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# A molecular dynamics study of the thermal conductivity of CaF$_2$ and UO$_2$

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**Abstract.** Previous experimental work has revealed an anomalous increase of thermal conductivity $\lambda$ in solid UO$_2$ above about 2000 K, which has been attributed to the effect of electronic excitations. The present molecular dynamics simulations of UO$_2$ and the closely related material CaF$_2$ are designed to test this explanation by providing quantitative results for the temperature dependence of $\lambda$ in the absence of electronic excitations. The simulation results for $\lambda$, obtained by the Green–Kubo technique, are in fair agreement with the (limited) experimental results for CaF$_2$. For UO$_2$, close agreement with experiment exists for $T < 2000$ K, but there is a large discrepancy for higher temperatures. This confirms the existence of an additional heat conduction mechanism in UO$_2$ at high temperatures.

## 1. Introduction

Uranium dioxide has been much studied over many years, because of its importance as the main constituent of the fuel in nuclear reactors (Marshall (1983); see also the collection of papers edited by Catlow (1987)). The thermal conductivity $\lambda$ of the material is a key quantity for understanding the performance of nuclear fuel (Washington 1973, Brandt *et al* 1967, Hyland 1983). The temperature dependence of $\lambda$ is known to be anomalous in UO$_2$. In most materials, $\lambda$ decreases monotonically with temperature $T$ in the solid state, the variation often going roughly as $1/T$ (Slack 1961). In UO$_2$, though, $\lambda$ goes through a pronounced minimum at about 2000 K, and increases by about 60% of the minimum value before the melting point is reached at 3120 K (Washington 1973, Brandt *et al* 1967, Hyland 1983). This paper presents the results of molecular dynamics (MD) simulations of UO$_2$, and the closely related material CaF$_2$, which have been used to calculate the thermal conductivity over a wide range of temperatures. We shall show that our results assist in interpreting the behaviour of $\lambda$ in UO$_2$.

   The most convincing explanation for the upturn in $\lambda$ at 2000 K is that it is due to electronic excitations (Harding and Martin 1989). UO$_2$ is a semiconductor, with a thermal band gap of about 2 eV (Bates *et al* 1967, Hampton *et al* 1988). This is small enough for there to be a substantial contribution to $\lambda$ from electrons and holes (the ambipolar contribution) above about 2000 K. The suggestion is, then, that $\lambda$ is dominated by lattice vibrations for $T < 2000$ K, but that above this temperature heat is carried by

the rapidly increasing population of electrons and holes. The main problem in refining this theory is that we do not really know how $\lambda$ would behave if lattice vibrations were the only contribution. Surprisingly, there are hardly any ionic materials apart from $UO_2$ for which $\lambda$ has been measured up to anywhere near the melting point. It must also be remembered that $UO_2$, like other materials having the fluorite structure, is a superionic conductor at high temperatures, with massive disorder on the oxygen sublattice and a very high ionic conductivity (Clausen *et al* 1984, Hutchings 1989). The behaviour to be expected of the vibrational contribution to $\lambda$ in such systems is unknown.

Our purpose is therefore to use MD simulation to study the form that $\lambda(T)$ would have in $UO_2$ in the absence of electronic excitations. For comparison, we have also studied $\lambda(T)$ for $CaF_2$, which has the same crystal structure as $UO_2$, but is rather better understood at the atomic level. Molecular dynamics simulation has been the main theoretical tool for studying superionic conductors, and there has been an extensive series of simulations of fluorite materials, including $CaF_2$, $SrCl_2$, $PbF_2$ and $Li_2O$ (Gillan 1989a, b, Chadwick *et al* 1988). The many comparisons with experiment that have been made show that the simulations reproduce the experimental results, often with surprising accuracy, and that the interaction models that have been developed are generally rather realistic.

Our MD calculations of $\lambda$ are based on the Green–Kubo relations, which allow transport coefficients to be deduced from time correlation functions involving spontaneous fluxes in full thermal equilibrium (Green 1954, Kubo 1966). Recent work has shown that this method is capable of giving the thermal conductivity of solids with quantitative accuracy (Sindzingre and Gillan 1990). The simulations of $UO_2$ employ a realistic rigid-ion interaction model recently developed by Sindzingre and Gillan (1988). This model is known to reproduce a number of the key physical properties of the material, including the observed oxygen disorder, and some of the thermodynamic quantities for the solid (Sindzingre and Gillan 1988, Gillan 1989a).

