Effect of Pores and He Bubbles on the Thermal Transport Properties of UO_2 by Molecular Dynamics Simulation

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Abstract:

The thermal conductivities of UO_2 single crystals containing nanoscale size pores and He gas bubbles are calculated using non-equilibrium molecular dynamics as a function of pore size and gas density in the bubble. As expected, the thermal conductivity decreases as pore size increases, while the decrease in thermal conductivity is determined to be more substantial than the predictions of traditional analytical models by Loeb and Maxwell-Eucken. However, the recent model of Alvarez, which is applicable when the phonon mean-free path is comparable to the pore size, is able to quantitatively reproduce the simulation results. The thermal conductivity of UO_2 of the small pores considered here is reduced further when the pore is filled with He gas. This surprising result is due to the penetration of the helium atoms into the lattice where they act as phonon scattering centers.

Keywords

Thermal conductivity, Porosity, Molecular dynamics

1 Introduction

The thermal conductivity of uranium dioxide (UO_2) fuel is one of its key performance metrics. The thermal conductivity of an electrical insulator such as UO_2 is sensitive to the microstructure of the material; irradiation causes significant microstructural changes, including the generation of both soluble and insoluble fission products, grain-size refinement (including the rim effect¹), development of off-stoichiometry and the development of porosity and gas bubbles. The focus of this work is on the effect of pores and bubbles on thermal transport properties².

Porosity is ubiquitous in UO_2 ; residual porosity is present from the fabrication process and is also generated during burnup. A certain amount of porosity can be desirable to minimize fuel swelling.² Depending on the exact specification, the density of as prepared fuel ranges from 80% to 95% of the theoretical density of UO_2 ; that is the porosity ranges from 20% to 5%. Typically, pore sizes in the freshly sintered fuel pellet are on the scale of tens of μm .² At high linear power rates such as are found in fast fission reactors, these initial pores are driven by the thermal gradient towards the center of the fuel pin, where they form a central void. In the process of microstructure evolution due to fission, bubbles are formed which are filled with the inert gases He, Kr and Xe due to their very low solubility in the UO_2 matrix. The typical size of these bubbles is much smaller than as-fabricated pores, on the scale of 10-1000 Å.^{3, 4} Larger bubbles tend to form at the grain boundaries, while the smaller bubbles remain in the interior of the grains. However, regardless of its origin, porosity reduces the thermal conductivity of the UO_2 . Therefore, understanding the contribution of the porosity to the thermal conductivity of UO_2 is important.

The contribution of the porosity to the thermal conductivity of UO_2 has received much attention over the years. Many analytical models have been proposed to describe its effects⁵⁻⁹. These models describe the thermal conductivity as functions of porosity fraction and/or temperature, with coefficients describing the porosity geometry. Fuel-performance codes such as FRAPCON adopt such analytical models for the effect of porosity on thermal transport¹⁰⁻¹².

Continuum modeling and meso-scale modeling have also been applied to investigate thermal conductivity of UO_2 with porosity¹³⁻¹⁵. Millett *et al.* reported that intergranular bubbles reduce the thermal conductivity to a greater degree than randomly-dispersed bubbles¹³. Similarly, Oh *et al.* calculated the thermal conductivity of UO_2 with intergranular and intragranular bubbles using finite difference methods, and found agreement between their results and an analytical model¹⁴. Hayes *et al.* also investigated the thermal conductivity of UO_2 using the finite element method¹⁵. Their findings included: i) continuum level simulations generally agree with analytical models due to Loeb and Maxwell-Eucken (see below for a detailed discussion of these models), ii) helium gas within a pore (i.e., a helium gas bubble) increases thermal conductivity via conduction through the gas, and iii) the contribution of radiation to thermal conductivity in UO_2 can be significant for pores with diameters larger than 100 μm .

