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# Describing oxygen self-diffusion in PuO<sub>2</sub> by connecting point defect parameters with bulk properties

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## Abstract

The description of oxygen self-diffusion over a range of temperatures and pressures is important in PuO<sub>2</sub> for nuclear fuel applications. Although there are limited experimental studies describing oxygen self-diffusion in PuO<sub>2</sub>, recent molecular dynamics studies extend the temperature range significantly. In the present study elastic and expansivity data is used in the framework of a thermodynamic model (known as the cBΩ model) to derive the oxygen self-diffusion coefficient in PuO<sub>2</sub> in the temperature range 1800 K to 3000 K. In the cBΩ model the defect Gibbs energy is proportional to the isothermal bulk modulus (B) and the mean volume per atom (Ω). The derived results are in good agreement with the most recent experimental and molecular dynamics data. Importantly, the present study extends the applicability of the model to nuclear fuel materials for the first time, where point defect parameters and behaviour are difficult to determine, particularly at the temperatures considered here.

**Keywords:** PuO<sub>2</sub>; self-diffusion

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## 1. Introduction

In recent years nuclear energy is being reconsidered as a way to meet future global energy demand while limiting greenhouse gas emissions. The custodianship of spent nuclear fuel – typically called nuclear waste – is a daunting political and scientific challenge that stands as a barrier between the promise of nuclear power and its successful technical utilization.

The primary component of conventional commercial nuclear fuel is  $\text{UO}_2$ . This can be mixed with other actinide oxides (for example  $\text{ThO}_2$  and  $\text{PuO}_2$ ) to form mixed oxide fuel (known as MOX fuel) [1-3]. The renaissance of the nuclear industry will require consideration of alternative nuclear fuel cycles and the sustainable utilization of spent fuel in so-called “closed fuel cycles”. Up to 95% of nuclear waste is burnable actinides. Hence, nuclear waste is a significant source of energy; in fact some would argue that it is more appropriate to be called “strategic fuel reserve” than “waste”, particularly if the issues surrounding non-proliferation can be successfully resolved. Detailed and accurate scientific knowledge of various waste components and their chemical and metallurgical properties is required in developing the safe utilization of waste for fuel purposes in appropriate proliferation-resistant technologies.

Additionally, the consideration of fuels based on thorium with high corrosion resistance, high melting point, and higher thermal conductivity (as compared to  $\text{UO}_2$ -based fuels) is of significant interest given the abundance of thorium in some countries [4-6]. The Th-U fuel cycle can lead to lower concentrations of long-lived transuranic elements and is perceived to be more proliferation-resistant, but there are still numerous unresolved issues that need to be clarified [7-9].

The association of the defect Gibbs energy ( $g^i$ ) and bulk properties in solids has been considered by the community for over 60 years, leading to a number of models [10]. Importantly, Varotsos and Alexopoulos [11-13] described  $g^i$  as being proportional to the isothermal bulk modulus  $B$  and the mean volume per atom  $\Omega$ , with  $c$  being the constant of proportionality (referred to hereafter as the  $cB\Omega$  model). In previous studies the  $cB\Omega$  model has been used to describe the defect processes in a number of materials [14-19], however it has not previously been employed to investigate oxygen self-diffusion in  $\text{PuO}_2$ .

As oxygen self-diffusion in  $\text{PuO}_2$  is vacancy-mediated the  $cB\Omega$  model can be applied as it is typically employed in systems with a single diffusion mechanism. Here we use the  $cB\Omega$  model to derive relations for the association of the oxygen self-diffusion coefficients in  $\text{PuO}_2$  with the isothermal bulk modulus and the mean volume per atom.

## 2. Methodology

The activation Gibbs energy ( $g^{\text{act}}$ ) in a crystal with a single diffusion mechanism can describe the diffusion process by the sum of the Gibbs formation ( $g^{\text{f}}$ ) and the Gibbs migration ( $g^{\text{m}}$ ) processes. The activation entropy  $s^{\text{act}}$  and the activation enthalpy  $h^{\text{act}}$  are given by [14,15]:

$$s^{\text{act}} = -\left.\frac{dg^{\text{act}}}{dT}\right|_P \quad (1)$$

$$h^{\text{act}} = g^{\text{act}} + Ts^{\text{act}} \quad (2)$$

The diffusion coefficient  $D$  is defined by:

$$D = fa_0^2ve^{-\frac{g^{\text{act}}}{k_B T}} \quad (3)$$

Where  $f$  is the diffusion correlation factor (which depends upon the diffusion mechanism and crystal structure),  $a_0$  is the lattice constant,  $\nu$  is the attempt frequency and  $k_B$  is Boltzmann's constant.