## 2. Technical background

### 2.1. Green–Kubo theory

The use of the Green–Kubo relations to calculate the thermal conductivity of solids and liquids by simulation has been described in several previous papers. The present work is based on the scheme outlined by Sindzingre and Gillan (1990). A key feature of this method is that it requires only simulations of the system in full thermal equilibrium. For reasons stressed in previous work (Sindzingre and Gillan 1990), this approach is much to be preferred over methods that involve the application of a temperature gradient, when calculating $\lambda$ for solids.

It will be enough here simply to recall the main points of the method. The thermal conductivity $\lambda$ of an ionic system can be expressed in terms of the phenomenological coefficients $L_{\alpha\beta}$ which relate the local *macroscopic* fluxes of charge $j_z$ and energy $j_e$ to the local gradients of electrochemical potential $\mu_z$ and temperature $T$. These coefficients are defined by the equations:

$$j_z = -L_{zz}\nabla(\beta\mu_z) - L_{ze}\nabla(-\beta) \tag{1a}$$

$$j_e = -L_{ez}\nabla(\beta\mu_z) - L_{ee}\nabla(-\beta) \tag{1b}$$

where $\beta = 1/k_B T$. Recognizing that $L_{ze}$ and $L_{ez}$ are equal (the Onsager reciprocal relation) the thermal conductivity is then given by:

$$\lambda = (L_{ee} - L_{ze}^2/L_{zz})/k_B T^2. \tag{2}$$

The coefficients $L_{\alpha\beta}$ can be expressed in terms of the correlation functions $C_{\alpha\beta}$ of the corresponding *microscopic* fluxes $J_\alpha$:

$$C_{\alpha\beta}(t) = \tfrac{1}{3}\langle J_\alpha(t) \cdot J_\beta(0)\rangle \tag{3}$$

where the average $\langle \ldots \rangle$ is taken in full thermal equilibrium. Then:

$$L_{\alpha\beta} = \frac{1}{\Omega}\int_0^\infty C_{\alpha\beta}(t)\,\mathrm{d}t \tag{4}$$

where $\Omega$ is the volume of the system (Allen and Tildesley 1987).

As noted by Sindzingre and Gillan (1988), there are useful alternative expressions for $\lambda$. If, instead of the fluxes $j_z$ and $j_e$, we work with the fluxes $j_z$ and $j_x$, where $j_x = j_e - xj_z$ for any arbitrary value of $x$, $\lambda$ is correctly given by:

$$\lambda = (L_{xx} - L_{zx}^2/L_{zz})/k_B T^2. \tag{5}$$

The $L_{\alpha\beta}$ coefficients appearing here are defined as in equation (4), but with the fluxes $J_z$ and $J_x$ replacing $J_z$ and $J_e$. Equation (5) is exactly equivalent to equation (2). This freedom to choose $x$ as we wish will turn out to be useful.

## 2.2. Interionic potentials

The simulations are based on rigid-ion pair potentials for CaF₂ and UO₂. The interaction model for CaF₂ is that of Gillan and Dixon (1980). This has the Born–Mayer–Huggins form, the potential between ions of types $i$ and $j$ being given by:

$$V_{ij}(r) = z_i z_j e^2/r + A_{ij}\exp(-r/\rho_{ij}) - C_{ij}/r^6. \tag{6}$$

The model assumes CaF₂ to be fully ionic, so that $z_+ = 2$, $z_- = -1$. For the values of the parameters $A_{ij}$, $\rho_{ij}$ and $C_{ij}$, and an explanation of the way these were chosen, see Gillan and Dixon (1980) and Gillan (1986). The model is known to reproduce faithfully a large variety of properties of the material at both low and high temperatures (Gillan and Dixon 1980, Gillan 1986, 1989b).