None of these approaches takes into account the atomic-level structure of the materials. There has been considerable work in recent years on using atomic-level simulation methods to characterize the thermal-transport properties of UO_2 , including the contributions of grain boundaries¹⁶, dislocations¹⁷, impurities present in mixed oxide fuels¹⁸⁻²⁰ and off-stoichiometry²¹⁻²³. The effect of porosity was considered at the atomic level in the context of nanoporous Si²⁴⁻²⁶, where a strong reduction of thermal conductivity was found, with a precise value that depended on the average pore size. An analytical approach to describe this behavior was developed on the basis of phonon hydrodynamics^{27, 28}. MD simulations were used to investigate the effect of nanoscale pores on thermal conductivity in SiC and the results demonstrated a larger effect than that predicted by the standard continuum model²⁹. Indirect contributions to the thermal conductivity of UO_2 from the atomic structure were considered by Colbert and coworkers³⁰. In that work, a model based on the Mathiessen rule³¹ was considered, and the contribution to thermal resistance from pores was deduced from the Casimir limit³², thus associating the phonon-pore scattering length with the mean pore-pore separation. In this model, the atomic structure of the pore was used to evaluate the thickness of the reconstructed layer at the inner surface of the pore which contributes to the effective pore-pore distance.

The effect of porosity on thermal transport in UO_2 has not yet been directly characterized at the atomic level. While there are a few atomistic simulation studies of pores in UO_2 ³³⁻³⁷, they have focused on phenomena such as migration under a thermal gradient³³, thermomechanical properties³⁴, interaction of the pores with each other³⁸ or with grain boundaries,³⁵ and re-solutioning of inert gases from bubbles in the lattice^{36, 37}. In this article, the thermal conductivity of porous UO_2 is characterized. Due to computational load restrictions, we considered only relatively small bubbles with radii less than 12 Å. As a result, our work is most relevant for small intragranular bubbles. This focus on small bubbles is appropriate because the details of the atomistic structure are expected to be most important precisely in this regime, where the size of the pores is comparable to the phonon mean free path in the material. We apply non-equilibrium molecular dynamics (MD) to establish the relative contributions of the pores, and helium gas within the pores, to the overall thermal conductivity of UO_2 . The results are compared with classical analytical results. The rest of the paper is organized as follows. In Section 2 we present the computational details of the MD simulations and discuss representative, successful analytical approaches. Section 3 presents the results and discussion for the empty pores, Section 4 analyses the findings for the gas-filled voids. Finally, Section 5 presents our conclusions.

2 Computational details

2.1 Structure of Simulation Cell and Simulation Procedure

The three-dimensionally periodic simulation supercell for the thermal conductivity simulations consists of two identical blocks each containing $10 \times 10 \times 20$ cubic non-primitive fluorite unit cells of UO_2 , both of which contain a pore or bubble, see Figure 1. One block is the mirror of the other and they join seamlessly at the center to the heat source, which is indicated by the red stripe in the center of the structure illustrated in Figure 1. The heat sink is indicated by the blue stripes at either end of the structure shown in Figure 1. Spherical pores of radii from 2 to 12 Å, with an interval of 2 Å, are considered. The pore is placed at the center of the $10 \times 10 \times 20$ unit-cell block. U atoms within the radius of the sphere are identified, and are removed along with two neighboring O ions, thereby maintaining charge neutrality within the simulation cell. The percentage of the simulation cell that is pore, i.e., % volume

porosity, varies from 0.01% ($r = 2 \text{ \AA}$) to 2.2% ($r = 12 \text{ \AA}$), which is the maximum percentage for which the supercell remains stable; experimentally the most relevant range for porosity varies from ~ 2 to $\sim 10 \%$,³⁹. To create a He bubble in the simulations, He atoms at a pre-specified density are placed randomly within the pore followed by equilibration of all the atoms associated with the structure.

Figure 1. 3-D periodic simulation cell containing $10 \times 10 \times 40$ cubic unit cells of UO_2 with two spherical pores ($r=8.0 \text{ \AA}$) filled with He atoms at a density of $2.88 \times 10^{28} \text{ atoms/m}^3$. Red (center) and blue stripes (ends) depict the heat source and heat sink regions, respectively. The direction of heat flow is indicated by the arrows. The inset shows the structure of a bubble with the He atoms shown in green.