In the present study we consider the cB $\Omega$  model in which the defect Gibbs energy  $g^i$  is related to the bulk properties of the solid via the relation [11-13]:

$$g^i = c^i B \Omega \quad (4)$$

Combining Eqs. (3) and (4) the following relation is obtained:

$$D = f a_0^2 \nu e^{-\frac{c^{act} B \Omega}{k_B T}} \quad (5)$$

$c^{act}$  is a constant that can be considered to be temperature- and pressure-independent at a first approximation [14,15]. If the pre-exponential factor  $f a_0^2 \nu$  can be calculated using Eq. 5, and by using a single experimental diffusivity  $D_i$  value at a temperature  $T_i$ ,  $c^{act}$  can be derived (single experimental measurement method [14,15]). This  $c^{act}$  can thereafter be used to derive the diffusivity  $D_i$  at any temperature  $T_i$  using Eq. 5, provided that the elastic data and expansivity are known for  $T_i$ . It is important to note that the cB $\Omega$  model can encapsulate anharmonic effects exhibited by the temperature decrease in B and by the thermal expansivity.

### 3. Results and discussion

The main reason to employ atomic-level simulation modelling on nuclear materials is that their properties are difficult to determine directly, particularly under operating conditions [20-28]. Recently, Cooper *et al.* [26] introduced a comprehensive potential set that describes the thermomechanical and thermophysical properties of AmO<sub>2</sub>, CeO<sub>2</sub>, CmO<sub>2</sub>, NpO<sub>2</sub>, PuO<sub>2</sub>, ThO<sub>2</sub> and UO<sub>2</sub> in a wide temperature range (300-3000 K). The potential model by Cooper *et al.* [26] introduces many-body interactions using the embedded atom method and successfully describes the elastic constants of the

actinide oxides. Importantly, it reproduces the Cauchy violation and the bulk modulus over a wide temperature range [26]. The efficacy of this model has been demonstrated to calculate the diffusion and defect process in CeO<sub>2</sub>, PuO<sub>2</sub>, ThO<sub>2</sub> and UO<sub>2</sub> [27-29].

The method of the single experimental measurement [14,15] described above is not unique and a drawback is that  $c^{act}$  is influenced by errors in the B,  $\Omega$ , and  $D_1$  values. These errors can be very significant if only one set of values is considered. Other methods have been used in previous studies to calculate  $c^{act}$  such as the compensation law [30,31] and the “mean value” method [17,18]. In the present study, to avoid errors in the pre-exponential factor and the molecular dynamics uncertainties, the mean value method is considered. The cB $\Omega$  model requires the expansivity and the isothermal bulk modulus data, and given the limited available experimental data the calculated values of Cooper *et al.* [26,29] were used here. These values are reported in Table 1 alongside the molecular-dynamics-derived oxygen self-diffusion coefficients in PuO<sub>2</sub> [26,29].

In the mean value method linear behaviour of  $\ln D_{MD}^{PuO_2}$  versus  $\frac{B\Omega}{k_B T}$  verifies the validity of the cB $\Omega$  model with the slope of the line being (refer to Eq. 5). Figure 1 reports the oxygen self-diffusion coefficients (adopted from [27]) in PuO<sub>2</sub> with respect to  $\frac{B\Omega}{k_B T}$ . It can be concluded from Figure 1 that a single cB $\Omega$  relation cannot describe the whole temperature range considered, as there is a change in behavior at about 2400 K. This is consistent with the superionic transition for PuO<sub>2</sub> which was calculated to occur near this temperature at the MD study of Cooper *et al.* [29] The superionic transition is effectively the transition between the fully crystalline low temperature and the superionic high temperature behavior, and occurs at a higher temperature for ThO<sub>2</sub> (above 3000 K) as compared to UO<sub>2</sub> (around 2650 K) [27,32]. From Figure 1, in the temperature range 1800-2400 K the oxygen diffusion

coefficients derived by the cB $\Omega$  model,  $D_{cB\Omega}^{PuO_2}$ , of PuO<sub>2</sub> with respect to the isothermal bulk modulus and the mean volume per atom is given by:

$$D_{cB\Omega}^{PuO_2} = 1.621e^{-\frac{0.3047B\Omega}{k_B T}} \cdot 10^{-3} m^2 s^{-1} \quad (6)$$

From Figure 1 the superionic high temperature regime (2500-3000 K) can also be described by the cB $\Omega$  model but with a different pre-exponential and  $c^{act}$  factor:

$$D_{cB\Omega}^{PuO_2} = 2.234e^{-\frac{0.0604B\Omega}{k_B T}} \cdot 10^{-8} m^2 s^{-1} \quad (7)$$

Figure 2 is the Arrhenius plot for oxygen self-diffusion coefficients in PuO<sub>2</sub> calculated by molecular dynamics [29] and derived by the cB $\Omega$  model using Eqs. (6) and (7). The linearity and excellent agreement between the molecular dynamics [29] and the cB $\Omega$  model testifies the efficacy of the model to describe PuO<sub>2</sub>. The discrepancies observed at the lower end of the temperature range can be attributed to the calculation of the diffusivities by molecular dynamics.