The model used here for UO₂ also has the functional form given in equation (6), except that the anion–anion interaction has a spline form at intermediate distances; for details of this model, see Sindzingre and Gillan (1988). The model reproduces the low-temperature properties of the bulk material, and is known to give a fairly satisfactory description of the properties of the high-temperature solid, including the experimentally observed superionic behaviour at $T > 2000$ K (Sindzingre and Gillan 1988, Gillan 1989a).

## 3. Simulation results

### 3.1. Calcium fluoride

We have performed a series of simulations of CaF₂ at temperatures ranging from 300 K up to the experimental melting point (1693 K). We have also made simulations at a number of different volumes at a temperature of 900 K.

**Table 1.** Calcium fluoride simulation results; $n$ is the number of steps, MV the molar volume and $\lambda$ the thermal conductivity. The time step used was $5.0 \times 10^{-15}$ s. ($a$) Thermal conductivity as a function of temperature. ($b$) Thermal conductivity as a function of volume. The experimental molar volume at 900 K is 25.6 cm$^3$.

| $T$ (K) | $n$ ($\times 10^3$) | MV (cm$^3$) | $\lambda$ (W m$^{-1}$ K$^{-1}$) |
|---|---|---|---|
| ($a$) | | | |
| 304 | 300 | 24.60 | 7.00 ± 0.39 |
| 501 | 100 | 24.80 | 4.62 ± 0.58 |
| 906 | 200 | 25.60 | 1.94 ± 0.05 |
| 1294 | 50 | 26.67 | 1.60 ± 0.09 |
| 1694 | 20 | 28.06 | 1.46 ± 0.29 |
| ($b$) | | | |
| 897 | 60 | 23.00 | 4.77 ± 0.45 |
| 898 | 50 | 24.30 | 2.34 ± 0.18 |
| 899 | 50 | 25.60 | 1.79 ± 0.09 |
| 898 | 50 | 26.90 | 1.80 ± 0.18 |
| 901 | 50 | 28.20 | 1.34 ± 0.18 |

All the simulations were done on a system of 32 cations and 64 anions, using a time step $\Delta t$ of $5.0 \times 10^{-15}$ s, which is sufficient to ensure conservation of the total energy to within 0.03% over the length of the runs. The volume of the simulated system was chosen so as to reproduce the experimental lattice constant at each temperature (Hutchings and Kjems 1986, private communication). As is usual with the calculation of transport coefficients, we found that long simulation runs were needed to achieve acceptable statistical accuracy. The length of run needed was greater at lower temperatures, for reasons that will become clear. Details of all our simulation runs on CaF$_2$ are given in table 1.

The three correlation functions $C_{\alpha\beta}(t)$ involving the fluxes of energy and electric charge were calculated during the course of the simulations. The functions were calculated for all available times $t = n\,\Delta t$ up to a chosen maximum value of $n$, with time origins taken at every step.

To illustrate our results, we show in figures 1 and 2 the correlation function $C_{ee}(t)$ for the energy flux and its time integral at our lowest and highest temperatures, 300 K and 1694 K. The forms of the curves at the two temperatures differ remarkably. At the high temperature, $C_{ee}(t)$ decays to zero within about 0.4 ps, so its time integral attains its plateau value within this time. At the low temperature, $C_{ee}(t)$ takes about ten times as long to decay. This is what one would expect, since the system is presumably almost harmonic at room temperature, and so the decay time for lattice vibrations is very long. At high temperatures, lattice vibrations in CaF$_2$ are well known, both from neutron scattering measurements and from previous MD simulations (Gillan 1986, 1990), to be highly damped.

A prominent feature of the low-temperature results is strong periodic oscillations. These were also observed in previous MD calculations of $C_{ee}(t)$ in alkali halides (Sindzingre and Gillan 1990). They are associated with vibration of the transverse optic (TO) mode, as may be verified by noting that the frequency of the oscillations (7.0 THz) agrees closely with the known TO frequency for our interaction model (Gillan 1986).