2.2 Simulation Methods

The interatomic interactions in ionic systems can be considered to consist of a long-range electrostatic component and a short-range, mainly repulsive component that accounts for the interaction of overlapping electron clouds. Here the interatomic description for the UO_2 -He system developed by Grimes *et al.*⁴⁰ is used. Specifically, the Buckingham potential:

$$V(r_{ij}) = A_{ij} \exp(-r_{ij} / \rho_{ij}) - \frac{C_{ij}}{r_{ij}^6} \quad (1)$$

is employed to describe the short-ranged U-U, U-O and O-O, while the Lennard-Jones potential:

$$V(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (2)$$

is utilized to describe the He-U, He-O and He-He short-ranged interactions. The parameters are given in Table I.

Table I. Parameters for the (a) Buckingham potentials, and (b) the Lennard-Jones potentials⁴⁰.

(a)			
Buckingham	A_{ij} [eV]	ρ_{ij} [$\text{\AA}$]	C_{ij} [$\text{eV}\text{\AA}^6$]
O-O	108	0.38	56.06
U-O	2494.2	0.34123	40.16
U-U	18600	0.27468	32.64

(b)		
Lennard-Jones	ϵ [eV]	σ [$\text{\AA}$]
He-O	0.0153864	2.400015
He-U	0.027106	2.019993
He-He	0.00219	2.559

The long range electrostatic interactions are determined using the direct-summation method, which involves truncation of the electrostatic force at a cutoff radius, with charge compensation on the truncated spherical surface⁴¹. This method is straightforward to implement and is computationally efficient with a cost that scales linearly with system size.

The technique has been successfully applied to a number of materials⁴²⁻⁴⁵. The appropriateness of using the direct-summation method for the UO₂ system has been established previously^{16, 21}, and in the context of the thermal transport simulations it was found to produce reasonable agreement with the exact Ewald summation⁴⁶.

The macroscopic definition of thermal conductivity, k , comes from Fourier's Law:

$$J = -k \frac{dT}{dx} \quad (3)$$

where J is the heat current and dT/dx is the temperature gradient. Here the 'direct method', involving the non-equilibrium MD (NEMD) simulation of heat flow through a system, of inducing temperature gradient is used⁴⁷.

2.3 Theoretical and phenomenological approaches

There are a large number of macroscopic approaches that describe the effect of porosity on thermal conductivity. Here the results of the MD simulation are compared against the predictions of particularly pertinent methods.

Thermal transport in porous materials, as applied to nuclear fuels, has been reviewed in a number of publications^{2, 8, 48}. The simplest theoretical models consider two phases as resistors connected in parallel⁷. While this approach leads to ambiguity⁴⁸, the standard result obtained by Loeb is:

$$\frac{k}{k_s} = 1 + P_c \left[\frac{\frac{k_p}{k_s} - 1}{1 + \frac{(1 - P_L) k_p}{P_L k_s}} \right] \quad (4)$$

where k_s is the thermal conductivity of the pure material, k_p is the thermal conductivity of the material in the pore, P_c is the fractional cross-sectional area of the pores, P_L is the fractional length of the pore.

If the pore is empty, then it is considered to have zero thermal conductivity, in which case the limit of Eq. 4 becomes:

$$\frac{k_{CorrLoeb}}{k_s} = 1 - P_c = 1 - P^{2/3} \quad (5)$$

where P now is the volume porosity. Franci and Kingerly⁴⁹ used a different definition of the P_c to the one used by Loeb² and arrived at an equation that is widely known as the Loeb equation:

$$\frac{k_{Loeb}}{k_s} = 1 - P \quad (6)$$

This equation, however, was found to be inadequate in some cases, particularly in UO_2 ^{6, 50}, which led to the introduction of the modified Loeb equation with the empirical constant α , which has been assigned values from 1.5 to 2.8, depending on stoichiometry:⁵¹

$$\frac{k_{ModLoeb}}{k_s} = 1 - \alpha P \quad (7)$$

More sophisticated models consider analogies between thermal transport and electrical transport, following the original work of Maxwell⁵². The resulting expression is known as the Maxwell-Eucken formula and is applicable for spherical pores:

$$\frac{k_{Maxwell}}{k_s} = \frac{1 - P}{1 + 0.5P} \quad (8)$$

Generalization of this equation for elliptically shaped pores^{53, 54} affects only the coefficient in front of P in the denominator of Eq. 8. It is thus common to rewrite it in the following form with parameter β :

$$\frac{k_{FRAPCON}}{k_s} = \frac{1 - P}{1 + \beta P} \quad (9)$$

A slightly modified version of this equation, developed by Biancheria⁵³, is used in the FRAPCON fuel performance code^{10, 12}.

