The comparative study of the specific heat capacity of uranium dioxide according to the fractal structure

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Abstract

In the present study, we investigate the effectiveness of existing methods for evaluating the heat capacity of uranium dioxide (UO_2) by considering the fractal structure of materials. Two well-known theoretical methods were investigated in this work which have the advantages of giving accurate and efficient calculation results for the heat capacities of uranium dioxide for a wide range of temperatures. To verify the effectiveness of these theoretical methods, we compare the calculation results with existing experimental data from the literature. Based on the concept of fractality, the results obtained in this work are useful for determining the best theoretical approaches, i.e., those that are more convenient and meaningful for the evaluation of the heat capacities of uranium dioxide. The approaches and results presented in this study can provide useful knowledge for accurate investigations of the physical properties of other nuclear fuels.

Keywords: Debye method; Einstein-Debye approximation; nuclear fuel; Uranium dioxide; heat capacity.

I. Introduction

It is well known that the accurate evaluation of the heat capacities of nuclear fuels is important for analysis of the other thermal properties, and these are significant features that need to be determined in detail (Crossland, 2012; Hore-Lacy, 2016; Allen, 2021; Hurley *et al.*, 2022). Nowadays, nuclear fuels are the most important sources of clean energy, and hence many theoretical and experimental methods of examining their physical properties have been developed (Terentyev, 2007; Yamada et al., 2000; Ronchi, 2007; Zhou *et al*., 2018; Inoue, 2000; Carbajo *et al*., 2001; Hiayuki *et al*., 1975; Muta *et al*., 2008; Vlahovic *et al*., 2018; Martin, 1988).. Determination of the temperature dependence of the heat capacities of nuclear materials is an important quantitate of fuel control in a reactor. In the literature, various theoretical and experimental approaches for calculating the heat capacities of nuclear fuels have been proposed (Martin, 1988; Kerrisk & David, 1972; Ronchi & Hyland, 1994; Yun *et al*., 2012; Sobolev & Lemehov, 2006; Pavlov *et al*., 2017; Oetting & Leitnaker, 1972; Takahasi *et al*., 1971; Bathellier *et al.,* 2021; Hyland & Ohse, 1986; Eser *et al*., 2020; Koç *et al*., 2011; Mehmetoglu, 2019; Kang et al., 2006). The authors of (Yun *et al*., 2012) applied the spin-polarized generalized gradient approximation to determine the thermal properties of UO_2. In the study in (Sobolev and Lemehov, 2006), a novel, efficient and high-resolution approach to the evaluation of various thermal properties of dioxides was presented. The authors of (Pavlov *et al.*, 2017) reported the results of calculations of the heat capacity, thermal diffusivity and thermal conductivity of UO_2 using solid state physics and laser flash measurements. The

Einstein-Debye method is a powerful approach that has also recently been applied to study the thermal properties of solids Eser *et al*., 2020; Koç *et al*., 2011; Mehmetoglu, 2019; Kang *et al*., 2006; Copuroglu, 2016).

Following the invention of fractal geometry, the study of the thermal properties of solids with a fractal structure has been of both great fundamental interest and practical importance. The Debye theory was modified by the authors (Hore-Lacy, 2016; Allen, 2021) based on the concept of fractality of the phonon spectrum, and the temperature dependence was studied over the range of values $1 < d < 3$. In the present work, the Einstein-Debye method is modified on the basis of the fractality structure of materials, and a new analytical approach is applied to calculate the heat capacities of uranium dioxide. In recent studies (Devyatko *et al.,* 2016; Lazarev *et al*., 1995; Rekhviashvili, 2010), the heat capacities of materials have been examined by considering the fractal character of materials.

In this work, we take into account the fractality structure of substances, and study the accuracy and efficiency of the Einstein-Debye approach (Cankurtaran & Askerov, 1996; Askerov & Cankurtaran, 1994) and theoretical methods that have been proposed (Rekhviashvili, 2010) for evaluation of the heat capacity of uranium oxide by comparing experimental data. The importance of uranium dioxide among nuclear fuels was best described in (Vlahovic *et al*., 2018) as follows: "Uranium dioxide is certainly one of the most studied nuclear materials because it is the fuel for almost all nuclear reactors worldwide. Consequently, the investigation of its thermodynamical properties in a wide range of conditions from normal operation to off normal and severe accidents is of prime importance for the nuclear industry." While the abovementioned fractal structure is described an accurate estimation of the thermal properties, it is necessary to choose the most efficient theoretical methods, which enable clear determination and estimates of the heat capacities and other physical properties of uranium dioxide.