The thermal conductivity $\lambda$ is obtained from the long-time value of the time integrals. At all temperatures except for 1694 K, the electrical conductivity is negligible, so the
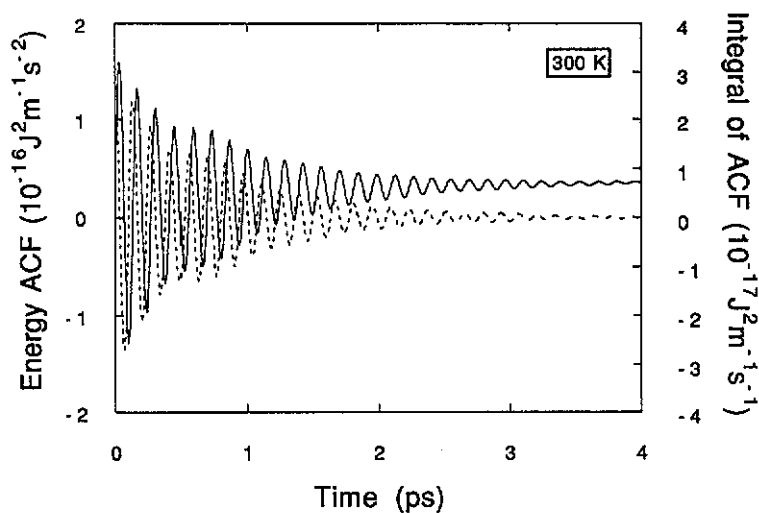
**Figure 1.** Energy flux autocorrelation function (ACF) $C_{ee}(t)$ (broken curve) and its time integral (full curve) for CaF$_2$ at 300 K.
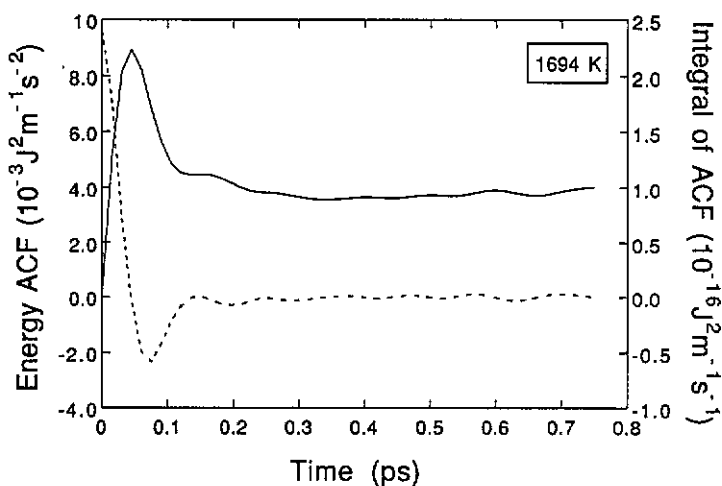


**Figure 2.** Energy flux autocorrelation function (ACF) $C_{ee}(t)$ (broken curve) and its time integral (full curve) for CaF$_2$ at 1690 K.

term $L_{ze}^2/L_{zz}$ (equation (2)) can be ignored. However, at 1694 K, this term is far from negligible, and is about the size of $L_{ee}$. Our results for $\lambda$ at two temperatures are shown in figure 3; these and a further three results appear in table 1. We have not made a systematic study of statistical errors. The error bars shown in the figure are estimated from the statistical fluctuations of the time integral at long times. Also shown in the figure are the available experimental data, which unfortunately extend only up to 420 K.