Finally, Ondracek and Schulz⁴⁸ introduced a more general expression that links together the effective thermal conductivity, a geometrical factor F (accounting for the

ellipsoidal shape of the pores) and orientation factor $\cos^2(\varphi)$ (that accounts for the pores' relative orientation):

$$\frac{k_{Ondracek}}{k_s} = (1 - P)^{\frac{\cos^2(\varphi)}{2F} - \frac{1 - \cos^2(\varphi)}{F - 1}} \quad (10)$$

Substituting values of $F=0.33$ and $\cos^2(\varphi)=0.33$ as valid for spherical pores,⁴⁸ one arrives at a simple expression: $\kappa_{Ondracek}/\kappa_s = (1 - P)^{3/2}$. Note that in the limit of $P \rightarrow 0$, Eq. 8 is equivalent to Eq. 10, and equivalent to the modified Loeb equation with $\alpha=1.5$.

The unsatisfactory performance of the simple approaches surveyed above in comparison to the experimental data^{8, 55} led to the introduction of phenomenological models. In particular, Aivazov and Domashnev started from Eq. 9 and observed that an especially good fit to the experimental data might be obtained if β were a linear function of porosity:⁵⁵

$$\frac{k_{Aivazov}}{k_s} = \frac{1 - P}{1 + nP^2} \quad (11),$$

with the value of $n=4$ for UO_2 being determined by Rhee⁸. Further refinements include the effects of temperature. In particular, Asamoto *et al.*⁵ fitted experimental data in UO_2 over the range $1073 \text{ K} < T < 2273 \text{ K}$ with $0.05 < P < 0.18$ and obtained a result, that we rewrite in the same form as Eqs. 4-11:

$$\frac{k_{Asamoto}}{k_s} = 1 + \frac{2008}{(1 + 11.66P)(T - 273.15)} \quad (12)$$

Additionally, Van Craeynest *et al.*⁹ fit data in the range $323 \text{ K} < T < 1273 \text{ K}$ by considering the coefficient α in the modified Loeb equation to be a function of temperature:

$$\frac{k_{Van\ Craeynest}}{k_s} = 1 - [2.58 - 0.58 \times 10^{-3}(T - 273.15)]P \quad (13)$$

We note that none of the expressions described above differentiate between porosity produced by a few large pores and porosity of equal volume caused by a larger number of

smaller pores. In the regime in which the phonon mean free-path, l , is much smaller than the pore radius, r , dependence on the overall porosity P alone is reasonable. However, when the mean free path is comparable to or longer than the pore radius, the size of the individual pore also becomes important. The mean free path in UO_2 is relatively short, on the scale of few nanometers; thus it is precisely the nanoscale pores considered in this work for which the effect on thermal conductivity is expected to be the most pronounced. Dependence on the size of the pores has been considered in the context of nanoporous silicon, a material with a far longer mean free path than UO_2 , and for which the effect is presumably much more important^{27, 28}. A model derived by Alvarez and coworkers²⁷ is analogous to hydrodynamic flow with particular attention to the limit in which the mean free path is greater than the obstacle size. In this limit, the generalization of the Fourier equation is mathematically equivalent to the Navier-Stokes equation. Resistance to the “flow of phonons” from spherical particles is then given simply by Stokes Law properly adjusted to the large Knudsen numbers and random distribution of particles. The resulting expression is:

$$\frac{k_{\text{Alvarez}}}{k_s} = \frac{1}{\frac{1}{k_{\text{Loeb}}} + \frac{9}{2} P(l/r)^2 \{1 + (0.864 + 0.29e^{-1.25r/l})l/r\}^{-1} \left[1 + \frac{3}{\sqrt{2}} \sqrt{P}\right]} \quad (14),$$

The first term in the denominator describes a geometrical reduction factor as produced by one of the approaches described above, for which we use the Loeb equation, though at small porosities the specific model used is not especially important. The second term in the denominator is an additional “resistance” from Stokes Law with corrections for the mean free path greater than the pore radius (term in curly brackets) and a random pore distribution (term in square brackets).

