Supporting information

On the thermodynamics of framework breathing: free energy model for gas adsorption in MIL-53

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1. Structural parameters for MIL-53(Cr)

		experiment			our model		
		lp	np	average	reference V_0	lp	np
a	Å	16.733	19.685		14.992	16.733	19.685
b	Å	13.038	7.849		14.992	13.021	7.877
c	Å	6.812	6.782	6.797	6.797	6.797	6.797
D	Å	21.213	21.192	21.202	21.202	21.202	21.202
V	$Å^3$	1486	1013		1528	1481	1054
α		90°	90°		90°	90°	90°
β		90°	104.9°		90°	90°	90°
γ		90°	90°		90°	90°	90°
δ		14.2°	46.5°		0°	14.2°	46.4
tan δ		0.25	1.05		0	0.25	1.05

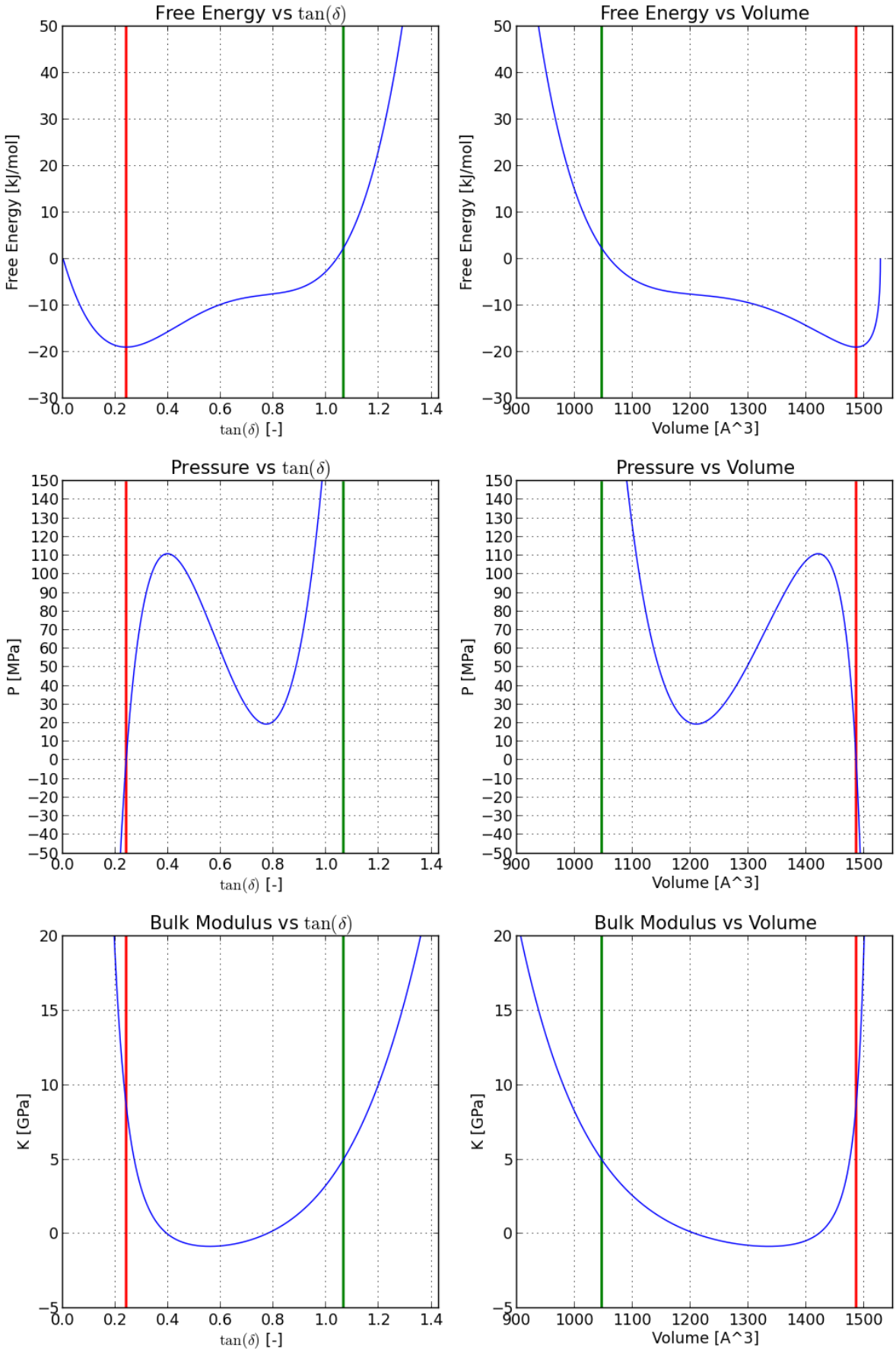
The experimental values are those reported by Serre et al. (2002).