2. Definition and expressions for the heat capacities of nuclear fuels

The specific heat capacities are defined in (Landau & Lifshits, 1959; Pässler, 2007) as follows:

$$C_P(T) = C_V(T)\left(1+\frac{A_0 T}{T_m}C_V(T)\right), \tag{1}$$

$$C_V(T) = 3N_A k_B M\left(T,\theta_D,\theta_E\right)\ , \tag{2}$$

where $A_0 = 5.1x10^{-3} J^{-1} K\, mol$, T is the absolute temperature, N_A is the Avogadro number, k_B is the Boltzmann constant, T_m is the melting temperature, and θ_D and θ_E are the Debye and Einstein temperatures, respectively.

Using a framework based on the Einstein and Debye approaches, the authors of (Cankurtaran & Askerov, 1996; Askerov & Cankurtaran, 1994) give the following relation for the $M(T,\theta_D,\theta_E)$ functions:

$$M\left(T,\theta_D,\theta_E\right) = L_V\left(T,\theta_D\right)+(s-1)A\left(T,\theta_E\right), \tag{3}$$

where s is the number of atoms at one lattice point. Due to the fractal structure of solids, analytical expressions for the $L_V(T,\theta_D)$ function can be defined in general form as:

$$L_V\left(T,\theta_D\right)=(d+1)D_d\left(1,\frac{\theta_D}{T}\right)-\frac{\theta_D}{T}\frac{d}{e^{\frac{\theta_D}{T}}-1}. \tag{4}$$

where d is the fractal dimension of the substances. For the special case where $d=3$, this corresponds to the Debye model. In Equation (4), the functions $D_n(\beta,x)$ are the fractional *d*-dimensional Debye functions:

$$D_d\left(\beta,\mathrm{x}\right)=\frac{n}{x^n}\int_0^x\frac{t^d}{(e^t-1)^\beta}dt. \tag{5}$$

where β can take integer and non-integer values, and $\beta=1$ corresponds to the Einstein-Debye approximation. The function $A(T,\theta_E)$ appearing in Equation (3) is the Einstein function, and is given by the formula:

$$A\left(T,\theta_E\right)=\left[\frac{\theta_E}{2T}\frac{1}{\sinh\left(\frac{\theta_E}{2T}\right)}\right]^2. \tag{6}$$

An expression for integer and noninteger d-dimensional Debye functions was obtained on the basis of the binomial expansion theorem, and has the form (Copuroglu, 2017; Copuroglu, 2022):

$$D_d(\beta,x)=\frac{d}{x^d}\lim_{N\to\infty}\sum_{i=0}^{N}(-1)^iF_i(-\beta)\frac{\gamma(d+1,(i+\beta)x)}{(i+\beta)^{d+1}} \tag{7}$$

where N is the upper value of the expansion. The functions $F_i(-\beta)$ and $\gamma(\alpha,y)$ appearing in this relation are the binomial coefficients and incomplete gamma functions, which are defined by the formulae (Gradshteyn & Ryzhik, 1980):

$$F_m(n)=\frac{1}{m!}\prod_{i=0}^{m-1}\left(n-i\right) \tag{8}$$

And

$$\gamma(\alpha,y)=\int_0^y t^{\alpha-1}e^{-t}dt, \tag{9}$$

respectively.

By the second efficient approximation, corresponding to the acoustic phonon branches within the Debye and optical Einstein models, we obtain the following form (Devyatko *et al*., 2016):

$$C_V(T)=3R\left[4D_3\left(\frac{\theta_D}{T}\right)-\frac{3\theta_D/T}{e^{\theta_D/T}-1}+\frac{2}{3}\sum_{i=1}^{3}\left(\frac{\theta_{Ei}}{T}\right)^2\frac{e^{\theta_{Ei}/T}}{(e^{\theta_{Ei}/T}-1)^2}\right]. \tag{10}$$

The characteristic temperatures in Equation (10) for approximating the specific heat of uranium dioxide are $\theta_D=168K;\theta_{E1}=391K;\theta_{E2}=629K;\theta_{E3}=836K$.