We have also obtained results for $\lambda$ at different volumes for temperatures close to 900 K (see table 1(b)). These results are plotted in figure 4. There appear to be no
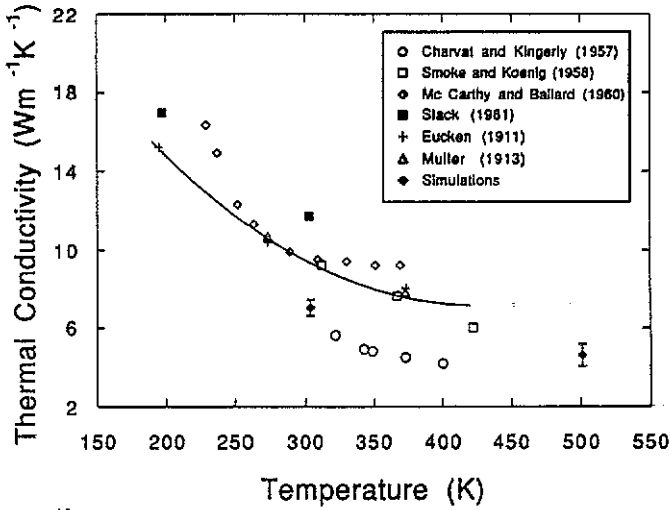
**Figure 3.** Simulated thermal conductivity $\lambda$ of $CaF_2$ at 300 and 500 K (filled diamonds) compared with experimental values; the full curve is an interpolation of experimental results due to Slack (1961), who gives references to experimental work.
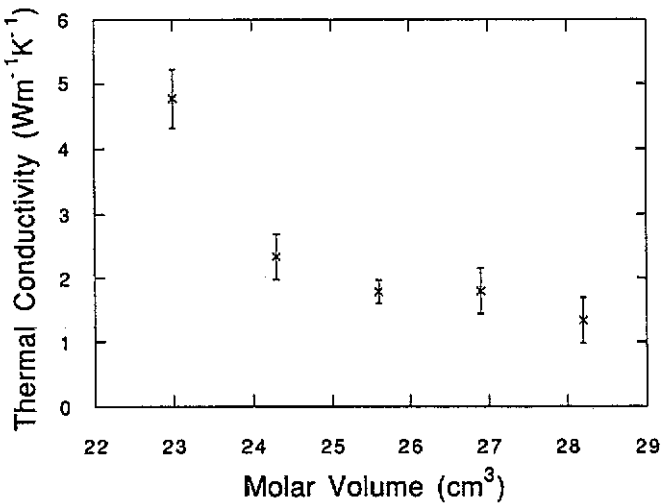


**Figure 4.** Simulated thermal conductivity of $CaF_2$ as a function of volume at 900 K.

experimental results for the volume dependence of $\lambda$ for $CaF_2$, although there are fairly plentiful results for alkali halides (Ross *et al* 1984). Such results show that $\lambda$ increases strongly as the crystal is compressed, exactly as we observe in the simulations.

## 3.2. Uranium dioxide

Simulations of $UO_2$ have been performed for the temperature range 1000–3000 K (the experimental melting temperature is 3120 K (Rand *et al* 1978)). The simulated system

**Table 2.** Simulated thermal conductivity $\lambda$ of uranium dioxide as a function of temperature; each sub-run consisted of 50 000 steps of $3.0 \times 10^{-15}$ s. $\lambda_{sp}$ is the estimated contribution to the thermal conductivity due to small polarons (Harding and Martin 1989) and MV is the molar volume.

| $T$ (K) | Sub-runs | Total time (ps) | MV (cm$^3$) | $\lambda$ (W m$^{-1}$ K$^{-1}$) | $\lambda_{sp}$ (W m$^{-1}$ K$^{-1}$) |
|------|------|------|------|------|------|
| 1003 | 5 | 750 | 25.15 | 3.8 | — |
| 1512 | 5 | 750 | 25.63 | 2.8 | — |
| 2000 | 4 | 600 | 26.16 | 2.3 | 0.29 |
| 2512 | 4 | 600 | 26.94 | 2.0 | 0.98 |
| 3007 | 4 | 600 | 27.93 | 1.5 | 2.00 |

consisted of 32 cations and 64 anions. The time step in all these simulations was $3 \times 10^{-15}$ s; we found that this shorter time step was needed to ensure adequate energy conservation. The volume at each temperature was taken from experiment (MacDonald 1985). The simulation runs were similar in length to those done on CaF$_2$ (see table 2).

The results for the correlation functions and their time integrals are qualitatively similar to those for CaF$_2$, and it would be superfluous to display them here. However, in analysing these results, we experienced some difficulty in extracting reliable results for $\lambda$ at high temperatures. We therefore studied the question of statistical errors in some detail.

The main cause of the difficulty is that at high temperatures $\lambda$ is given by the difference of two terms (equation (2)), which are comparable in magnitude, and whose values both suffer from substantial statistical noise. Any uncertainty in the two terms will therefore have a gross effect on $\lambda$. Because of this, it is not satisfactory to estimate separately the asymptotic values of $L_{ee}$, $L_{ze}$ and $L_{zz}$ for substitution into equation (2). We have found that this difficulty can be overcome if one recognizes that the statistical errors in the $C_{\alpha\beta}$ are correlated—in other words there is a cancellation of errors between the two terms in equation (2), which can be exploited.