3 Results and Discussion

3.1 Thermal conductivity of UO_2 as a function of porosity

Figure 2. Temperature profile of UO_2 calculated by non-equilibrium molecular dynamics for a pore-free system and for a system with pore radii of $r=12.0$ Å.

Temperature profiles from MD simulations for a pore-free system and for the system with pores of uniform radii $r=12.0$ Å are given in Figure 2. Since the heat flux used is the same in each case, the steeper gradient for the system with pores indicates that the pores reduce the thermal conductivity. The MD results for the dependence of the thermal conductivity on the porosity volume fraction are shown as the solid squares in Figure 3. Since each simulation provides two data points for thermal conductivity due to the periodic boundary conditions, the difference between them can be used to assess statistical accuracy of the simulations. Each of the linear regression fits to the temperature profile in turn carries a statistical uncertainty. These error sources were combined to produce the error estimates shown as error bars in Figures 3 and 4.

Figure 3. Effect of porosity on effective thermal conductivity from analytical models described in the text and MD simulations. The left panel shows models that describe random pore positions, while the right panel shows the Loeb and Alvarez models that describe the pore arrangement used in MD simulations. The Alvarez model uses a phonon mean free path of 3.6 nm.

For the lowest porosity considered in the MD simulations, 0.01% ($r = 2 \text{ \AA}$), the simulations yield no discernible effect on the effective thermal conductivity of the system. However, at higher porosities, the thermal conductivity has a greater and more complex effect than predicted by the simple analytical models. It decreases sharply between $P=0.1$ and $\sim 0.7\%$, followed by a slow, almost linear reduction at higher porosities, reaching a reduction of $\sim 28\%$ for $P = 2.2\%$ ($r = 12 \text{ \AA}$).

The MD results for the thermal conductivity are compared to the empirical equations discussed above in Fig. 3a. The model due to Alvarez²⁷ predicts only a slightly greater thermal conductivity than the MD data, while all the other models considered significantly underestimate the reduction of the thermal conductivity. A likely source of the disagreement between the MD simulation and other approaches is the distribution of lattice pores within the simulated system. Namely, periodic boundary conditions effectively arrange all pores in a single plane and due to the relatively small dimension of the UO_2 supercell in the direction perpendicular to heat flow, the effect of the lattice pore as a barrier for thermal flow can be magnified beyond that of the random distribution assumed in the analytical approaches. The models due to Loeb (Eq. 5) and Alvarez (Eq. 14) can be adjusted to include not only a random distribution of pores, but also to a specific geometry. The results of these calculations are provided in the right panel of Figure 3b and it is clear that both models predict a greater

reduction of thermal conductivity than models using a random distribution of pores. In particular, the results of the Alvarez model fall within the error bars for all the considered porosities.

Clearly, accounting for the dimension of the pore relative to the phonon mean free path is an important feature for the Alvarez model that makes it stand out from all of the other approaches. This is not particularly surprising since continuum level theories (represented by Eqs. 5-10) break down when the mean free path of the phonons becomes comparable to the defect dimensions. At the same time, the smallest pores considered here constitute a small fraction of the pore-size distribution in the real material; thus our MD predictions may over-emphasize their contribution relative to the larger-sized pores accounted for by the analytical models (Eqs. 11-13). Nevertheless, our results suggest that small pores can be a more important contributor to the thermal conductivity degradation of the UO_2 than previously realized, and that the Alvarez model is quite successful in predicting the thermal conductivity for the smallest pores in UO_2 .

