

# Can hematite nanoparticles be an environmental indicator?

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## 1 Chemical potential of water vapour

At low temperatures and under high pressures, water vapour behaves differently from ideal gases, and should be treated as a real gas. We have used the van der Waals equations to describe the states of water vapour, as

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT, \quad (1)$$

where  $V_m$  is the molar volume,  $R$  is the gas constant,  $a$  and  $b$  are empirical parameters, and  $P$  and  $T$  are respectively the pressure and the temperature of water vapour. In our calculations,  $a = 5.536 \text{ L}^2 \text{ bar mol}^{-2}$ , and  $b = 0.03049 \text{ L mol}^{-1}$ . [Reference: R.C. Weast, Handbook of chemistry and physics (53rd ed.), Cleveland: Chemical Rubber Co. 1972.] It is apparent from Fig. S1 that the deviation in equation of state of water vapor from ideal gas is apparently large at low temperatures and under high pressures, and is small at high temperatures and under low pressures.

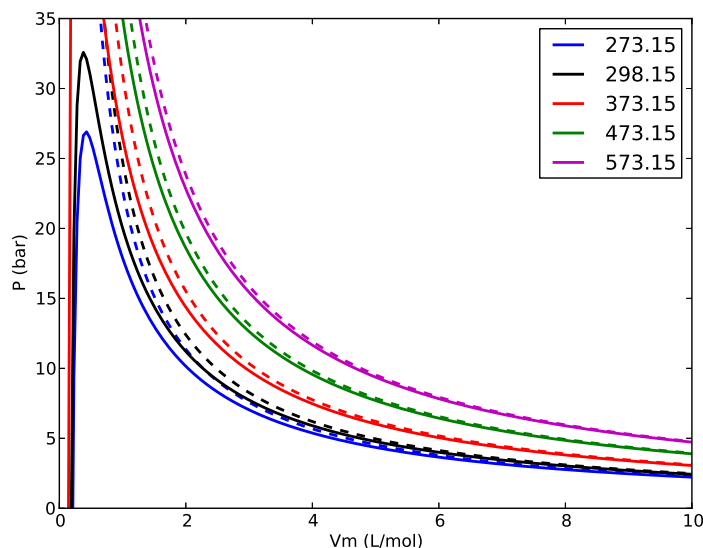


Fig. S1 Compare the pressure of van der Waals equation of water vapour and an ideal gas

We calculate the chemical potential difference of water vapour using the differential form of Gibbs free energy:

$$dG = v dP - S dT. \quad (2)$$

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Here  $S$  is the entropy. The integration can be divided into two parts, one is an isothermal process in which  $dT$  is zero, the other is an isobaric process in which  $dP$  is zero. The chemical potential change ( $\Delta\mu$ ) in the isobaric process can be calculated solely from heat capacity, while in the isothermal process  $\Delta\mu$  depends on the equation of state. Water vapor may condensate into liquid water when the pressure is larger than the saturated vapour pressure. In such an condensation process the chemical potential remains constant. We have treated approximately the liquid water as an incompressible liquid. In our calculations, the saturated vapour pressure is calculated using the three-parameter Antoine equation

$$\log_{10} P_{\text{sat}} = a - b/(c + t) . \quad (3)$$

If  $P_{\text{sat}}$  takes the unit of mmHg,  $t$  takes the unit of degree Celsius, then the parameters are used as  $a = 8.07131$ ,  $b = 1730.63^\circ\text{C}$ , and  $c = 233.426^\circ\text{C}$  for the temperature range of  $[0^\circ\text{C}, 100^\circ\text{C}]$ , and  $a = 8.14019$ ,  $b = 1810.94^\circ\text{C}$ , and  $c = 244.485^\circ\text{C}$  for the temperature range of  $[100^\circ\text{C}, 374^\circ\text{C}]$ . A minor discontinuity in the saturated pressure at  $t = 100^\circ\text{C}$  is present which is negligible for the thermodynamic calculations. Fig. S2 shows a comparison of the chemical potentials calculated using van der Waals equation and the ideal gas law. It is apparent that the chemical potential of the gas phase (under low pressures) is much more sensitive to pressure than the liquid phase (under high pressures).

