Electronic Supplement to the paper

A New Paradigm on the Chemical Potentials of Components in Multi-component Nano-Phases within Multi-phase Systems

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Supplement A. Some simple examples of nano-equilibria

First let us suppose that the nano-phase is a liquid ($\alpha = l$), which is surrounded by a large vapor phase ($\beta = v$). The chemical potential of component $i$ in this vapor phase ($\mu_i(v)$, J/mol) is written as:

$$\mu_i(v) = \mu^0_i(v) + R \cdot T \cdot \ln \left( \frac{p_i}{p^0} \right) \quad (A1a)$$

where $\mu^0_i(v)$ (J/mol) is the standard chemical potential of component $i$ in the vapor phase, corresponding to the standard pressure of $p^0 = 10^5$ Pa, $R = 8.3145$ J/molK is the universal gas constant, $T$ (K) is the absolute temperature, $p_i$ (Pa) is the partial pressure of component $i$ in equilibrium with the liquid nano-droplet. The latter can be obtained by substituting Eq-s (2) of the main text) and the above Eq.(A1a) into Eq.(1) of the main text:

$$p_i = p_i^\infty \cdot e^{\mu_i^b(l)} \cdot \sigma_{i/v}$$ \quad (A1b)

$$p_i^\infty = p^0 \cdot e^{\left( \frac{\mu_i^b(l) - \mu_i^0(v)}{R \cdot T} \right)}$$ \quad (A1c)

where $p_i^\infty$ (Pa) is the equilibrium vapor pressure of component $i$ above a large liquid phase with $r = \infty$, $r$ (m) is the radius of the liquid droplet. Eq.(A1b) is a generalized Kelvin equation. If $z = 2/r$ is substituted into Eq.(A1b), the classical Kelvin equation is obtained in accordance with the Kelvin paradigm. If $z = A_{sp,\alpha}$ from Eq.(8g) and parameters of Table 1 are substituted into Eq.(A1b), the new equations according to the new paradigm are obtained (see Table 2). Please, note: Eq.(A1b) can be applied also to calculate the equilibrium vapor pressure around a solid nano-phase, if $\mu_i^b(l)$ is replaced by $\mu_i^b(s)$ in Eq.(A1c) and if subscripts “l” are replaced by subscripts “s” in Eq.(A1b).

Now, suppose that the nano-phase is a pure solid phase ($\alpha = s$), which is surrounded by a large liquid phase ($\beta = l$). The chemical potential of a diluted component $i$ in this large liquid phase ($\mu_i(l)$, J/mol) is written as:
\[
\mu_{i(l)} = \mu_{i(l)}^o + R \cdot T \cdot \ln x_{i(l)} + L_o
\]  
(A2a)

where \( x_{i(l)} \) (dimensionless) is the mole fraction of component \( i \) in the diluted liquid solution, \( L_o \) (J/mol) is the interaction energy between components \( i \) and \( j \) in the liquid solution. The bulk chemical potential of component \( i \) in a one-component solid nano-phase is written as the standard chemical potential of a pure solid phase:

\[
\mu_{i(s)}^b = \mu_{i(s)}^o \tag{A2b}
\]

Substituting Eq-s (A2a-b, 2) into Eq.(1), the equilibrium solubility of the pure solid component \( i \) in the liquid \( i-j \) solution is expressed as:

\[
x_{i(l)} = x_{i(l)}^\infty \cdot \exp \left[ \frac{z \cdot V_{m,i(s)} \cdot \sigma_{s/l}}{R \cdot T} \right] \tag{A2c}
\]

\[
x_{i(l)}^\infty = \exp \left[ \frac{\mu_{i(s)}^o - \mu_{i(l)}^o - L_o}{R \cdot T} \right] \tag{A2d}
\]

where \( x_{i(l)}^\infty \) (dimensionless) is the equilibrium solubility of a large pure solid phase \( i \) in the liquid solution. Eq.(A2c) is a generalized Ostwald-Freundlich equation. If \( z = 2/r \) is substituted into Eq.(A2c), the classical Freundlich equation is obtained, in accordance with the Kelvin paradigm. If \( z = A_{sp,\alpha} \) from Eq.(8g) and parameters of Table 1 are substituted into Eq.(A2c), the new equations according to the new paradigm are obtained, which are also in agreement with the Ostwald equation (see Table 2).

