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New helium equation of state for pressurized nanobubbles in UO₂: matrix calculated via molecular dynamics simulations

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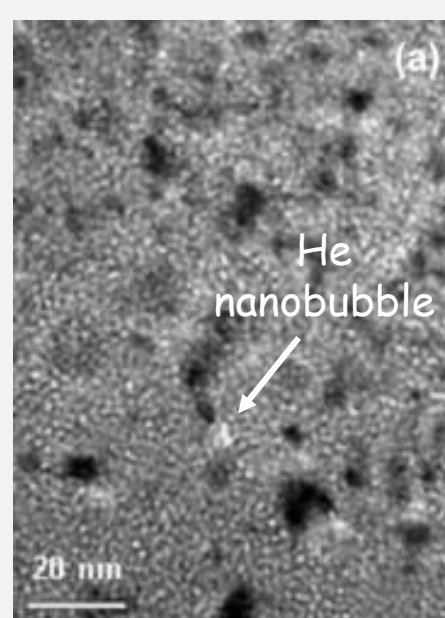
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Motivation

During storage helium atoms accumulate in spent fuel via α -decay. These helium atoms may cluster into nanoscopic bubbles (c.f. opposite Figure), which could change the physical properties of spent fuel. To estimate the impact of such bubbles, it is essential to possess a good thermodynamical model for helium interacting with the surrounding matrix including states at high pressures and temperatures. Therefore, MD simulations are carried out to establish a new equation of state (EOS) for helium in nanobubbles embedded in UO₂ matrix.

T. Wiss et al. JNM 451 (2014) 198

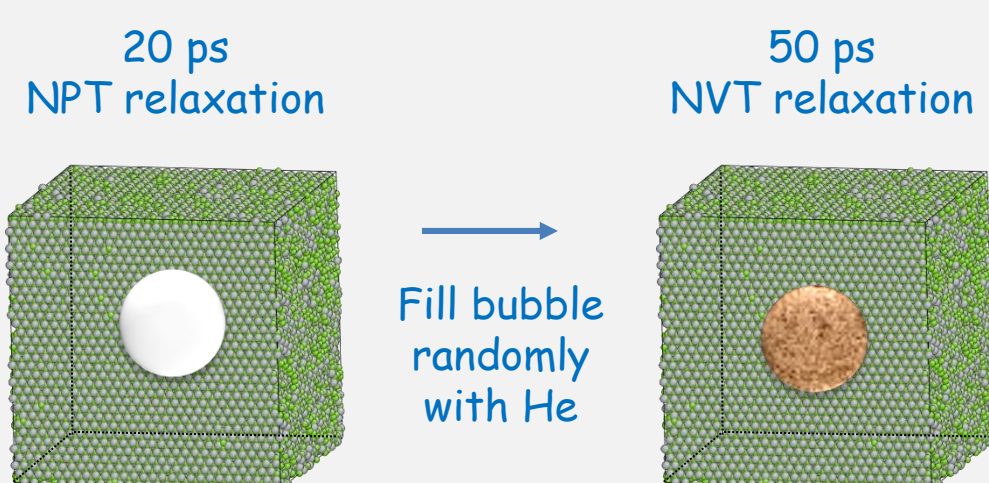


TEM bright field images of the U_{0.9}Pu_{0.1}O₂ (1.7×10¹⁹ α.g⁻¹) showing bubbles of about 1-2 nm diameter

Method

Bubble:

- Bubbles sizes: **1 to 10 nm**
- Temperatures: **300 to 900 K**
- Helium concentration: **3×10⁻² to 0.4 mol.cm⁻³** (0.3 → 3.3 n_{He}/n_{vac})