In our model, we assume that (1) *c* is constant, (2) *D* is constant, and (3) the unit cell stays orthorhombic. The diagonal length *D* and cell parameter *c* are indeed approximately constant, and are estimated as the average between the experimental lp and np values. We then derived the remaining cell parameters for the reference shape with volume V_0, the lp shape and np shape. Choosing a cell parameter *a*, the cell parameter *b* is calculated from $b^2 = D^2-a^2$. These cell parameters have been used in all our Monte Carlo simulations.

The positions of the framework atoms are reported as partial coordinates in the original experimental paper by Serre et al. (2002). In the Monte Carlo simulations, the framework is kept rigid, with the framework atoms located at these partial coordinates. A series of shapes δ was investigated by varying *a/b* while keeping $D^2=a^2+b^2$ constant. We used the same partial coordinates for the framework atoms in each of these shapes.

2. Free energy profile of the empty host

The four parameters of the free energy profile of the empty host was fitted using six conditions. The resulting free energy profile, pressure profile, and bulk modulus are shown as a function of the parameter tan(δ) and as a function of the unit cell volume. The pressure is the negative of the derivative of profile with respect to volume (Section III in main document). The pressure is also the negative of the diagonal elements of the stress tensor in case of isotropic stress (S.I.6, formula 12).


Free Energy vs $\tan(\delta)$
Free Energy [kJ/mol]
$\tan(\delta)$ [-]
Free Energy vs Volume
Free Energy [kJ/mol]
Volume [A^3]
Pressure vs $\tan(\delta)$
P [MPa]
$\tan(\delta)$ [-]
Pressure vs Volume
P [MPa]
Volume [A^3]
Bulk Modulus vs $\tan(\delta)$
K [GPa]
$\tan(\delta)$ [-]
Bulk Modulus vs Volume
K [GPa]
Volume [A^3]

3. Pore volume and host-guest interaction calculations

The lp geometry of MIL-53(Cr) is constructed from the crystallographic data reported in the paper by Serre et al.(2002). The *c* vector, assumed to have constant length in this model, is estimated as the average between the lp and np shape (c = 6.797 Å). Similarly, the constant diagonal length D is calculated as the average of the diagonal in the lp and np phase (D = 21.20 Å). The framework is modeled as rigid with a simulation box of 2x3x4 unit cells. The CH_4 molecule interacts with the framework through Lennard-Jones interactions (Salles et al., 2008). CH_4 is modeled as a rigid molecule. CO_2 is also modeled as a rigid particle but has 3 charges to simulate its quadrupole moment, leading to electrostatic interactions in addition to Lennard-Jones interactions. Electrostatic interactions are computed with an Ewald sum beyond the cutoff radius of 12. In the Monte Carlo simulation 10^5 insertions are performed.

Adapted formula for pore volume

The pore volume V_p has been derived from Monte Carlo simulations with Widom insertions for a range of shapes.

In the standard procedure, a helium atom is inserted (and immediately removed) repeatedly at random positions for N_{trials} attempts, and its energy ΔU_i is calculated using Lennard-Jones interactions between the framework and the atom. The pore volume fraction V_p/V is estimated as the Rosenbluth factor

$$\frac{V_p}{V} = \frac{\sum_i^{N_{\mathrm{trial}}} \exp(-\Delta U_i / k_B T)}{N_{\mathrm{trial}}}$$

Indeed, when helium is inserted on top of a framework atom, the energy is very high and the contribution of this attempt to the sum is zero. When helium is inserted inside a pore, it barely interacts and the contribution to the sum is approximately one.

In our simulations, we have performed insertions with a CO_2 or CH_4 probe. Because these molecules may have favorable interactions, the Rosenbluth factor is no longer a plausible estimation of the pore fraction, and we have adapted the procedure. When the inserted molecule overlaps with a framework atom, the contribution is again almost zero, but when the interaction is favorable ($\Delta U_i < 0$), the contribution is simplified to $1/N_{trial}$. This procedure amounts to counting how often a molecule can be inserted favorably, and adding how often a molecule may be inserted unfavorably with a Boltzmann probability. The resulting maximum number of particles per unit cell V_p/b, with b the van der Waals parameter, is then an overestimation as it assumes perfect packing.

4. Force field parameters

* helium - framework interactions: Lennard-Jones
* methane - framework interactions: Lennard-Jones
* carbon dioxide - framework interactions: Lennard-Jones, Coulomb

The Lennard-Jones interactions make use of the Lorentz-Berthelot mixing-rules.
The Coulomb interactions are calculated with an Ewald summation beyond the 12 A cutoff.
Potentials are truncated and not shifted.

