# Method for the prediction of the particle attachment to the bubble in oil at elevated temperatures

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ABSTRACT

In three phase catalytic reactions or in floatation the position of particles in respect to the gas/liquid interface is a crucial parameter affecting the efficiency of those processes. It is commonly assumed that three phase interactions are described by the contact angle, and in general the higher the contact angle the greater the probability of particle attachment to the gas/liquid interface. Contact angles are notoriously difficult to measure accurately for porous particles of wide size distribution and/or irregular shape. Also, it is practically impossible to measure the contact angles at high temperature/pressure e.g. at the conditions typical in many catalytical reactors.
Here a new method, based on the thermodynamical description of interfacial/surface energies, enabling prediction of the position of particles in three phase solid/gas/liquid systems is discussed. In this method the surface energy of catalyst particles at elevated temperatures is measured using inverse gas chromatography enabling the calculation of total interaction energy between three phases and the prediction of the position of particles in gas/liquid dispersion. The predictions were in very good agreement with experimental results obtained with the bubble pick up method.

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## 1. Introduction

The position of solid particles in respect to fluid/liquid interface might critically affect the efficiency of flotation processes [1,23,32], stability of emulsion [2,3,31] as well as overall reaction rate in multiphase catalytical reactors [18,20,34,39,40]. The prediction of the position of the solid particles in gas/solid/liquid systems (in the bulk of liquid or at the interface between gas and liquid) is rather difficult and the simple method based on the values of contact angle is not always accurate. According to this method it is commonly accepted that in gas/liquid/solid dispersions, the particles might stay on the gas/liquid interface when the three phase contact angle $\theta > 0°$ [5,39,40] and the larger the contact angle the stronger the attachment. Whilst indication of the position of particles based on the value of the contact angle is simple and straightforward the measurements of the contact angle between particles and liquids as such might be challenging [27,28]. Even at room temperature/pressure such measurements for porous particles (catalyst) are not straightforward and it is practically impossible to obtain accurate values of contact angles at the elevated temperature/ pressure typical for many multiphase catalytical reactors. The contact angles measured at room temperature might be different from the

contact angle at an elevated temperature since the surface tension and surface/interfacial energy depend on the temperature [19].

In this work, the position of solid particles in gas/solid/oil dispersions has been investigated theoretically and experimentally. The theoretical considerations are based on a thermodynamical description of the work of adhesion/cohesion [19] applied to a macroscopic system. This methodology enables prediction of the particles' most favourable position, i.e. whether they tend to remain in the bulk of the liquid or at the gas/liquid interface.

The work associated with the particle detachment from the gas/ liquid interface can be expressed in terms of surface energies between: gas/solid ($\gamma_{sg}$), gas/liquid ($\gamma_{lg}$) and solid/liquid ($\gamma_{sl}$) as illustrated in Fig. 1.

The energy of the particle detachment ($\Delta E$) can be expressed in terms of the work of adhesion between solid/liquid and gas/solid ($W_a = \gamma_{lg} + \gamma_{sg} - \gamma_{sl}$) and the work of liquid cohesion ($W_c = 2\gamma_{lg}$) [19]:

$$\Delta E = W_c - W_a = \gamma_{lg} + \gamma_{sl} - \gamma_{sg}. \tag{1}$$

For the $\Delta E > 0$, $\gamma_{lg} + \gamma_{sl} > \gamma_{sg}$ the attraction between gas and solid is stronger than the attraction between liquid and solid, therefore the particles tend to adhere/attach to the gas/liquid interface. For the $\Delta E < 0$, $\gamma_{lg} + \gamma_{sl} < \gamma_{sg}$ liquid displaces gas on the solid surface and totally wets the solid therefore the particles tend to stay in the liquid. Therefore, if the surface energies between gas/liquid ($\gamma_{lg}$), gas/solid ($\gamma_{sg}$)

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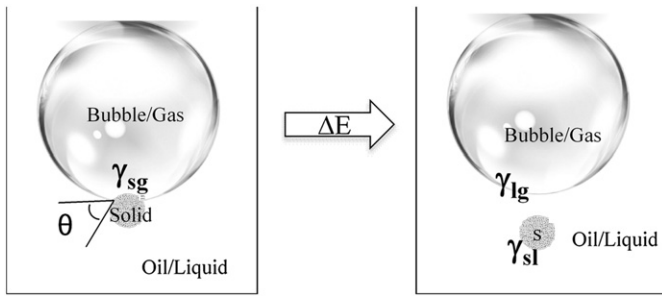E-mail address: e.nowak@bham.ac.uk (E. Nowak).

**Fig. 1.** Energy associated with particle detachment from the gas/liquid interface.

and solid/liquid ($\gamma_{sl}$) are known it is possible to predict the position of the particles in gas/liquid dispersion. Whilst the energy between gas and pure liquids (surface tension, $\gamma_{lg}$) is readily available in the tables of physical properties [44] the gas/solid surface energies ($\gamma_{sg}$) and solid/liquid interfacial energy ($\gamma_{sl}$) strongly depend on the treatment of the solid surfaces [35]; therefore are not available in the literature and they have to be measured.