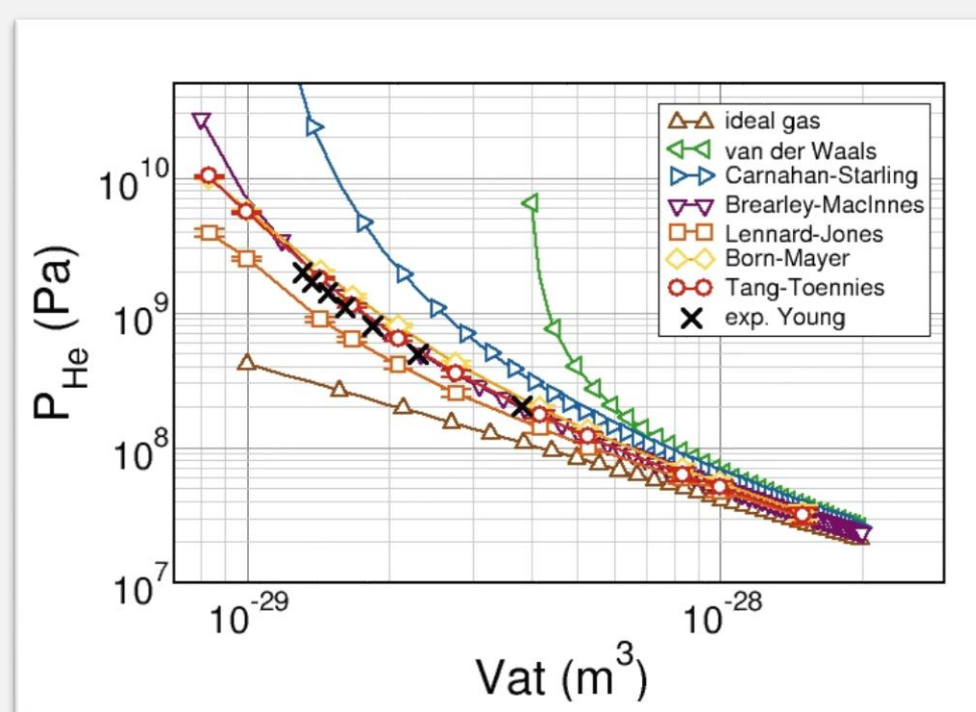
$$P_{He} = \left\langle \frac{N_{He} k_B T}{\Omega} + \frac{1}{3\Omega} \sum_{i=1}^{N_{He}-1} \sum_{j>i} \vec{r}_{ij} \cdot \vec{f}_{ij} \right\rangle$$

Potentials:

- UO₂: **Morelon** Phil Mag 83 (2003) 1533
- UO₂-He: **Lennard-Jones** JNM 172 (1990) 123
- He-He: **Tang-Toennies** JCP 118 (2003) 4976

$$\phi_{He-He}(r) = A \exp\left(\frac{-r}{\rho}\right) - f_6 \left(\frac{r}{\rho}\right) \frac{C}{r^6} - f_8 \left(\frac{r}{\rho}\right) \frac{D}{r^8} - f_{10} \left(\frac{r}{\rho}\right)$$

where $f_{2n} \left(\frac{r}{\rho}\right) = 1 - \exp\left(-\frac{r}{\rho}\right) \sum_{k=0}^{2n} \left(\frac{r}{\rho}\right)^k \frac{1}{k!}$



Comparison of EOS for pure He calculated by MD simulations.

He EOS embedded in UO₂

The hard-sphere formalism based on Carnahan-Starling model is used to fit the new EOS. However, we account herein for the interactions between the UO₂ matrix and the He atoms.