3.2 Effect of He Density on Thermal Conductivity

We now proceed to examine how filling the pore with gaseous helium (He) at various concentrations further affects the thermal conductivity of the UO_2 . Intuitively, we expect that filling the pore with a material that has a non-zero thermal conductivity would lead to an increase in the overall thermal conductivity. To quantify this intuition, we first examine the prediction of the Loeb equation. Gaseous He has a relatively high thermal conductivity, 0.3 W/m-K at 800 K⁵⁶; the density of the gas in the pore is unimportant since in the case of an ideal gas of hard spheres the thermal conductivity is independent of pressure for a given temperature. As radiative thermal transfer is expected to be small under these conditions¹⁵, the thermal conductivity of He gas inside the pore will represent pore conductivity, k_p . Thus for a porosity of 2.2% ($r = 12 \text{ \AA}$), the Loeb equation predicts an enhancement of 1.1% for He-filled bubbles relative to empty pores.

Turning now to the MD simulation results, Figure 4 provides the effect of various He-gas densities on the thermal conductivity relative to pores of the same size. The presence of He has little effect on k for the $r=4.0 \text{ \AA}$ case. However, as the pore size increases to $r=8.0 \text{ \AA}$

and, particularly to $r=12.0 \text{ \AA}$, the presence of He in the pore results in a significant decrease in the thermal conductivity (as much as 1.39% for $r=8.0 \text{ \AA}$, and 8.76% for $r=12.0 \text{ \AA}$). This result is completely contrary to our intuition that the filling the pore with gas should lead to an increase in the thermal conductivity. It is also completely contrary to the predictions of the empirical formulas.

Figure 4. Deviation of thermal conductivity, $\Delta k/k_p$ (%) as a function of helium density within the lattice pores ($\times \text{atoms/m}^3$).

To determine the origin of this decrease, it is instructive to examine the distribution of He in and around the pore. Figure 5 illustrates the radial distribution functions for U, O, and He atoms for the case of pores with $r=12.0 \text{ \AA}$. The figure indicates that the He atoms are not confined to the bubble, but diffuse, or penetrate, into the UO_2 lattice. These He atoms in the lattice are mainly inserted as interstitials within UO_2 octahedral site; in the case of the $r=12 \text{ \AA}$ bubble with a He density of 1.49, about 75% of the He atoms are in such sites, as indicated by Figure 5(b). This is consistent with previous experimental and computational studies^{57, 58}.

Gas bubbles dissolution into the UO_2 matrix does happen under irradiation environment due to the interaction of the bubble with fission spikes.^{3, 59} In these conditions the resolution layer thickness was estimated using the SRIM (Stopping and Range of Ions in Matter) software⁶⁰ by Noirot⁶¹ who obtained the penetration length of He into UO_2 to be around $20 \text{ \AA}$. In our simulation the diffusion length is shorter because there is no irradiation:

examination of Figure 5(b) and Figure 5(d) reveals that in MD simulations this thickness approaches 6-8 Å. While the details of the resolution process may be different in irradiated fuel and our simulation, the conclusion that gas in the pores will cause overall reduction of thermal conductivity should remain valid.

Figure 5. Radial distribution of U, O, and He atoms within a sphere of $r=12$ Å. The total number of each atom within the sphere is plotted versus the distance from the pore center. (a) Initial He density in the pore ($\times 10^{28}$ atoms/m³) is 0.72, and the number of He atoms, n_{He} , is 54, (b) initial He density = 1.49 and $n_{\text{He}}=108$, (c) initial He density = 1.8 and $n_{\text{He}}=130$, and (d) initial He density = 2.5 and $n_{\text{He}}=181$.

Figure 6 illustrates the number and fraction of He atoms that have penetrated into the UO_2 lattice after 600 ps. While the fraction of atoms that penetrates the lattice does not depend on He density, the total number of He atoms that penetrate into the UO_2 lattice increases with the He bubble density.

Figure 6. Number (red) and fraction (blue) of He atoms inside the UO₂ lattice as a function of initial He density within the pore for $r=12.0\text{\AA}$.

