Electronic Supplementary Information for "Size-Dependent Pressure-Induced Amorphization: A Thermodynamics panorama"

Denis Machon[*,1] and Patrice Mélinon[1]

1 Institut Lumière Matière, UMR 5306 Université Lyon 1-CNRS, Université de Lyon 69622 Villeurbanne cedex, France

*denis.machon@univ-lyon1.fr

1- Determination of the Gibbs energy including the interfacial energy term

The expression of the Gibbs energy including the surface energy term and considering isothermal compression reads

$$dG = V.dP + \gamma.dA \qquad (1)$$

One can derive directly the effect of the particle radius r by replacing dA by $8\pi r$dr assuming a spherical particle. This seeming obvious step nevertheless requires an underlying assumption that is that no surface reconstruction takes place during the compression path. This assumption is consistent with considering an average interfacial energy γ. This treatment does not hold anymore if we consider nanoparticles under vacuum without any capping molecule. For a free particle, the morphology is derived from the Wulfs'construction [E. Ringe, R. P. Van Duyne, L. D. Marks, *Nano Lett.*, 2011, 11, pp 3399–3403] with associated γ(hkl) surface energies, (hkl) is related to the external facets.

The molar Gibbs energy is then expressed as

$$dG_m = \frac{V}{n}.dP + \frac{8\pi r \gamma}{n}.dr \qquad (2)$$

where n is the number of mole in the system (i.e., in the nanoparticle) and $\frac{V}{n} = V_m$ is the molar volume of the phase.

The equality of the crossed derivatives yields

$$\left(\frac{\partial V}{\partial r}\right)_P = \left(\frac{8\pi r \partial \gamma}{\partial P}\right)_r \tag{3}$$

Leading to $\left(\frac{\partial \gamma}{\partial P}\right)_r = \frac{r}{2}$ thus to $\gamma(r,P) = \frac{r}{2}P + \gamma_0(r)$ (4)

γ_0 is the contribution of the interfacial energy at ambient pressure. Note that this relation is similar to the Laplace-Young equation.

On the other hand, $V_m = \left(\frac{\partial G_m}{\partial P}\right)_r$ and the integration at constant r leads to

$$G_m = P.V_m + f(r) \tag{5}$$

Differentiating with respect to r at constant P yields

$$\left(\frac{\partial G_m}{\partial r}\right)_P = \frac{4\pi.r^2}{n}.P + f'(r) \tag{6}$$

According to (2), one also has $\left(\frac{\partial G_m}{\partial r}\right)_P = \frac{8\pi\gamma.r}{n}$ (7)

By identification between eqs (6) and (7), and using eq.(4), one obtains

$f'(r) = \frac{8\pi.r\gamma_0}{n}$ which, after integration, yields

$$f(r) = \frac{4\pi.r^2.\gamma_0}{n} + C \tag{8}$$

As $n = \frac{V}{V_m}$ where V_m is the molar volume of the phase, one obtained

$f(r) = \frac{3\gamma_0}{r}.V_m + C$, leading to the final expression using eq.(5)

$$G_m = P.V_m + \frac{3V_m\gamma_0}{r} + G_0 \tag{9}$$