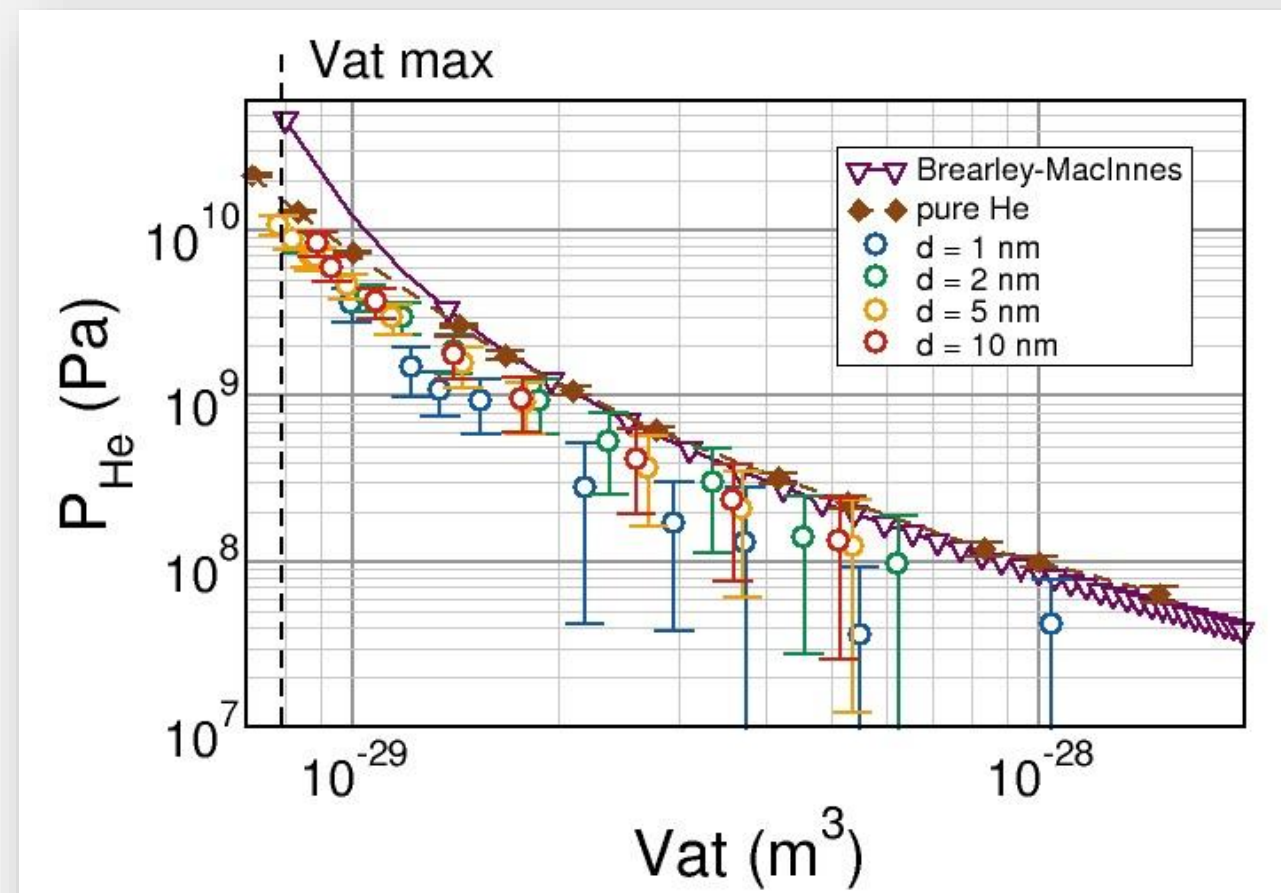
The new parameters for the He EOS are:

$$P_{He} = \frac{k_B T (1 + y + y^2 - y^3)}{V_{at} (1 - y)^3}$$

$$\text{Packing factor } y = \frac{1}{V_{at}} \frac{\pi d^3}{6}$$

Hard-sphere diameter

$$d = \sigma \left[A - B \ln\left(\frac{T}{\varepsilon}\right) \right]$$



$$d = 2.973 \left[0.8414 - 0.05 \ln\left(\frac{T}{10.985}\right) \right] \quad \begin{matrix} d \text{ in } [\text{\AA}] \\ T \text{ in } [\text{K}] \end{matrix}$$

$$V_{at \text{ max}} = 7.8 \times 10^{-30} \text{ m}^3$$

⇒ Allows more He atoms in bubbles than with previous EOS (I Brearley & D MacInnes JNM 95 (1980) 239)

Mechanics of nanobubbles

Damage:

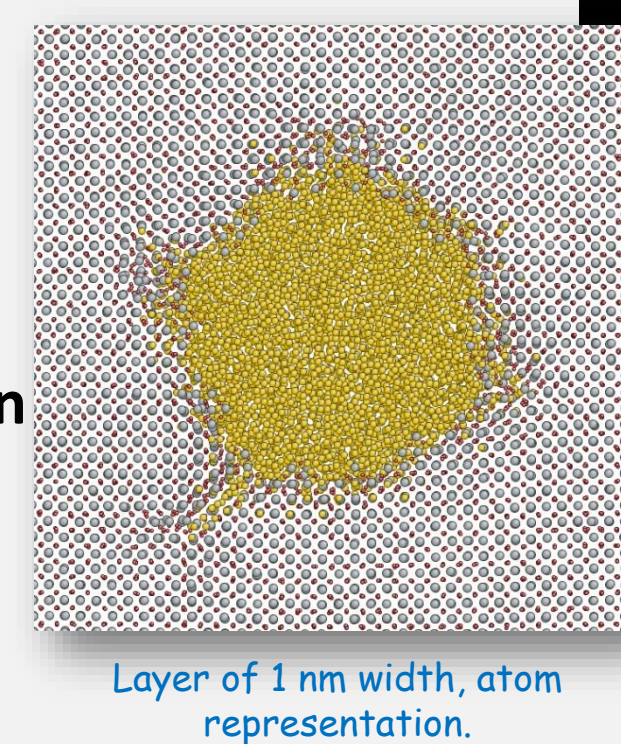
- For diameter < 5 nm ⇒ **No damage** found
- For diameter ≥ 5 nm both **nano-cracks** and **dislocations** appear at the bubble surface for He concentration ≥ 2.4 n_{He}/n_{vac} (5 nm) and ≥ 1.9 n_{He}/n_{vac} (10 nm)

Critical pressures:

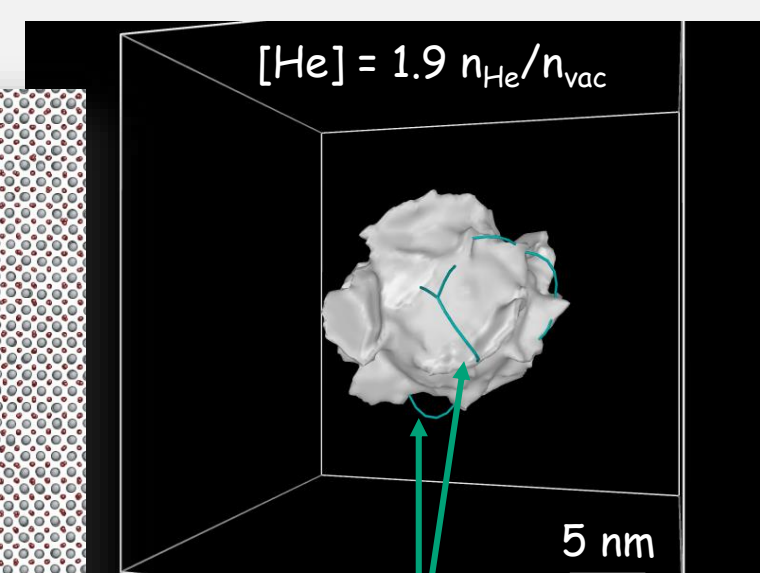
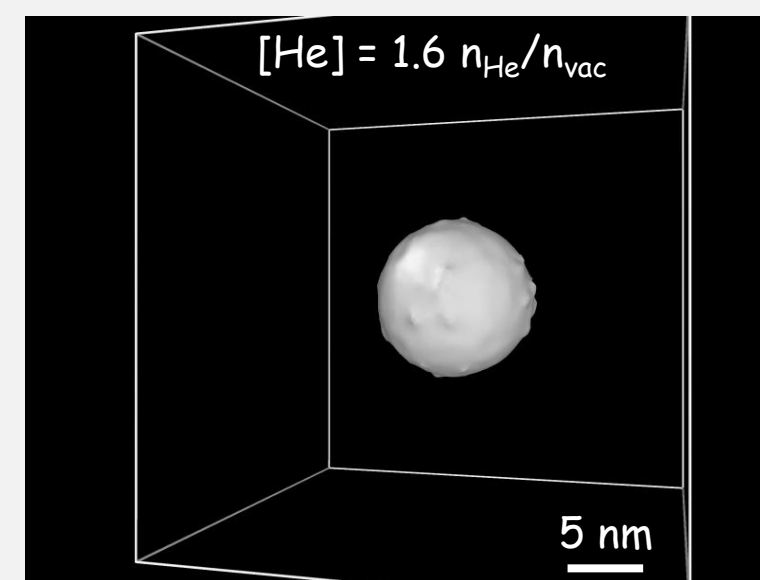
- 5 nm: P_{He}^{crit} = 10.4 GPa
- 10 nm: P_{He}^{crit} = 6.5 GPa