The parameters are based on the parameters of the force field developed by Salles et al. (2008). Mass and charge are reported in atomic units, the radius in Angstrom, the LJ-parameter epsilon in joule and the LJ-parameter sigma in angstrom.

Parameters of framework

type	element	mass	charge	radius	epsilon	sigma
Cr	Cr	51.9961	1.031	1.2	7.543	2.69007
Oh	O	15.9994	-0.637	1	85.526	3.12
Oc	O	15.9994	-0.506	1	105.65	2.96
Ho	H	1.00794	0.291	0.8	0	0
Hc	H	1.00794	0.1393	0.8	19.267	2.44833
Ca	C	12	0.6126	0.8	74.378	3.61815
Cb	C	12	-0.0739	0.8	74.378	3.61815
Cc	C	12	-0.0739	0.7	74.378	3.61815

Parameters of adsorbates

type	element	mass	charge	radius	epsilon	sigma
C_co2	C	12.0107	0.6512	0.7	80.524	2.757
O_co2	O	15.9994	-0.3256	0.7	28.07	3.033
He	He	4.002602	0	1	10.9	2.64
CH4_sp3	CH4	16.04246	0	1	148	3.73

5. LEGENDRE TRANSFORM WITH RESPECT TO VOLUME

The constant $(n, N, \bar{\bar{\eta}}, T)$ ensemble. Assume $F(n, N, \bar{\bar{\eta}}, T)$ is the free energy of the constant $(n, N, \bar{\bar{\eta}}, T)$ ensemble with constant number n of unit cells of the host framework, number N of particles, shape (definition $\bar{\bar{\eta}}$ in Eq. 2) and temperature T. The shape is a generalization of the thermodynamic quantity 'volume' for a gas. The transition from the constant $(n, N, \bar{\bar{\eta}}, T)$ ensemble to the constant $(n, \mu, \bar{\bar{\sigma}}, T)$ ensemble, with constant external chemical potential μ and Cauchy stress tensor $\bar{\bar{\sigma}}$, is realized by a Legendre transform. This transform starts from the first law of thermodynamics, so we need the infinitesimal amount of work associated with a change in shape $(d\bar{\bar{\eta}})$ under constant stress. The equivalent of this term for a simple system containing only gas is the well-known $-PdV$ term. The expression for a system containing a solid is somewhat more elaborate because solids resist to shear. In case the stress-strain relations can be linearalized, the familiar infinitesimal work term is given by $\bar{\bar{\sigma}} : d\bar{\bar{\epsilon}}$, where $\bar{\bar{\sigma}}$ is the Cauchy stress tensor and $\bar{\bar{\epsilon}}$ is the infinitesimal Cauchy strain tensor. For the purpose of this work, where relatively large deformations of the unit cell are observed, the finite strain tensor should be considered. In the next section, this infinitesimal work is calculated when the stress results from isotropic pressure and it is found that the work term reduces to the standard $-PdV$ term under the set of assumptions. This simplifies the transform to the constant P ensemble.

Infinitesimal work for shape change under constant stress $\bar{\bar{\sigma}}$. The elements of the asymmetrical gradient deformation tensor $\bar{\bar{\alpha}}$ are defined as the derivatives of the deformed material positions $\mathbf{x}$ with respect to the reference material position $\mathbf{X}$,

$$\alpha_{i,j} = \frac{\partial x_i}{\partial X_j} \tag{1}$$

where i, j are Cartesian indices. This tensor has size 3×3 and describes the deformation state of the unit cell: it expresses the amount of deformation $\mathbf{x} - \mathbf{X}$ of a material point depending on the original reference position $\mathbf{X}$ of the material point. The corresponding finite Lagrangian strain tensor $\bar{\bar{\eta}}$ is then given by

$$\bar{\bar{\eta}} = \frac{1}{2}(\bar{\bar{\alpha}}^T \bar{\bar{\alpha}} - 1) \tag{2}$$

and is conveniently a symmetric tensor. The work-conjugate tensor to $\bar{\bar{\eta}}$ is known as the second Piola-Kirchhoff stress tensor, which is defined as

$$\bar{\bar{S}} = (\det \bar{\bar{\alpha}}) \;\; \bar{\bar{\alpha}}^{-1}.\bar{\bar{\sigma}}.(\bar{\bar{\alpha}}^T)^{-1} \tag{3}$$