The interfacial energy between a solid and liquid consists of their surface energies reduced by the energy of the interactions between them due to polar and non-polar (dispersive) forces [12,14]. Depending on the physical properties of the solid and liquid (polarity, dielectric constant etc.) the interactions can be either entirely due to the dispersive forces or it can also have the polar components [14,38]:

$$\gamma_{sl} = \gamma_{sg} + \gamma_{lg} - 2\left(\gamma_{sg}^d \cdot \gamma_{lg}^d\right)^{1/2} - 2\left(\gamma_{sg}^p \cdot \gamma_{lg}^p\right)^{1/2}. \quad (2)$$

The systems investigated here consist of non-polar oil, therefore interactions with catalyst particles can occur only due to dispersive forces. In such a case the interaction energy can be calculated from Fowkes [12,13]:

$$\gamma_{sl} = \gamma_{sg} + \gamma_{lg} - 2\left(\gamma_{sg}^d \cdot \gamma_{lg}^d\right)^{1/2} \quad (3)$$

and the change of system energy from:

$$\Delta E = 2\gamma_{lg} - 2\left(\gamma_{sg}^d \cdot \gamma_{lg}^d\right)^{1/2}. \quad (4)$$

This means that the energy of the particle attached to the bubble can be determined if the dispersive component of the surface free energy of the particle is known since the dispersive component of gas/liquid interaction is equal to the surface tension of the non-polar oil.

The interfacial energy between a solid and gas strongly depends on the processing methods, e.g. solids processed at low temperature have a different surface energy than the same solid processed at high temperature; also chemical treatment affects surface energy as it might change the zeta potential [35].

Recently inverse gas chromatography (IGC) has been employed to measure the dispersive component of the surface energy of both porous and non-porous solid particles [4,6,7,15,21,36,42]. In inverse gas chromatography net retention volume/time depends on the strength of the interactions between a fluid (probes) and adsorbent (solids) [41]:

$$V_N = jF(t_r - t_0)CT. \quad (5)$$

The retention volume is related to the adsorption energy of the solid phase [15,22]:

$$\Delta G_{ads} = -RT \ln V_N + const \quad (6)$$

where the constant depends on the type of chromatographic column and selected reference state.

The adsorption of probe molecules is caused by dispersive and polar interactions and can be related to the work of adhesion by Grajek et al. [15]:

$$\Delta G_{ads} = -N_A a W_{adh} \quad (7)$$

where $a$ is a molecular area of an adsorbed molecule [10,11]:

$$a = 1.09 \cdot 10^{14} \left(\frac{M}{\rho N_A}\right)^{2/3}. \quad (8)$$

The relation between the adsorption energy and the work of adhesion enables calculation of the surface energy of solid particles from a measured retention volume. Because non-polar liquid adsorption can occur only due to dispersive forces the dispersive component of the particle surface energy can be obtained from Newell et al. [25]:

$$RT \ln V_N = 2N_A \left(\gamma_s^d\right)^{1/2} a \left(\gamma_l^d\right)^{1/2} + const \quad (9)$$

and it is equal to the slope of the line defined by Eq. (9) in $(RT\ln V_n)$ versus $((\gamma_l^d)^{1/2})$ coordinates. This means that when the particle surface energy in the presence of a non-polar liquid is known the position of catalyst particles in gas/solid/oil systems can be predicted. It is worth stressing here that this approach enables the calculation of surface energy at an elevated temperature/pressure e.g. conditions frequently occurring in industrial applications.

In this work inverse gas chromatography was used to measure the surface energy of selected catalyst particles at elevated temperatures. The results were compared with the predictions based on the values of contact angle [28] and validated against experimental results obtained with the bubble pick up method [39,40].

## 2. Experimental

Two sets of experiments were carried out.

In the first set the dispersive components of the surface energy of catalyst particles in (i) the set of consecutive alkanes of monotonically increasing molecular size and (ii) in the non-polar viscous (VARA oil) and non-viscous (n-decane) liquids were measured. The measurements carried out with alkanes were aimed at verification of the theoretical method used for prediction of the position of particles in gas/solid/liquid suspensions discussed above. The measured dispersive component of the surface energy of the particles with paraffin oil and with n-decane were used to predict the position of particles in such systems and to compare the results with the prediction based on the values of the contact angle [26].

In the second set of experiments the attachment of the catalyst particles to a single bubble suspended in the paraffin oil and in the n-decane was investigated and the results were compared with the theoretical predictions based on the dispersive components of surface energy and on the contact angle.

### 2.1. Materials

The following catalyst supports supplied by Johnson Matthey were investigated: $Al_2O_3$ ($d_{32} = 16$ μm), $SiO_2$ ($d_{32} = 13$ μm), and $ZrO_2$ ($d_{32} = 26$ μm); details of all physical properties can be found elsewhere [28]. The viscous oil supplied by Johnson Matthey (Heavy Liquid Paraffin VARA 600/240 PB, CAS No: 8042-47-5; EINECS No: 2324558) fulfils the DAB/BP/USP and FDA regulation 21 CFR 178.3570 on the purity requirements. A range of alkanes ($C_6H_{14}$, $C_7H_{16}$, $C_8H_{18}$, $C_9H_{20}$ and $C_{10}H_{22}$) was purchased from Sigma-Aldrich. The properties of liquids used are listed in Table 1.