



# Equilibrium orientations of non-spherical and chemically anisotropic particles at liquid–liquid interfaces and the effect on emulsion stability

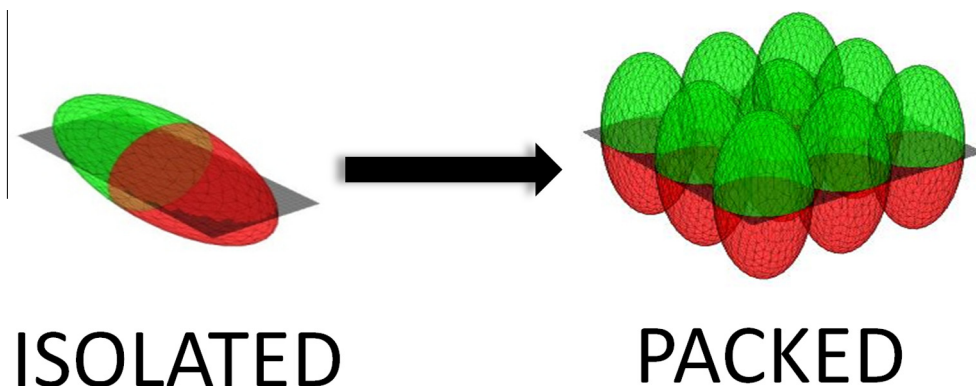


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## GRAPHICAL ABSTRACT



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## ABSTRACT

The effective stabilization of emulsions by solid particles, a phenomenon known as Pickering stabilization, is well known to be highly dependent on the wettability and the adhesion energy of the stabilizer employed at the liquid–liquid interface. We present a user-friendly computational model that can be used to determine equilibrium orientations and the adhesion energy of colloidal particles at interfaces. The model determines the free energy profile of particle adsorption at liquid–liquid interfaces using a triangular tessellation scheme. We demonstrate the use of the model, using a variety of anisotropic particles and demonstrate its ability to predict and explain experimental observations of particle behaviour at interfaces. In particular, we show that the concept of hydrophilic lipophilic balance commonly applied to molecular surfactants is insufficient to explain the complexity of the activity of colloidal particles at interfaces. In addition, we show the importance of the knowledge of the free energy adsorption profile of single particles at interfaces and the impact on overall free energy of emulsification of packed ensembles of particles. The delicate balance between optimization of adhesion energy, adsorption dynamics and particle packing is shown to be of great importance in the formation of thermodynamically stable emulsions. In order to use the model, the code is implemented by freely available software that can be readily deployed on personal computers.

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## 1. Introduction

The ability of particles to adsorb onto soft, deformable interfaces, for example to adhere to and thus stabilize emulsion droplets, has been studied in great detail since the inception of the topic over 100 years ago by Ramsden and Pickering [1,2]. They found that inorganic particulates were capable of emulsifying oils and serve as surfactants, and noted that particle stabilized emulsions were often superior, in terms of resistance to de-emulsification, to emulsions that use molecular surfactants. A quantitative theoretical description of this effect was given by Pieranski for the case of a sphere of uniform surface tension in the absence of any imposed external force fields [3]. He demonstrated that the main cause of particle adhesion to the interface was due to energy minimization as a result of removal of an area of liquid–liquid interface and that, as a result of this, the energy to remove a particle from the interface is typically much greater than  $k_B T$ , rendering particle adhesion often effectively irreversible.

One important factor in the stability of the emulsions and foam materials listed above is the particle morphology and surface chemistry which govern the overall particle wettability and the strength with which it is adhered to the interface [4]. Whilst spheres are the most studied particulate emulsifier experimentally, there have also been reports on the interfacial activity of discs [5–7], cylinders [7–10], ellipsoids [11–13], cubes [14–16], dumbbells [17–21] and hemispheres [22–25], aided by advances in the measurement of the adsorption of colloids to liquid–liquid interfaces [26–28]. In addition, new synthetic routes to complex nanoparticles have allowed us to explore the use of chemically anisotropic ‘Janus’ particles as surfactants [29,30]. Thus, Kim et al. used colloidal dumbbells synthesized by seeded emulsion polymerization to stabilize hydrocarbon in water emulsions and illustrated the ability of these particles to outperform spherical particles of the same surface groups [17].

