-miscible liquid. The particles are then transferred by centrifugation or mere sedimentation. The transfer is, unlike a liquid-liquid extraction, not only driven by thermodynamic effects such as favorable solubility, but is based on an additional mechanical work input. Here the transfer of a colloidal particle system is discussed on the example of SiO₂ particle dispersions with regards to the influence of particle size, viscosity, density and an emphasis on the effects of interfacial forces. For small particles it was found that hydrophilic and hydrophobic forces dominate and hinder the transfer as particles adsorb to the interface, which can be countered by an increase of centrifugation forces or reduction of surface forces with surfactants. The transfer is described in detail with a model to lay out the influence of all parameters, revealing a threshold size for a successful transfer at given conditions. The model is applied and tested on different SiO₂ suspensions for verification.

1. Introduction

Colloidal nanoparticles are commonly used in industrial applications and products. The properties of those colloidal systems are mainly governed by their size in the micron- to nanometer range. In this size domain, the extremely large surface area leads to desired or beneficial effects that are utilized for scientific or industrial applications. The

colloidal stability is highly dependent on the interaction of the surface with the continuous phase [1,2]. In order to be stable, there have to be either repulsive forces in form of electrostatic or steric hindrance between the particles or a reduction in mobility by increasing the viscosity of the continuous phase. There are several examples for a necessary change of the continuous phase by buffer exchange, re-suspension or transfer. This transfer can be done by mechanical separation with

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filtration and thermal drying followed by re-dispersion, which often leads to aggregation during the process. The exposure of the particles to a gas phase can also have a negative impact with occurring reactions or oxidation. Once repulsive forces, as described by DLVO theory, are overcome, the particle-particle adhesion is too strong to reverse the particles to a homogenous distribution. A more direct approach is the immediate transfer by sedimentation, layering the suspension above a second liquid without mixing and forcing the particles to transfer by introducing a directional acceleration with a centrifuge. When the position of the particles is monitored, the centrifugal force can be adjusted until there is a successful transfer.

The technical application of a direct phase transfer has several potential options. It can be used for a) an immediate change of the continuous phase i.e. for storage after synthesis, avoiding prolonging and complicated procedures, b) as an analytical procedure to measure the force needed to transfer, quantifying the work needed and thereby quantifying a hydrophobic or –philic force, c) a way to coat particles, when the surface will be covered by educts present in the continuous phase and d) as a mean to produce liposomes from an emulsion, where aqueous emulsion droplets are transferred into a continuous water phase.

A transfer of colloidal particles is described in literature for a number of different particle systems, but is usually based on the higher affinity of a solute to an extract, regularly implying a chemical reaction, making it de facto a liquid-liquid phase extraction. Vigorous stirring or mixing will expose the particles to the extraction phase, which then remain in the extract due to better solubility. This is especially the case for metal based colloids like Au, Ag, Pt, Pd and magnetite particles, which has been described extensively [3–9]. All processes have in common that surfactants, salts or other reactants are used to modify the particle surface or the interface. A “spontaneous” transfer of Au and Pd particles from toluene to water by the use of reversible binding 4-dimethyl-aminopyridine is described by Gittins et al., emphasizing the advantage of reversibility over covalent binding or precipitation protocols [5]. Zhao et al. and Manchunsky et al. use centrifugation to propagate the transfer, but still depend on at least one additional excipient that does modify the particle surface [6,7]. The choice of surfactant has a large impact on the transfer yield and agglomeration size [8,9]. Nanoparticles can be synthesized on the interface of liquid-liquid systems using the reduction in interfacial energy, which also places them easy to access for subsequent modification for transfer [3,10]. Larger particles or masses can be easily transferred through immiscible phases, as described for sediment flows loaded with sand [11], and are not dependent on interfacial forces, due to their size far above colloidal systems, while nanoparticles need ultracentrifugation to create sufficient forces in sedimentation [12].