3. Numerical Results and Discussion

In this study, the heat capacities were investigated by considering the fractal properties of solids and applying this approach to the nuclear fuel UO_2. By using a modified Einstein-Debye method that took into account the fractal structure, we obtained formulae for the heat capacities based on the d fractal dimensional Debye functions. In (Copuroglu, 2017; Copuroglu, 2022), a general expression was used for the Debye functions of the whole values of d fractional dimensions. The approach presented in this study is very helpful in explaining the fractal phenomena of solids, and is particularly appropriate and significant for descriptions of the fractal dimensions of substances. We report results from the use of modified analytical expressions for the heat capacities for various values of the fractal dimension d with appropriate comparisons with experimental data and results in the literature. Figures 1–3 show the temperature dependence of the calculated heat capacity for various values of the fractal dimension d, compared with previously reported experimental values.

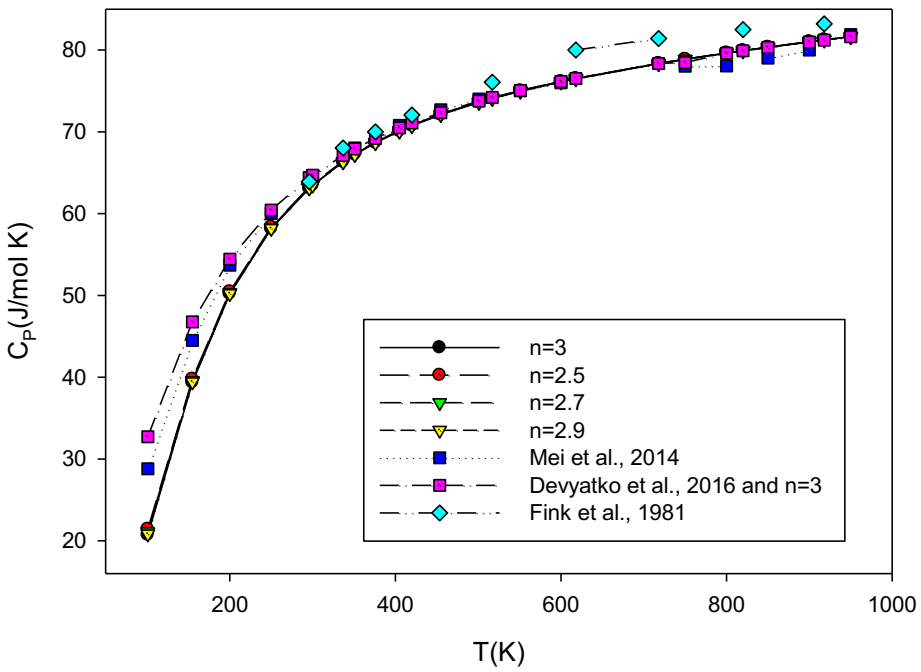

Fig. 1. A comparative values of C_P heat capacity of uranium dioxide with various fractal dimension ($\theta_D = 377$ and $\theta_E = 535$)