The tensor $\bar{\bar{S}}$ is symmetric and depends on the Cauchy stress tensor $\bar{\bar{\sigma}}$. The explicit expression for the infinitesimal work by the stress $\bar{\bar{\sigma}}$ is given by

$$V_0 \bar{\bar{S}} : d\bar{\bar{\eta}} = V_0 \det \bar{\bar{\alpha}} \sum_{ijkl} \sigma_{k,l} \alpha^{-1}_{i,k} \alpha^{-1}_{j,l} d\eta_{i,j} \tag{4}$$

In the present model, the unit cell undergoes deformations under the restrictions of a constant diagonal length D and constant angles α, β, γ. A point $\mathbf{r}$ with fractional coordinates (x', y', z') has in the reference open shape the Cartesian coordinates $\mathbf{X}(X, Y, Z) = (x'a_0, y'b_0, z'c_0)$ with $a_0 = b_0 = D/\sqrt{2}$ (tetragonal). In the deformed shape, the Cartesian coordinates read $\mathbf{x}(x, y, z) = (x'a, y'b, z'c) = (a/a_0 X, \sqrt{D^2 - a^2}/a_0 Y, Z)$ since $b = \sqrt{D^2 - a^2}$ and $c = c_0$. The elements of $\bar{\bar{\alpha}}$ can be calculated by taking the derivative of the deformed positions with respect to the original positions, e.g.

$$\alpha_{x,x} = \frac{\partial x}{\partial X} = \frac{\partial (a/a_0 X)}{\partial X} = \frac{a}{a_0} \tag{5}$$

$$\alpha_{x,y} = \frac{\partial x}{\partial Y} = \frac{\partial (a/a_0 X)}{\partial Y} = 0 \tag{6}$$

and similar for the other elements of $\bar{\bar{\alpha}}$. The tensor expresses how much the (x, y, z) coordinates of a material point change in the x, y, z directions due to the deformation. For convenience we choose to express all elements as a function of the lattice length a, such that we find

$$\bar{\bar{\alpha}} = \begin{pmatrix} \frac{a}{a_0} & 0 & 0 \\ 0 & \frac{\sqrt{D^2 - a^2}}{a_0} & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{7}$$

The diagonal form of the deformation tensor is a consequence of the angles α, β, γ being kept constant and is certainly no general feature of $\bar{\bar{\alpha}}$. The determinant of $\bar{\bar{\alpha}}$ is given by

$$\det \bar{\bar{\alpha}} = \frac{a\sqrt{D^2 - a^2}}{a_0^2} = \frac{V}{V_0} \tag{8}$$

and is a measure for the change in density, while the inverse of $\bar{\bar{\alpha}}$ and the inverse of its transpose is calculated as

$$\bar{\bar{\alpha}}^{-1} = \begin{pmatrix} \frac{a_0}{a} & 0 & 0 \\ 0 & \frac{a_0}{\sqrt{D^2 - a^2}} & 0 \\ 0 & 0 & 1 \end{pmatrix} = \left(\bar{\bar{\alpha}}^T\right)^{-1} \tag{9}$$

The Lagrange strain tensor is easily constructed from $\bar{\bar{\alpha}}$ using the definition in Eq. 2,

$$\bar{\bar{\eta}} = \frac{1}{2}\begin{pmatrix} \frac{a^2}{a_0^2} - 1 & 0 & 0 \\ 0 & \frac{D^2-a^2}{a_0^2} - 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{10}$$

and its differential (considering a as the only degree of freedom)

$$d\bar{\bar{\eta}} = \frac{1}{a_0^2}\begin{pmatrix} a & 0 & 0 \\ 0 & -a & 0 \\ 0 & 0 & 0 \end{pmatrix} da \tag{11}$$

When assuming that the external stress $\bar{\bar{\sigma}}$ is due to an isotropic pressure P, such that $\sigma_{i,j} = -P\delta_{i,j}$, the second Piola-Kirchhoff stress tensor $\bar{\bar{S}}$ reads,

$$\bar{\bar{S}} = -\frac{V}{V_0}P\begin{pmatrix} \frac{a_0^2}{a^2} & 0 & 0 \\ 0 & \frac{a_0^2}{D^2-a^2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{12}$$

Taking all terms together, the derivation leads to the infinitesimal work expression for a shape change under constant pressure

$$V_0\bar{\bar{S}} : d\bar{\bar{\eta}} = -VP\left(\frac{1}{a} + \frac{-a}{D^2-a^2}\right)da \tag{13}$$

$$= -P(ac\sqrt{D^2-a^2})\frac{D^2-2a^2}{a(D^2-a^2)}da \tag{14}$$

$$= -P\frac{D^2-2a^2}{\sqrt{D^2-a^2}}\,c\,da \tag{15}$$

$$= -PdV \tag{16}$$

since the differential of the volume V could be recognized,

$$dV = d\left(ac\sqrt{D^2-a^2}\right) = \frac{D^2-2a^2}{\sqrt{D^2-a^2}}\,c\,da \tag{17}$$

So ultimately the infinitesimal work term for a volume change under constant pressure for the MIL-53 structure amounts to the standard $-PdV$ term, and the tensor quantity $\bar{\bar{\eta}}$ can be simplified to the use of a scalar quantity V. The Legendre transform from a constant V ensemble to a constant P ensemble is then realized by adding a term $+PV$ to the free energy expression.