Here we have established the validity of the cB $\Omega$  model for PuO<sub>2</sub> and in a recent study for UO<sub>2</sub> and ThO<sub>2</sub>. In future work we will aim to use the cB $\Omega$  model to progress to the understanding of the diffusion and thermophysical properties in mixed oxide fuels. Additionally, other defect properties such as formation entropies and enthalpies can be calculated for a range of temperatures and pressures, complementing the available literature.

#### 4. Conclusions

1. This study has applied the cB $\Omega$  model, for the first time, to the study of transport properties of nuclear fuel materials, namely PuO<sub>2</sub>. The defect Gibb's energy is related to the bulk properties of the material, specifically the bulk modulus and the mean

volume per atom. The method has been used to calculate the rate of oxygen self-diffusion in  $\text{PuO}_2$ .

2. There is excellent agreement between results obtained from molecular dynamics simulations and the derived oxygen self-diffusion coefficients in  $\text{PuO}_2$  in the temperature range 1800-2400 K. It was shown that the cB $\Omega$  model adequately describes oxygen self-diffusion in  $\text{PuO}_2$  by considering two regimes, above and below the high-temperature superionic transition between the fully crystalline low temperature and superionic high temperature behaviour.

3. The cB $\Omega$  model can therefore be applied to calculate defect volumes, formation and migration enthalpies and entropies over a range of temperatures and pressures. The findings presented could be relevant to the broader goal of advancing proliferation-resistant technologies in order to harvest the energy potential of spent fuel (i.e., nuclear waste).

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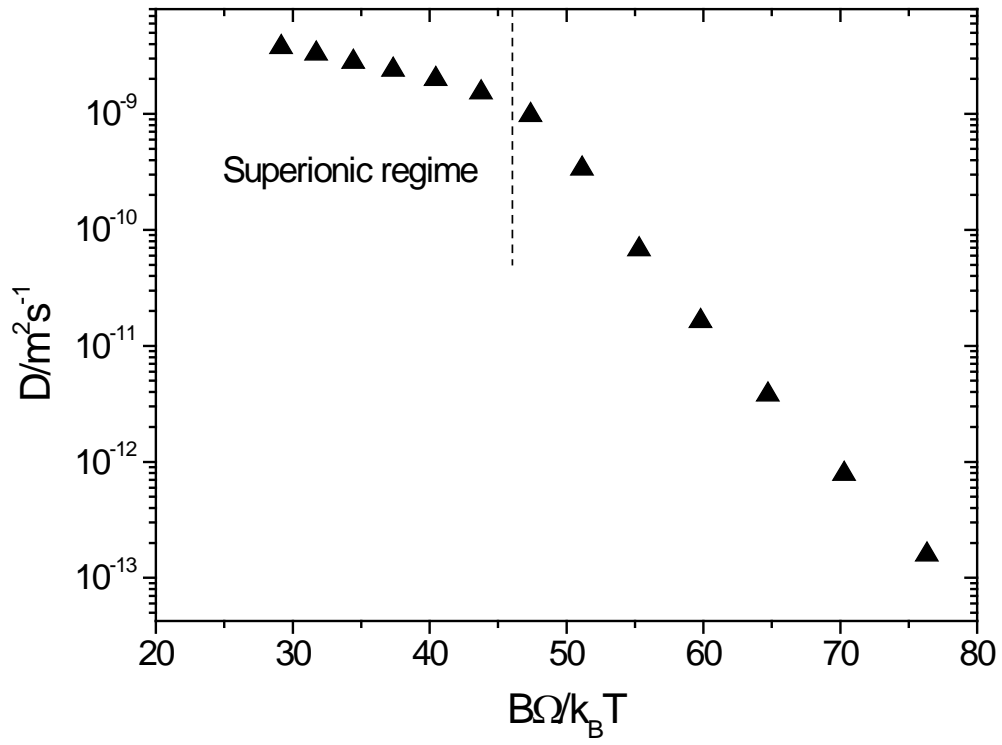
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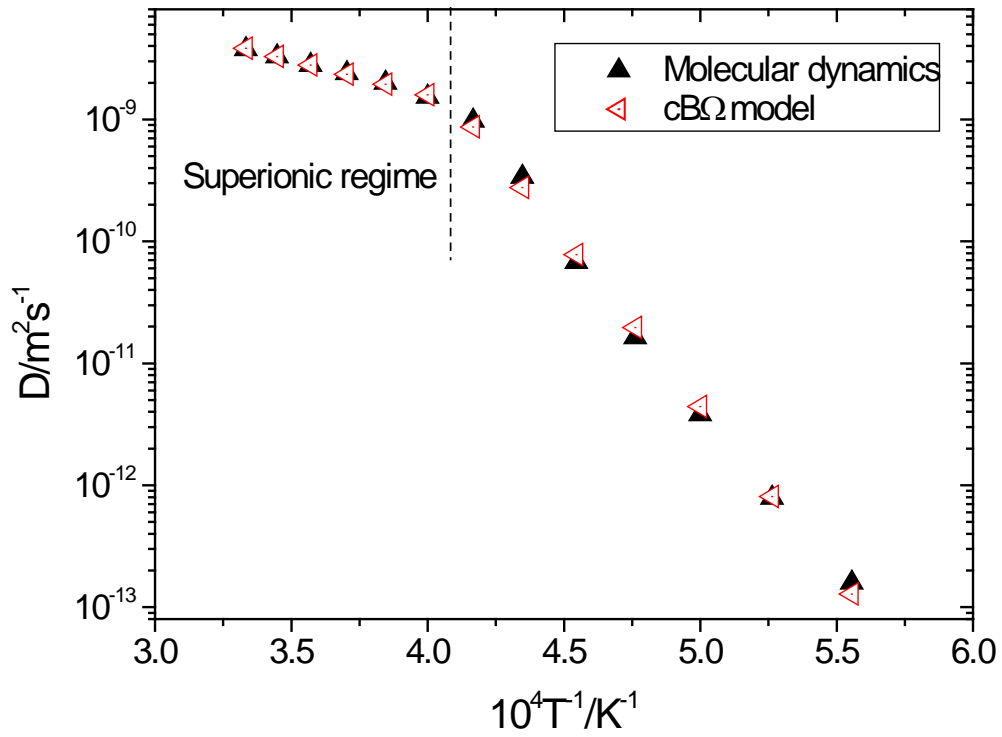
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**Table 1.** Derived and molecular dynamics [27] self-diffusion coefficients in PuO<sub>2</sub>, elastic and expansivity data [26] used in the cBΩ model.