The theoretical description of how such complicated nanoparticles orientate at liquid–liquid interfaces is of the utmost importance and governs the extent to which they are adsorbed, the type of emulsion and ultimately their ability to stabilize an emulsion. While the theoretical case for a sphere has been extensively researched [31–33], more complicated shape and chemically anisotropic particles present difficulties due to the extensive derivations that are required for analytical solutions as the particle shape deviates from a sphere. The case for a chemically anisotropic sphere has been studied by several groups who have shown that amphiphilic spheres orientate to minimize free energy and can potentially give thermodynamically stable emulsion systems [34–36]. Ellipsoidal and cylindrical particles have been shown to orientate according to capillary interactions between particles at interfaces and their orientation is guided by such adhesive bonds [37–39]. In addition, high aspect ratio nanocellulose has been shown to bend due to capillary interactions, inducing a very high surface coverage and highly stable emulsion systems [40].

Recently the effects of both chemical and shape anisotropy have been observed in simulations on amphiphilic cylinders and dumbbells with the orientation being dictated by the balance of shape and chemical nature of the particle surfaces [41]. We present here a program that allows users to predict surface activity of particles of any shape or chemistry in a simple user-friendly manner. The calculation is based on a triangular tessellation scheme originally introduced by de Graaf et al. [42] which allows for the free energy profile of a particle at an interface to be determined from which equilibrium orientations can be predicted. We show the application of the method to a broad spectrum of particle morphologies in the hope that it will aid in the synthesis by design of colloidal surfactants. The surface chemistry and morphologies selected

herein are chosen to exemplify the necessary factors that must be considered when designing particulate emulsifiers and to highlight the complementary nature of the effects of particle surface, shape and packing. In particular, it is shown that there are marked differences between the steric and chemical factors applied to conventional molecular surfactants and their colloidal counterparts.

## 2. Calculating the free energy surface of shape and chemically anisotropic particles

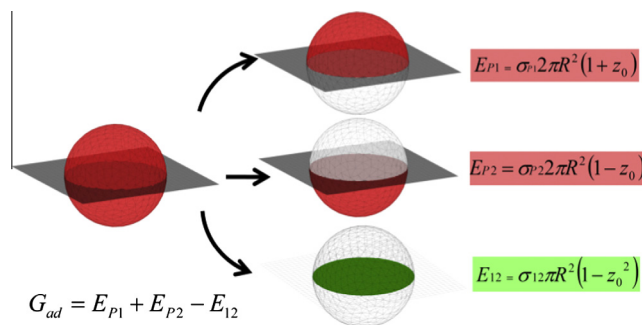
The work of Pieranski demonstrated that the surface activity of spherical colloidal particles could be explained using surface tension arguments. In essence, he demonstrated that the adsorption free energy ( $G_{ad}$ ) of a colloidal particle is equal to the sum of the three areas shown in Fig. 1 that arise from penetration of a sphere into an interface. While the case for a sphere can be easily solved analytically, upon introducing anisotropy there is often no analytical solution but the general solution (Eq. (1)) still holds.

$$G_{ad} = A_{P1}\sigma_{P1} + A_{P2}\sigma_{P2} - A_{12}\sigma_{12} \quad (1)$$

where  $A$  corresponds to area and  $\sigma$  is the interfacial tension and the subscripts correspond to the particle ( $P$ ) and liquid phases 1 and 2. Hence for a given particle position the free energy at this orientation can be calculated if the corresponding areas and interfacial tension values are known. In order to calculate the surface areas of a given particle we use a triangular tessellation scheme in which the particle surface is divided into a series of tessellating triangles that define the surface. For most particle morphologies (spheres, cubes, ellipsoids dumbbells etc.) the shape can be approximated by a superellipsoidal model where the location of the  $x, y, z$  points can be given by Eq. (2) where  $x, y$  and  $z$  denote the coordinates of the point,  $r_x, r_y$ , and  $r_z$  are the particles  $x, y$  and  $z$  radii respectively, and  $n_1$  and  $n_2$  acts as the ‘squareness’ parameter in the  $z$  axis and the  $x$ – $y$  plane respectively with  $0 < n_1, n_2 < \infty$ .

$$\left(\frac{x^{2/n_2}}{r_x} + \frac{y^{2/n_2}}{r_y}\right)^{n_2/n_1} + \frac{z^{2/n_1}}{r_z} = 1 \quad (2)$$

The details of how this can be implemented for complex particle morphologies are provided in the Supporting information. In general, the model can handle any morphology that can be processed as a series of interconnecting triangles and highly anisotropic particles can be constructed in computer aided design programs and imported easily into the program (see Fig. 2), although the assumptions of the model limit the practical applicability for certain highly complex morphologies with significant capillary interactions.



**Fig. 1.** Free energy change upon adsorption of colloidal particle of radius,  $R$ , at the liquid–liquid interface. The interface energy,  $G_{ad}$ , depends on the particle position with respect to the interface given by  $z_0$  (where  $z_0 = 1$  it is immersed in phase 1 and where  $z_0 = -1$  it is immersed in phase 2) and the various interfacial tension,  $\sigma$ , values.

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