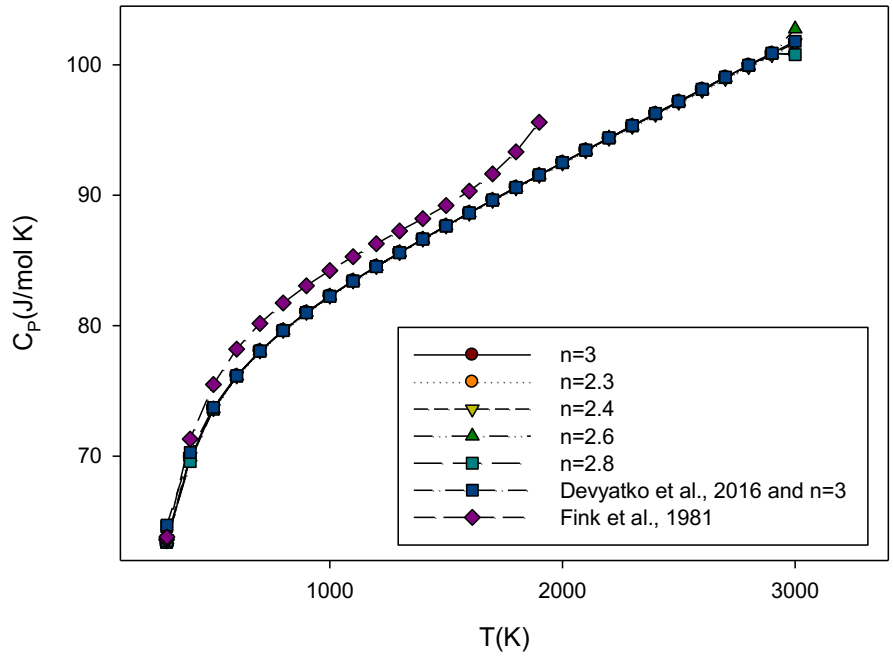

Fig. 2. A comparative values of C_P heat capacity of uranium dioxide with various fractal dimension ($\theta_D = 377$ and $\theta_E = 535$)

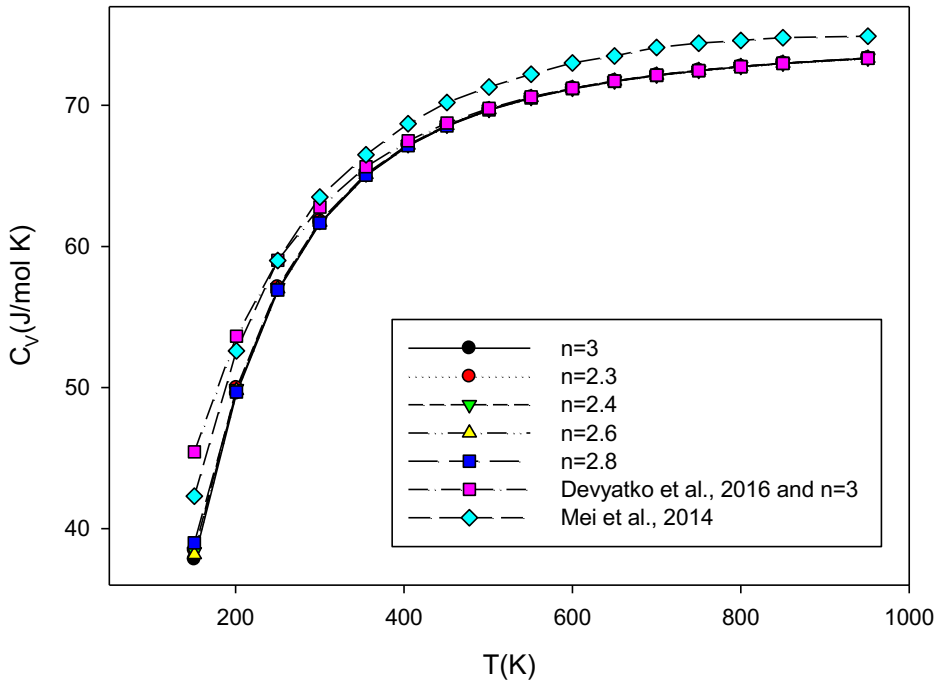

Fig. 3. A comparative values of C_V heat capacity of uranium dioxide with various fractal dimension ($\theta_D = 377$ and $\theta_E = 535$)

Figures 1–3 show that there is acceptable agreement between the calculated and experimental results for uranium dioxide. We calculated the heat capacity of uranium dioxide for several various values of the fractal dimension d in order to study the fractal structure behavior of solids. Using the fractality model, we can obtain good results in comparison with those in (Devyatko *et al*., 2016)and experimental data. It can be seen from Figure 1 that the difference between our calculated results and experimental data for the range $T < 250\,K$ is larger than for the range $T > 250\,K$. In addition, the best fit with the experimental results is found for $d = 2.3$, as shown in Figures 1–3. Our theoretical results suggest that, in principle, it is possible not only to evaluate the thermal properties but also to determine the fractal dimensions of substances. Hence, the value $d = 2.3$ can be considered the fractal dimension of UO_2, and ensures that the calculation results are in excellent agreement with the results reported in the literature.

4. Conclusion

As can be seen from the results of this study, the solid structure is more convenient to the fractal character. An evaluation method based on the fractal character is a natural approach for investigating the other thermal properties of material systems.