Equivalent to **Griffith criterion** for brittle fracture:

$$P_{He}^{crit} = \frac{K_{Ic}}{\sqrt{\pi \cdot d}}$$



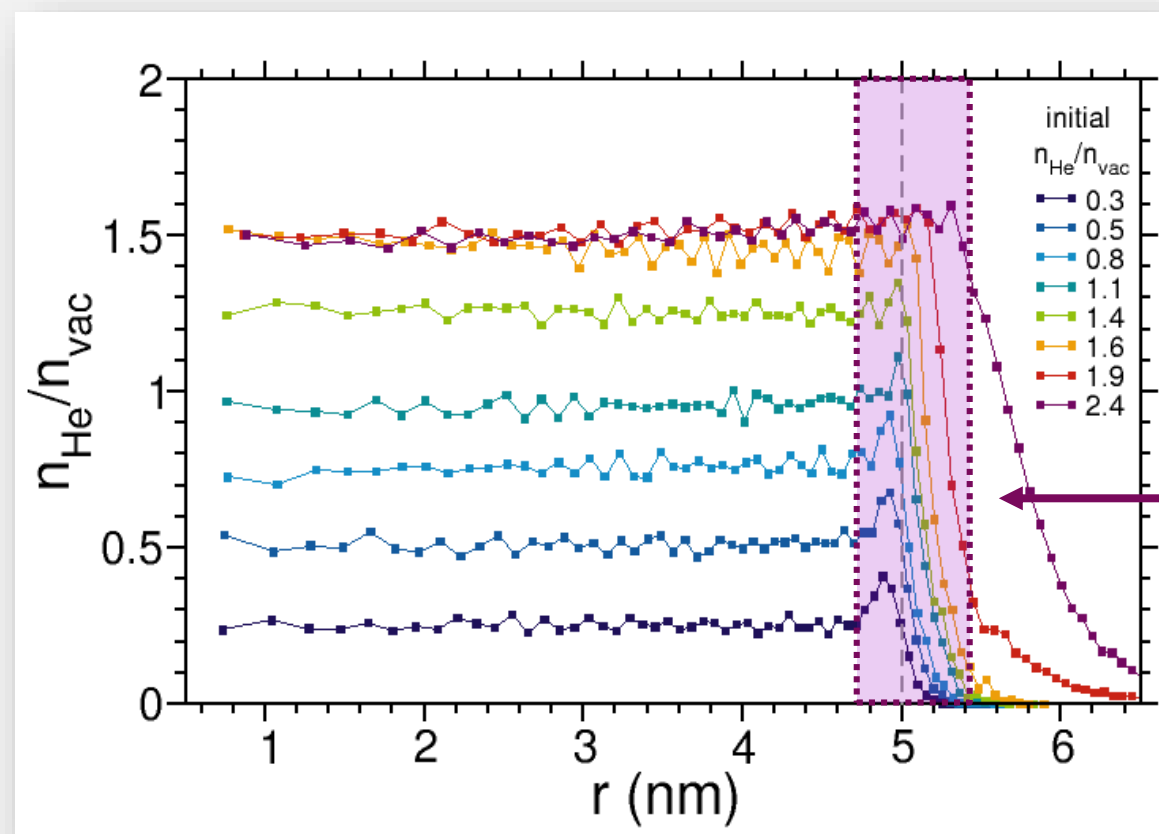
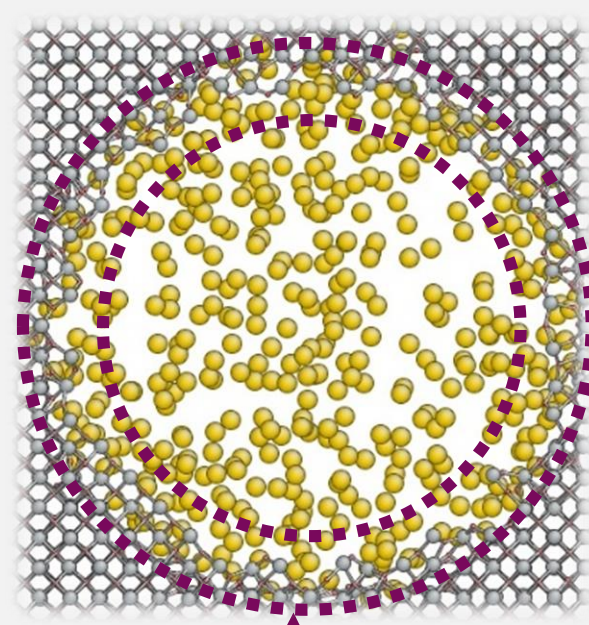
Layer of 1 nm width, atom representation.