From the results in Figure 4 - 6, it is possible to construct a coherent picture of the origin of the thermal conductivity of pores and He bubbles. The decrease in the thermal conductivity in He-filled pores originates from the infiltration of the He atoms into surrounding UO₂ lattice. These He atoms act as scattering centers for the heat-carrying phonons, as well as inducing displacements of U and O atoms in their vicinity. To assess the contribution of such interstitial He atoms to the thermal conductivity of UO₂, we determine the thermal conductivity of a single crystal of UO₂ with 80 He atoms inside a perfect-crystal region of diameter $r=20\text{ \AA}$. This results in density of 0.2×10^{28} atoms/m³ which approximately corresponds to the density of He atoms in the UO₂ lattice in the case of initial He density in the pore of 1.8×10^{28} atoms/m³ in Figure 6. The thermal conductivity of UO₂ containing this He interstitial cluster is decreased to $\kappa_l/\kappa_s = 0.91$. Such a measurable reduction in effective thermal conductivity convincingly demonstrates that dissolved He atoms from the bubble are responsible for the lower thermal conductivity of the bubble structure in comparison with the empty pore.

While the additional reduction from He penetration into the UO₂ lattice is substantial for the nanoscale pores, it is expected to have far weaker influence for micron-sized pores.

This is due to the fact that the He atoms' penetration depth is unlikely to change significantly for the larger pore and should remain on the scale of 1-2 nm. Consequently, the thickness of the layer with reduced thermal conductivity relative to the size of the pore is much smaller for a microscale pore. In addition, an increase in the thermal conductivity due to the non-zero He gas conductivity is expected for large pores. We thus expect that microscale pores filled with He will have larger thermal conductivities than empty pores.

4 Conclusions

In this work we have elucidated for the first time the details of the thermal transport properties of porous UO_2 using non-equilibrium molecular dynamics and compared the results with the available analytical models. We find that the reduction of the thermal conductivity due to nanoscale pores is far more substantial than that predicted by the classical Loeb analysis or similar approaches. Instead, satisfactory agreement is found with the model due to Alvarez that takes into account the fact that the phonon mean free path is greater than or comparable with the characteristic pore dimension. Our findings also indicate that the smallest intragranular pores may have a more significant impact on the thermal transport in UO_2 than previously realized.

Gas filled bubbles, on the other hand, are unexpectedly found to further reduce the thermal conductivity compared with the empty pores. A detailed investigation reveals that this is due to the re-solution of the He atoms within the UO_2 lattice surrounding the bubble. For larger bubbles, however, we expect this effect to be insignificant, and their thermal conductivity to be slightly larger than that of the empty pore due to the possibility of the thermal transport through the gas.

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Figure Captions

Figure 1. 3-D periodic simulation cell containing $10 \times 10 \times 40$ cubic unit cells of UO_2 with two spherical pores ($r=8.0 \text{ \AA}$) filled with He atoms at a density of $2.88 \times 10^{28} \text{ atoms/m}^3$. Red (center) and blue stripes (ends) depict the heat source and heat sink regions, respectively. The direction of heat flow is indicated by the arrows. The inset shows the structure of a bubble with the He atoms shown in green.

Figure 2. Temperature profile of UO_2 calculated by non-equilibrium molecular dynamics for a pore-free system and for a system with pore radii of $r=12.0 \text{ \AA}$.

Figure 3. Effect of porosity on effective thermal conductivity from analytical models described in the text and MD simulations. The left panel shows models that describe random pore positions, while the right panel shows the Loeb and Alvarez models that describe the pore arrangement used in MD simulations. The Alvarez model uses a phonon mean free path of 3.6 nm .

Figure 4. Deviation of thermal conductivity, $\Delta k/k_p$ (%) as a function of helium density within the lattice pores ($\times \text{atoms/m}^3$).

Figure 5. Radial distribution of U, O, and He atoms within a sphere of $r=12 \text{ \AA}$. The total number of each atom within the sphere is plotted versus the distance from the pore center. (a) Initial He density in the pore ($\times 10^{28} \text{ atoms/m}^3$) is 0.72, and the number of He atoms, n_{He} , is 54, (b) initial He density =1.49 and $n_{\text{He}}=108$, (c) initial He density =1.8 and $n_{\text{He}}=130$, and (d) initial He density =2.5 and $n_{\text{He}}=181$.

Figure 6. Number (red) and fraction (blue) of He atoms inside the UO_2 lattice as a function of initial He density within the pore for $r=12.0 \text{ \AA}$.