References

Allen, M. (2021) Improving nuclear fuel safety. *Physics World*, 34. pp 33-36.

Askerov, B. M., & Cankurtaran, M. (1994) Isobaric specific heat and thermal expansion of solids in the Debye approximation. *Physica Status Solidi (b)*, 185. pp 341-348.

Bathellier, D., Lainet, M., Freyss, M., Olsson, P., Bourasseau, E. (2021) A new heat capacity law for UO_2, PuO_2 and (U, Pu) O_2 derived from molecular dynamics simulations and useable in fuel performance codes. *Journal of Nuclear Materials*, 549. pp 152877.

Crossland, I. (2012) Nuclear Fuel Cycle Science and Engineering. Woodhead Pub., London. pp. 151.

Carbajo, J.J., Yoder, G.L., Popov, S.G., Ivanov, V.K. (2001) A review of thermodynamical properties of MOX and UO2 fuels. *Journal of Nuclear Materials*, 299. pp 181-198.

Copuroğlu, E. (2016) Heat Capacity Study on the Evaluation of Uranium Nitride Using Einstein-Debye Approximation. *AKU Journal Sciience and Engineering,* 16. pp 517-520.

Copuroglu, E. (2022) Theoretical estimation of entropy of solids by using integer and non-integer n-dimensional Debye functions. *Physica A*, 593. pp 126915.

Copuroglu, E. (2017) Analytical evaluation of heat capacities of structural stainless steels by using n-dimensional integer and noninteger Debye functions, *International Journal of Steel Structure*, 17. pp 739-742.

Cankurtaran, M., & Askerov, B. M. (1996) Equation of state, isobaric specific heat, and thermal expansion of solids with polyatomic basis in the Einstein-Debye approximation. *Physica Status Solidi (b)*, 194. pp 499-507.

Devyatko, Y. N., Novikov, V.V., Khomyakov, O.V., Chulkin, D.A. (2016) A model of uranium dioxide thermal conductivity. *Inorganic Matererials: Applied Research*, 7. pp 409-418.

Eser, E., Duyuran, B., Bölükdemir, M.H., Koç, H. (2020) A study on heat capacity of oxide and nitride nuclear fuels by using Einstein-Debye approximation. *Nuclear Engineering and Technology*, 52. pp 1208-1212.

Fink, J.K., Chasanov, M.G., Leibowitz, L. (1981) Thermodynamics properties of uranium dioxide, Argonne National Laboratory, Argonne, Villains, pp.183.

Gradshteyn, I.S., & Ryzhik, I. M. (1980) Tables of Integrals, Series and Products, Academic Press, New York, pp. 1020.

Hore-Lacy, I. (2016) Uranium for Nuclear Power. Woodhead Pub., London. pp. 93.

Hurley, D.H., El-Azab, A., Bryan, M.S., Cooper M.W.D., Dennett, C.A., Gofryk, K., He, L., Khafizov, M., Lander, G.H., Manley, M.E., Mann, J.M., Marianetti, C.A., Rickert, K., Selim, F.A., Tonks, M.R., Eharry, J.P. (2022) Thermal energy transport in oxide nuclear fuel, *Chemical Reviews*, 122. pp 3711-3762.

Hisayuki, M., Ken-ichi, S., Mitsuo, I., Hiromi, A., Tomoo, K. (1975) Electrical resistivity and lattice parameter of uranium monocarbide. *Journal of Nuclear Materials*, 57. pp 93-97.

Hyland, G.J., & Ohse, R.W. (1986) The heat capacity and enthalpy of condensed UO2: Critical review and assessment. *Journal of Nuclear Materials*, 140. pp 149-170.

Inoue, M. (2000) Thermal conductivity of uranium-plutonium oxide fuel for fast reactors. *Journal of Nuclear Materials*, 282. pp 186-195.

Kerrisk, J. F., & David, G. C. (1972) Smoothed values of the enthalpy and heat capacity of UO_2. *Nuclear Technology*, 16. pp 531-535.

Koç, H., Eser, E., Mamedov, B. A. (2011) Calculation of heat capacity of the nuclear fuels UO2 and NpO2 using integer and non-integer n-dimensional Debye functions. *Nuclear Engineering Design,* 241. pp 3678-3682.