Burgers vector: $\frac{1}{2} \langle 110 \rangle$

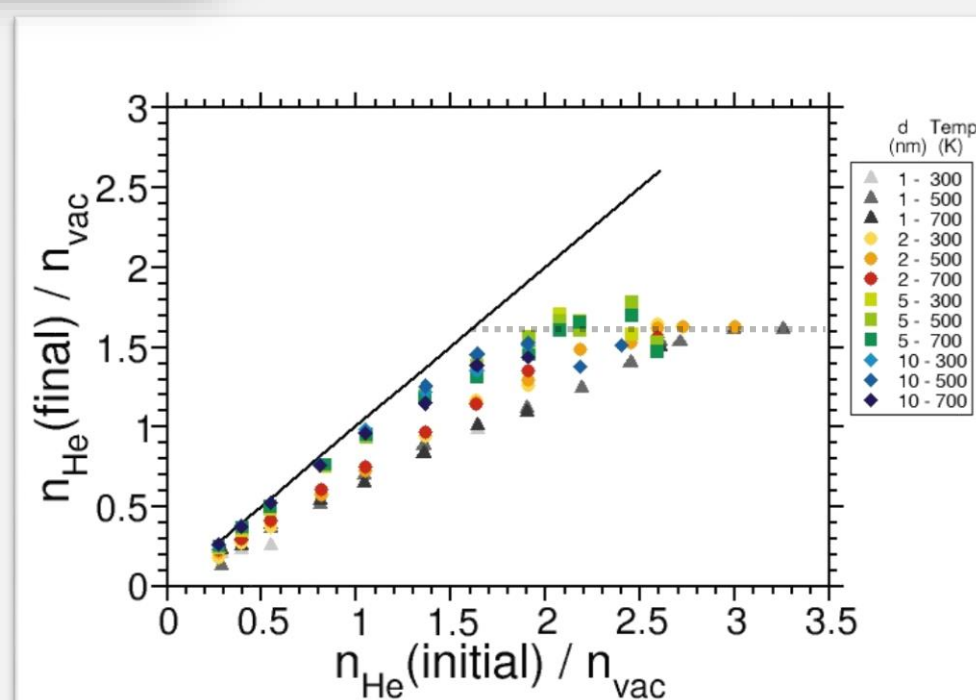
He spatial distribution in bubble

We observe an inhomogeneity in the He atom distribution inside the nanobubble. A **boundary layer** of ~1 nm thickness appears at the bubble surface where He atoms are more concentrated.



Boundary layer 0.4 - 1 nm

A **concentration limit** is found for He atoms inside the nanobubble. This maximum concentration is equal to **1.6 n_{He}/n_{vac}**. Beyond this threshold, the He atoms diffuse into the UO₂ matrix.



Conclusions

A series of MD simulations have been carried out to determine the He equation of state inside nanobubble embedded into UO₂ matrix. To facilitate its implementation into fuel performance codes, we use the same hard-sphere formalism than in the Brearley-MacInnes model. We observe an inhomogeneity in the He atom distribution inside the nanobubble with a boundary layer of about 1 nm thick appearing at the bubble surface where He atoms are more concentrated. We found also a concentration limit for the He atoms inside the nanobubble, which equals 1.6 n_{He}/n_{vac}. For bubble diameters higher than 5 nm nano-cracks or dislocations appear at the bubble surface. At this length-scale, the critical pressure for the crack onset is equivalent to the values calculated with the Griffith criterion for brittle fracture.

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