Another example for the direct phase transfer in colloidal systems can be found in a method to produce liposomes by transferring water-in-oil emulsion droplets into an aqueous phase, as first described by Träuble et al. [13]. and further advanced by other authors [14,15]. There are discrepancies in the reports of the particle sizes, which range from several micrometers for giant unilamellar vesicles for cell sized membrane models [16,17] to nanometer range, which would be required for the use as pharmaceutical relevant liposomes [18]. Generally, studies dealing with nanoparticles are not investigating the functionality or deformation of liposomes, while successful transfer without leakage is only shown for larger models [19]. Overall, no publication is discussing the necessary centrifugation speed to transfer liposomes and do not give a success rate for the transfer, e.g. by monitoring the colloid's concentration or particle size distribution throughout the transfer.

The direct transfer faces two major challenges, which are the need to stabilize a particle in two different media, usually having an oppositional hydrophilic/hydrophobic character and the passage of the particles through the interface of the two liquids, possibly in opposition to the thermodynamically more favorable solvent. The interaction of

solvent and particle are often described by solubility parameters. One of the most established, the Hansen solubility, describes affinity of particles with solvents depending on van der Waals forces, polarity and hydrogen bonding [20]. This is put to use to stabilize nanoparticles [21,22], but is elaborate to measure. The surface energy of particles in different solvents, also in combination with surfactants, is a research topic of interest for foam and emulsion stability [23–25]. The adhesion of colloidal particles to liquid interfaces is well described in literature, mostly regarding the stabilization of interfaces in pickering emulsions [26,27]. At small sizes, the adhesion is several magnitudes larger than the thermal energy of the particles, effectively trapping them on the interface and changing the surface tension [28]. In contrast to a complete phase transfer, there are no directional forces relevant and were therefore not further considered in these publications. The wettability of nanoparticles can be measured with a Wilhelmy film balance and scanning angle reflectometry on exposed surfaces [29–31], but are not applicable at liquid-liquid interfaces. The interfacial tension changes with the adsorption of nanoparticles, which can interact strongly with surfactants, even to a synergetic extent [32–34]. Approaches to calculate the surface energy of nanoparticles at the interface are often closely related to the synthesis and reaction enthalpy [10]. With a controlled application of centrifugal force, there is the prospect to quantify the affinity of the particles to both media with a mechanical force to form a simplified and straightforward method.

During the transfer several forces act on the particles, which are highly dependent on the size. In short, for nanoparticles the surface forces are more dominating, while for larger particles volumetric forces are more relevant. This is caused in general by the ratio of surface to volume that is several magnitudes larger for nanoparticles, which is key knowledge for every consideration in colloidal technology. Here SiO₂ was used, which is available in different size distributions and can be dispersed in hydrophobic and hydrophilic media, even though it has a hydrophilic character due to the exposed oxygen group. In this particular case, particles above several millimeters were observed to easily pass the interface, while smaller particles with size distributions in the nanometer to micrometer range accumulate at the interface and do not pass immediately. It was therefore fundamental to understand the contribution of the acting forces depending on the size, which is laid out by an analytical approach to estimate the threshold forces. The approach is evaluated and matched with experimental results.

The transfer is not well described, even though used in several applications. Understanding the close dependency of the force needed for a successful transfer to size and surface energy is crucial to advance the method towards colloidal systems. The theoretical approach presented here will help to select the appropriate experimental parameters and materials for a phase transfer. Additionally the procedure of transferring particles can be beneficial as a supplementary method for quantifying affinity of a particle suspension to solvents.

2. Material and methods

The two non-miscible fluids used for proof was purified water and squalene oil (C₃₀H₅₀) from sigma-Aldrich with 98 % purity and a density of 0.89 g/ml. Colloidal particles were SiO₂ glasses with different size distributions. Macroscopic SiO₂ glass spheres “Silibeads” in the size range of 1–3 mm and a density of 2.5 g/cm³ were purchased from Sigmund Lindner AG, Germany. Colloidal particles were kindly provided by Quarzwerke GmbH, Germany, product Sikron SF300, SF600, SF800 with a mean size $d_{3,50}$ of 10, 3 and 2 μm. More detailed size distributions are attached in the supporting information Fig. S1. Suspensions were dispersed with a 400 W and 20 kHz frequency sonifier from Branson Ultrasonics. The suspension was layered carefully on top of a water phase of WFI grade quality. The phase transfer of micron sized particles was monitored with a Stingray F033 B camera system from Allied Vision Technologies GmbH, which was also used for contact angle measurements. For colloidal dispersions the phase transfer was

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