Kang, K.H., Song, K.C., Yang, M.S., Lee, S.H.,. Ko, J.B, Kim, S.W. (2006) Thermal expansion of a simulated fuel with fission products forming solid solutions, *International Journal of Thermophysics*. 27. pp 161.

Landau, L. D., & Lifshits, E. M. (1959) Statistical Physics, Pergamon Press, London, pp. 252.

Lazarev, V.B., Izotov, A.D., Gavrichem, K.S., Shebershneva, O.V. (1995) Fractal model of heat capacity for substances with diamond-like structures, *Thermochemistry Acta*, 269. pp 109-116.

Muta, H., Kurosaki, K., Uno, M., Yamanaka, S. (2008) Thermal and mechanical properties of uranium nitride prepared by SPS technique. *Journal of Materials Science*, 43. pp 6429-6434.

Martin, D. G. (1988) The thermal expansion of solid UO_2 and (U, Pu) mixed oxides—a review and recommendations. *Journal of Nuclear Materials*, 152. pp 94-101.

Mehmetoglu, T. (2019) Use of Einstein-Debye method in the analytical and semi empirical analysis of isobaric heat capacity and thermal conductivity of nuclear materials. *Journal of Nuclear Materials,* 527. pp 151827.

Mei, Z.G., Stan, & M., Yang, J. (2014) First-principle study of thermodynamical properties of uranium dioxide. *Journal of Alloys and Compounds*, 414. pp 282-286.

Oetting, F.L., & Leitnaker J.M. (1972) The chemical thermodynamic properties of nuclear materials I. Uranium mononitride. *The Journal of Chemical Thermodynamics*, 4. pp 199-211.

Pavlov, T.R., Wenman, M.R., Vlahovic, L., Robba, D., Konings, R.J. M., Uffelen, P.V., Grimes, R. W. (2017) Measurement and interpretation of the thermo-physical properties of UO_2 at high temperatures: the viral effect of oxygen defects. *Acta Materialia*, 139. pp 138-154.

Pässler, R. (2007) Dispersion-related theory for heat capacities of semiconductors. *Physica Status Solidi (b)*, 244. pp 4605-4623.

Ronchi, C. (2007) Thermophysical properties affecting safety and performance of nuclear fuel. *High Temperature*, 45. pp 552-571.

Rekhviashvili, & S. Sh. (2010) Equation of State of a Solid with Fractal Structure. *Technical Physics Letters*, 36. pp 798-800.

Ronchi, C., & Hyland, G.J. (1994) Analysis of recent measurements of the heat capacity of uranium dioxide. *Journal of Alloys And Compounds*, 213. pp 159-168.

Sobolev, V., & Lemehov, S. (2006) Modelling heat capacity, thermal expansion, and thermal conductivity of dioxide components of inert matrix fuel. *Journal of Nuclear Materials*, 352. pp 300-308.

Terentyev, D. (2007) Molecular dynamics study of oxygen transport and thermal properties of mixed oxide fuels, *Computational Material Science*, 40. pp 319-326.

Takahashi, Y., Murabayashi, M., Akimoto, Y., Mukaibo, T. (1971) Uranium mononitride: heat capacity and thermal conductivity from 298 to 1000 K. *Journal of Nuclear Materials*, 38. pp 303-308.

Vlahovic, I., Staicu, D., Küst, A., Konings, R.J.M. (2018) Termal diffusivity of UO_2 up to the melting point, *Journal of Nuclear Materials*, 499. pp 504-511.

Yun, Y., Legut, D., Oppeneer, P.M. (2012) Phonon spectrum, thermal expansion and heat capacity of UO_2 from first-principles. *Journal of Nuclear Materials*, 426. pp 109-114.

Yamada, K., Kurosaki, K., Uno, M., Yamanaka, S. (2000) Evaluation of thermal properties of uranium dioxide by molecular dynamics. *Journal of Alloys and Compounds*, 307. pp 10-16.

Zhou, W.Z., Revankar, S.T., Liu, R. Beni, M.S. (2018) Microstructure-Based Thermal Conductivity and Thermal Behavior Modeling of Nuclear Fuel UO_2-BeO. *Head Transfer Engineering*, 39. pp 760-774.

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