Suppose that the nano-phase is a pure solid phase \((\alpha = s)\), which is surrounded by a large pure liquid phase \((\beta = l)\). The chemical potential of component \( i \) in this large liquid phase \( (\mu_{i(l)}, \text{J/mol}) \) is written as:

\[
\mu_{i(l)}^b = H_{i(l)}^o - T \cdot S_{i(l)}^o
\]  
(A3a)

where \( H_{i(l)}^o \) (J/mol) is the standard enthalpy of pure liquid phase \( i \), \( S_{i(l)}^o \) (J/molK) is the standard entropy of pure liquid phase \( i \). The bulk chemical potential of component \( i \) in a solid nano-phase is written as:

\[
\mu_{i(s)}^b = H_{i(s)}^o - T \cdot S_{i(s)}^o
\]  
(A3b)

Substituting Eq-s (A3a-b, 2) into Eq.(1), the equilibrium melting point of the solid nano-phase \((T_{m,i}, \text{K})\) can be expressed as:

\[
T_{m,i} \approx T_{m,i}^\infty - \frac{z \cdot V_{m,i(s)} \cdot \sigma_{s/l}}{\Delta_m S_{i}^o}
\]  
(A3c)
where $T_{m,i}^\infty$ is the standard melting point of the large solid phase, $\Delta_m S^o_i \equiv S_{i(l)}^o - S_{i(s)}^o$ (J/molK) is the standard melting entropy of pure phase $i$. When Eq.(A3c) is derived, the chemical potential difference between pure liquid and solid phases is written approximately as:

$$\mu^b_{i(l)} - \mu^b_{i(s)} \approx \Delta_m S^o_i \cdot (T_{m,i}^\infty - T).$$

Eq.(A3c) is a generalized Gibbs-Thomson equation. If $z = 2/r$ is substituted into Eq.(A3c), the classical Gibbs-Thomson equation is obtained, in accordance with the Kelvin paradigm. If $z = A_{sp,\alpha}$ from Eq.(8g) and parameters of Table 1 are substituted into Eq.(A3c), the new equations according to the new paradigm are obtained (see Table 2). Let us mention that the solid/liquid equilibrium can also take place in other morphologies, leading to different equations, among which Eq.(A3c) is only the simplest one (for details see [25, 31]).

**Supplement B. On the ratio of surface atoms / molecules in nano-phases**

Let us denote the mole fraction of surface atoms /molecules to all atoms / molecules within a nano-phase by $x_s$ (dimensionless), defined as:

$$x_s \equiv \frac{N_s}{N} \quad (B1)$$

where $N$ (dimensionless) is the number of all atoms /molecules within the nano-phase, $N_s$ (dimensionless) is the number of atoms / molecules in the surface monolayer of the nano-phase. These quantities can be written as:

$$N = \frac{V_\alpha}{V_{m,\alpha}} \cdot N_{Av} \quad (B2)$$

$$N_s = \frac{A_\alpha}{\omega_\alpha} \cdot N_{Av} \quad (B3)$$

where $N_{Av} = 6.023 \times 10^{23}$ 1/mol is the Avogador number, $\omega_\alpha$ (m$^2$/mol) is the molar surface area of phase $\alpha$. Substituting Eq-s (B2-3) into Eq.(B1) and taking into account the definition written by Eq.(4f), the final equation is obtained as:

$$x_s = A_{sp,\alpha} \cdot \frac{V_{m,\alpha}}{\omega_\alpha} \quad (B4)$$

As follows from Eq.(B4), the ratio of surface atoms / molecules in a nano-phase is proportional to the specific surface area of the nano-phase. Eq.(B4) is the same as Eq.(9) of the main text.