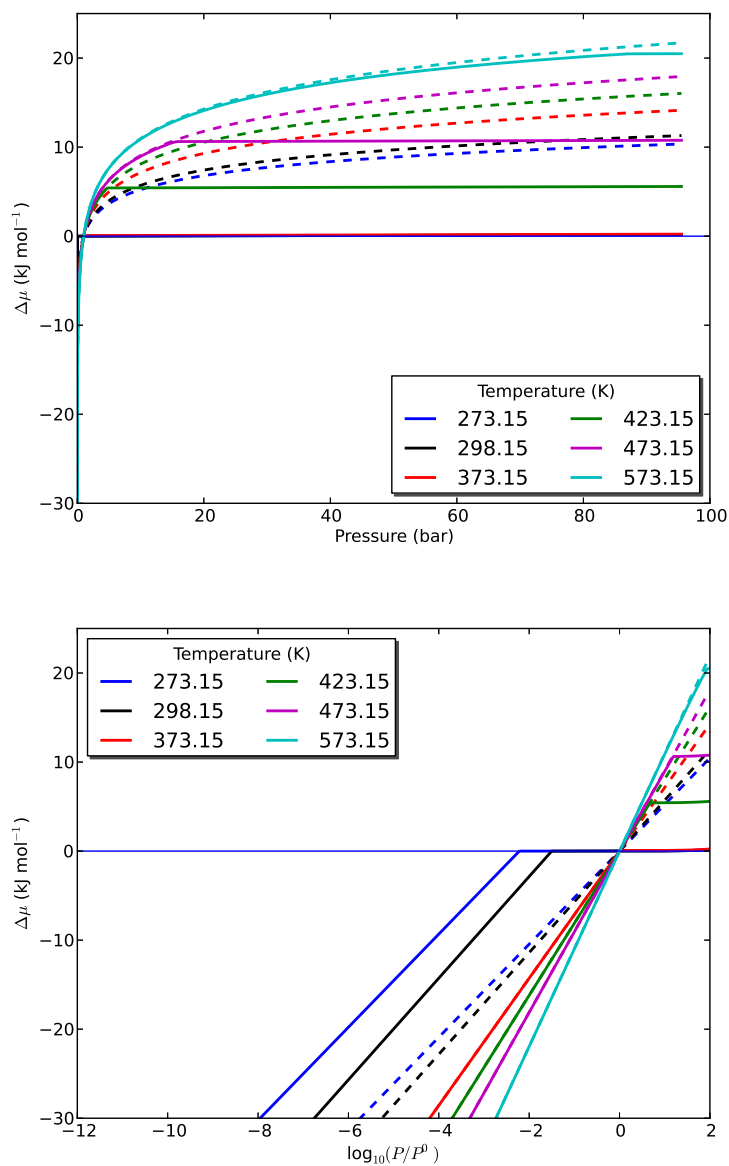
## 2 $T$ - and $P$ -dependence of formation energies of nanoparticles

Hematite nanocrystals of different shapes have different formation energies. Even the shapes are fixed (that is, the fractional surface areas are constant), the surface terminations still are variable in response to changing environmental conditions. We have selected several shapes and plotted their formation energies as functions of temperature (Fig. S1) and partial pressure of water vapour (Fig. S2), to show such variations. The selected shapes correspond to minimum formation energy of the particle under certain environmental conditions.

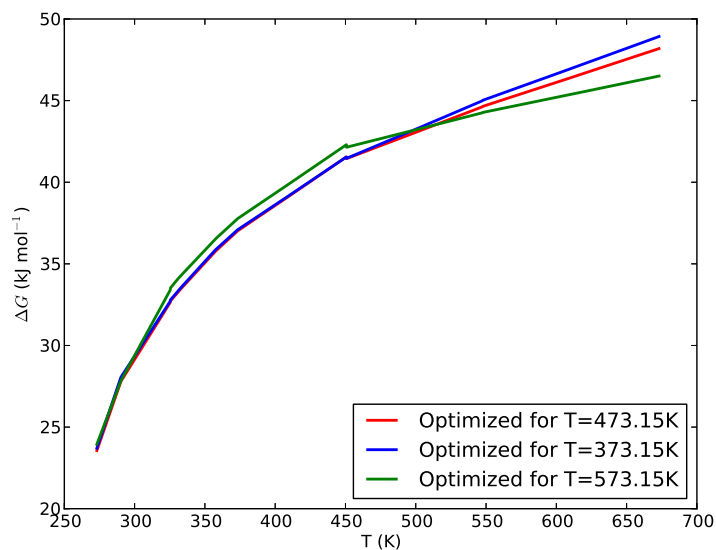
## 3 Estimation of errors

We also tested the effects of the approximations used in the exchange-correlation functionals, and found the surface energies calculated using PBE+ $U$  are smaller, by 0.1–0.3 J m<sup>-2</sup>, than those using local density approximation with corrections of Coulomb interactions (LDA+ $U$ ) (see Fig. S5). The relative order of thermodynamic stability of the terminations may change when different functionals are used. This would cause a level of uncertainties to the calculated surface energies and the phase boundaries between different terminations or morphologies. This is especially problematic for the terminations with close surface energies. However, such uncertainties are reduced in our case because the surface energies depend strongly on the surface chemistry of the terminations, so that the surface energies of different hydroxylation differ largely (see refs. 38, 39, and 40 in the main texts). But, the uncertainties due to functionals are generally not negligible, and should be considered with other uncertainties in the computations.