T / K	B / 10 <sup>11</sup> Nm <sup>-2</sup>	Ω / 10 <sup>-30</sup> m <sup>3</sup>	$D_{MD}^{PuO_2}$ / m <sup>2</sup> s <sup>-1</sup>	$D_{cB\Omega}^{PuO_2}$ / m <sup>2</sup> s <sup>-1</sup>	$\frac{D_{cB\Omega}^{PuO_2} - D_{MD}^{PuO_2}}{D_{MD}^{PuO_2}}$ %
1800	137.46	13.80	$1.59 \times 10^{-13}$	$1.28 \times 10^{-13}$	-19
1900	132.83	13.88	$7.88 \times 10^{-13}$	$8.08 \times 10^{-13}$	3
2000	128.20	13.94	$3.80 \times 10^{-12}$	$4.42 \times 10^{-12}$	16
2100	123.57	14.03	$1.63 \times 10^{-11}$	$1.97 \times 10^{-11}$	21
2200	118.94	14.12	$6.78 \times 10^{-11}$	$7.78 \times 10^{-11}$	15
2300	114.31	14.21	$3.37 \times 10^{-10}$	$2.76 \times 10^{-10}$	-18
2400	109.68	14.32	$9.71 \times 10^{-10}$	$8.69 \times 10^{-10}$	-11
2500	105.05	14.38	$1.53 \times 10^{-9}$	$1.59 \times 10^{-9}$	4
2600	100.42	14.46	$1.99 \times 10^{-9}$	$1.94 \times 10^{-9}$	-3
2700	95.79	14.53	$2.40 \times 10^{-9}$	$2.34 \times 10^{-9}$	-3
2800	91.16	14.60	$2.80 \times 10^{-9}$	$2.79 \times 10^{-9}$	0
2900	86.53	14.68	$3.29 \times 10^{-9}$	$3.29 \times 10^{-9}$	0
3000	81.90	14.75	$3.75 \times 10^{-9}$	$3.84 \times 10^{-9}$	2



**Figure 1.** The oxygen self-diffusion coefficients in  $\text{PuO}_2$  with respect to  $\frac{B\Omega}{k_B T}$



**Figure 2.** The Arrhenius plot for oxygen self-diffusion coefficients in  $\text{PuO}_2$  calculated by molecular dynamics [27] and derived by the cBΩ model. The dashed line roughly divides the part where the superionic regime is applicable (described by Eq. 7) to the part where the material is fully crystalline (described by Eq. 6).