

# Adsorption dynamics in Pickering emulsions

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## 1. INTRODUCTION

Emulsions composed of two immiscible fluids are usually prepared using surfactants. On the other hand, colloidal particles or granular materials can also stabilize macroemulsions. Such emulsions are called “Pickering emulsions” which was found about hundred years ago. Pickering emulsions are conceptually interesting because colloidal particles are surface active even though their surface is chemically homogeneous. This is in contrast with surfactants which have hydrophilic and hydrophobic parts. In this paper, we discuss the adsorption dynamics of colloidal particles to a flat liquid-liquid interface. We pay attention how the wettability of the particle with respect to the two liquids affects the adsorption kinetics.

## 2. FORMULATION

We first consider a situation in which a single spherical particle of diameter  $a$  adsorbs at an interface between liquid 1 and liquid 2. Let  $\sigma_{1p}$ ,  $\sigma_{2p}$ ,  $\sigma_{12}$  be the 1-particle, 2-particle, 1-2 interfacial tensions. Then the wettability of the colloidal particle can be defined by the following dimensionless quantity:  $\gamma \equiv (\sigma_{1p} - \sigma_{2p})/\sigma_{12}$ . Notice that the adsorption of particles occurs due to the elimination of unfavorable 1-2 interface.

As for the adsorption dynamics, we start with the following Ward–Tordai equation [1];

$$\phi_0(\tilde{t}) + \phi_1(\tilde{t}) = \frac{1}{\sqrt{\pi}} \left[ 2\phi_b \sqrt{\tilde{t}} - \int_0^{\tilde{t}} d\tau \frac{\phi_1(\tau)}{\sqrt{\tilde{t} - \tau}} \right] + 2\phi_b, \quad (1)$$

where  $\phi_0(\tilde{t})$  is the particle concentration at the interface,  $\phi_1(\tilde{t})$  is concentration at the sub-surface layer, and  $\phi_b$  is the bulk concentration. Here the dimensionless time is defined as  $\tilde{t} = Dt/a^2$ , where  $D$  is the diffusion constant. We further assume that the concentration at the interface changes according to the difference between the chemical potentials at the interface and the sub-surface layer. Based on the free energy formulation for surfactant adsorption [2], the time evolution of  $\phi_0(\tilde{t})$  is given by

$$\frac{\partial \phi_0}{\partial \tilde{t}} = \phi_1 \left[ \log \frac{\phi_1(1 - \phi_0)}{\phi_0} + \alpha(1 + \gamma)^2 + \beta\phi_0 \right], \quad (2)$$

where  $\alpha = \pi(a/2)^2\sigma_{12}/k_B T$  is the adsorption energy, and  $\beta$  is the interaction energy between the particles at the interface. We obtain  $\phi_0(t)$  and  $\phi_1(t)$  by solving Eqs. (1) and (2) simultaneously.

## 3. RESULT

By changing the particle wettability  $\gamma$ , we have numerically obtained characteristic time needed for adsorption. We show that this time scale is well explained by the asymptotic solution of the Ward–Tordai equation (1), i.e.,  $\tilde{t}^* \sim (\phi_{0,\text{eq}}/\phi_b)^2$  where  $\phi_{0,\text{eq}}$  is the Frumkin adsorption isotherm. This means that the adsorption takes place via a diffusion limited process. We have also calculated the dynamical surface tension which is in agreement with recent experiment results.

By extending the above formulation, we are able to calculate the adsorption dynamics of two different types of colloidal particles having different wettability. For certain conditions, we predict that the dynamical exchange of adsorbed particles can take place.

## REFERENCES

1. Ward, A. F. H. and Tordai, L., “Time-dependence of boundary tensions of solutions,” *J. Chem. Phys.*, **14**, 453–461, (1946).
2. Diamant, H. and Andelman, D., “Kinetics of surfactant adsorption at fluid-fluid interfaces,” *J. Phys. Chem.*, **100**, 13732–13742, (1996).