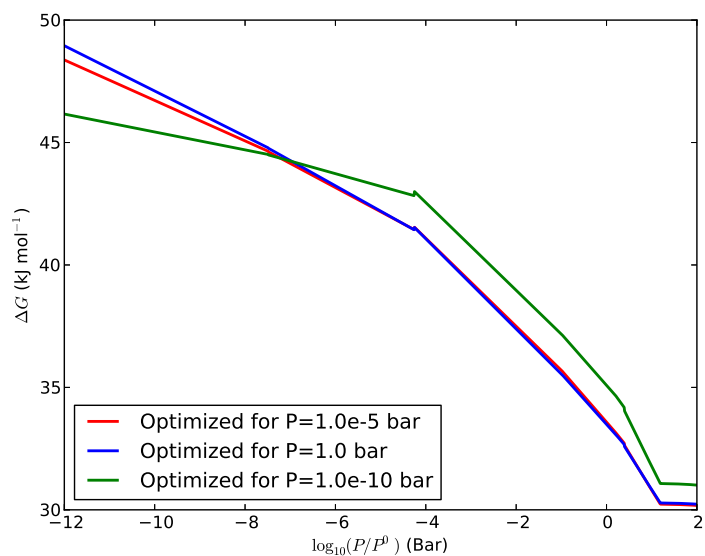
The surface energies from calculations carry uncertainties of several sources: the incompleteness of plane wave basis sets, and the sampling of Brillouin zone using discrete  $k$ -points, the interference of image cells in periodic boundary conditions, the approximation in exchange correlation functionals, to name a few. We have set the convergence criteria of surface energy calculations to be 5 mJ m<sup>-2</sup> (or 0.005 J m<sup>-2</sup>). If we assume a spherical nanoparticle, the error in surface energy calculation ( $\delta_s$ ) will cause an error in the



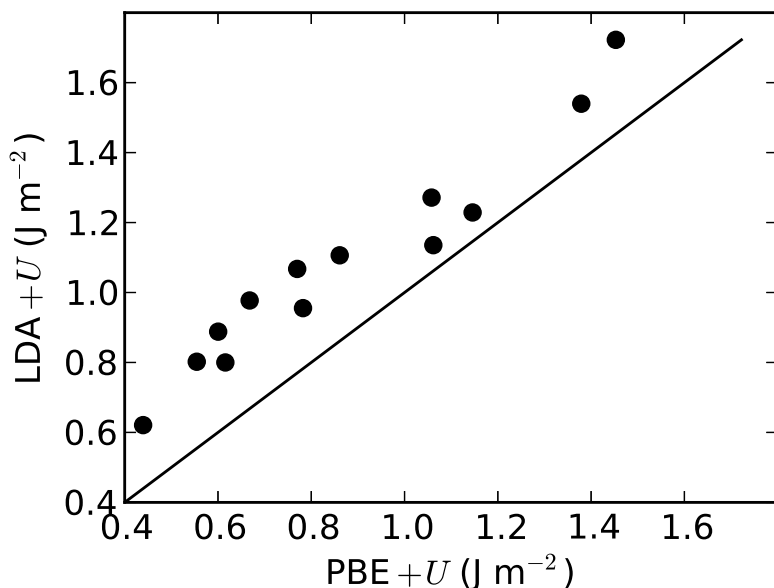
**Fig. S2** Comparison of chemical potentials calculated using van der Waals equation (solid lines) and ideal gas law (dashed lines), in linear and logarithm axis, at several temperatures. The reference of the chemical potentials are the state of the shown temperature and 1 atm.



**Fig. S3** Formation energies of hematite nanocrystals of selected shapes as functions of temperature. The partial pressure of water vapour is atm for all the three shapes.



**Fig. S4** Formation energies of hematite nanocrystals of selected shapes as functions of partial pressure of water vapour. The temperature is 298.15 K for all the three shapes.



**Fig. S5** Comparison of surface energies using LDA+ $U$  and PBE+ $U$ . The surface energies correspond to the thermodynamic standard state. A guide line is provided where the surface energies using LDA+ $U$  and PBE+ $U$  are equal.

formation energy of the nanoparticle ( $\delta_{\text{np}}$ ) as

$$\delta_{\text{np}} = \frac{\frac{1}{4}\pi d^2 \delta_s}{\frac{1}{6}\pi d^3 / V_m} = \frac{1.5V_m \delta_s}{d}, \quad (4)$$

where  $d$  is the diameter of the nanoparticle, and  $V_m$  is the molar volume, which is  $3.103 \times 10^{-5} \text{ m}^3/\text{mol}$  for hematite. It is immediately seen that  $\delta_{\text{np}}$  is inversely proportional to  $d$ . We give a few values of  $\delta_{\text{np}}$  to show the error. At  $d = 3 \text{ nm}$ ,  $\delta_{\text{np}} = 0.78 \text{ kJ mol}^{-1}$ , and at  $d = 10 \text{ nm}$ ,  $\delta_{\text{np}} = 0.23 \text{ kJ mol}^{-1}$ . Such a level of error small and acceptable for evaluating the thermodynamic stabilities.