The key assumption for this derivation is that the angles α, β, γ do not change in the deformations, such that the structure keeps its orthorhombic shape. In reality, the unit cell becomes triclinic at intermediate pressures (narrow-pore shape) with a change of about 15 degrees of the β angle. The other assumptions are that the linkers have constant length (constant diagonal D) and the stress tensor is caused by an isotropic pressure. In case of n unit cells with V_0 the volume of a single unit cell in the reference tetragonal shape ($\delta = 0$), the expression as a function of δ reads

$$PV = nPV_0 \cos\delta \tag{18}$$

Legendre transform to the constant (n, μ, P, T) ensemble. Assume F is the free energy of the $(n, N, \bar{\bar{\eta}}, T)$ ensemble, implying that F is a function of the natural variables $n, N, \bar{\bar{\eta}}, T$. Above we have shown that the infinitesimal work term associated with the variable $\bar{\bar{\eta}}$ can also be written as a function of the variable V,

$$dF = -SdT - PdV + \mu dN + \mu_n dn \tag{19}$$

In this last equation μ_n denotes the chemical potential of the host material, which has the interpretation of the free energy change when a unit cell were to be added to the crystal ($n \to n + 1$). A free energy that is a function of the variables n, μ, P, T is constructed by a Legendre transform with respect to N and V,

$$X(n, \mu, P, T) = \min_{N,V} \left[F(n, N, V, T) + PV - N\mu\right] \tag{20}$$

Or,

$$X(n, \mu, P, T) = F + PV - N\mu \tag{21}$$

such that

$$dX = -SdT + VdP - Nd\mu + \mu_n dn \tag{22}$$

Equation 21 is the correct free energy expression for MIL-53, assuming isotropic pressure, an orthorhombic unit cell, and constant linker length.

Remark: Legendre transform to constant $(n, \mu, \bar{\bar{S}}, T)$ ensemble. The free energy F is a function of the natural variables $n, N, \bar{\bar{\eta}}, T$. It is then straightforward and tempting to construct a free energy Y that is function of the variables $n, \mu, \bar{\bar{S}}, T$ by a Legendre transform with respect to N and $\bar{\bar{\eta}}$,

$$Y(n, \mu, \bar{\bar{S}}, T) = \min_{N, \bar{\bar{\eta}}} \left[F(n, N, \bar{\bar{\eta}}, T) - V_0 \bar{\bar{S}} : \bar{\bar{\eta}} - N\mu \right] \tag{23}$$

or

$$Y(n, \mu, \bar{\bar{S}}, T) = F - V_0 \bar{\bar{\eta}} : \bar{\bar{S}} - \mu N \tag{24}$$

such that

$$dY = -SdT - V_0 \bar{\bar{\eta}} : d\bar{\bar{S}} - Nd\mu + \mu_n dn \tag{25}$$

This is because the second Piola-Kirchhoff tensor $\bar{\bar{S}}$ is the work-conjugate tensor to $\bar{\bar{\eta}}$. Working out the term $-V_0 \bar{\bar{\eta}} : \bar{\bar{S}}$ gives

$$V_0 \bar{\bar{\eta}} : \bar{\bar{S}} = -V_0 \frac{V}{V_0} P \frac{1}{2} \left(\frac{a^2 - a_0^2}{a^2} + \frac{D^2 - a^2 - a_0^2}{D^2 - a^2} + 0 \right) \tag{26}$$

$$= PV \left(1 - \frac{a_0^2 (D^2 - a^2) + a_0^2 a^2}{2a^2 (D^2 - a^2)} \right) \tag{27}$$

$$= PV - P \frac{V_0^2}{V} \tag{28}$$

This is *not* the familiar PV term. In the case of MIL-53, the constant $\bar{\bar{S}}$ ensemble differs from the constant P ensemble, because $\bar{\bar{S}}$ is dependent on $\bar{\bar{\alpha}}$. The experimental setup asks for the constant P ensemble, and therefore the correct free energy is the one in equation 21.