We have found two ways of doing this. In the first method, we use the time-dependent integrals:

$$\xi_{\alpha\beta}(t) = \int_0^t C_{\alpha\beta}(t)\,\mathrm{d}t \tag{7}$$

in place of the $L_{\alpha\beta}$ in equation (2) to form the time-dependent quantity $\lambda(t)$:

$$\lambda(t) = (\xi_{ee}(t) - \xi_{ze}^2(t)/\xi_{zz}(t))/k_B T^2. \tag{8}$$

We then use the asymptotic value of $\lambda(t)$ to estimate $\lambda$. The result of doing this for the temperature 3007 K is shown in figure 5. The figure shows $\lambda(t)$ calculated from four subruns of 50 000 time steps. From the spread of these results an uncertainty of about 15% in the thermal conductivity is indicated.

The second method we have employed makes use of the freedom to express $\lambda$ in different ways, as in equation (5). By a suitable choice of $x$ we can reduce the statistical errors in the two terms in equation (5). The error in the second term can be minimized if we choose $x$ so that $L_{xz}$ is zero, because the errors in $L_{xz}$ and $L_{zz}$ are then multiplied
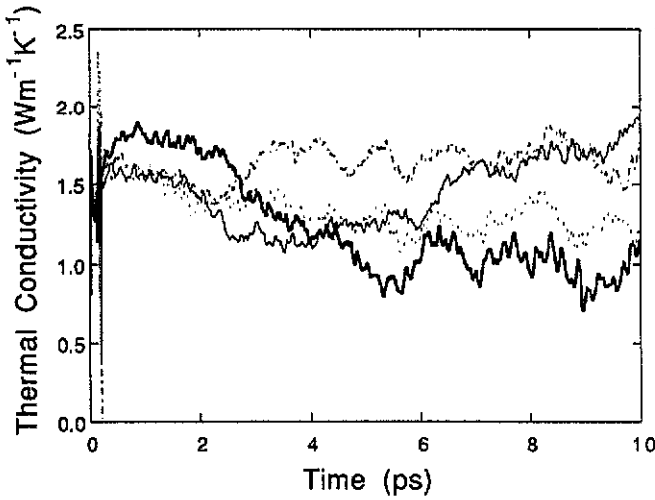
**Figure 5.** Thermal conductivity as a function of time $\lambda(t)$ calculated from 50,000 time-step sub-sections of the simulation run for UO$_2$ at 3007 K.

by zero. We can always choose $x$ in this way, since $L_{xz} = L_{ez} - xL_{zz}$, and $L_{zz}$ is non-zero by definition in the high-temperature region where we experience difficulty.

It turns out that this choice of $x$ also minimizes the errors in the first term. The reason for this is that the RMS error in the long-time value of a correlation function integral like $\xi_{xx}(t)$ is proportional to the asymptotic value itself, i.e. $L_{xx}$ in this case. If we make the second term zero, we automatically minimize the first term, and hence the error in the first term. The conclusion is that we do best by choosing $x = L_{ez}/L_{zz}$. Of course, because of statistical errors, we cannot know exactly what this $x$ is, but since we are dealing with minimization, an approximately correct value of $x$ should suffice. In the second method, then, having chosen $x$ in this way, we obtain $\lambda$ simply from the asymptotic value of $L_{xx}$. Our results for the time integral $C_{xx}(t)$ at 3007 K with an appropriate value of $x$, are illustrated in figure 6.

The two methods outlined here seem rather different, but in fact come to much the same thing. The reason is that if we have chosen $x$ so that $L_{xz}$ is zero, then in the second method $\lambda$ is obtained as $L_{xx}/k_B T^2$. But since $\xi_{xz}(t)$ then fluctuates about zero at long times, $\xi_{xz}(t)^2/\xi_{zz}(t)$ is small, so $L_{xx}$ is essentially the same as the asymptotic value of $\xi_{xx}(t) - \xi_{xz}(t)^2/\xi_{zz}(t)$. But it is readily shown that this latter quantity is independent of $x$ for all $t$, so we arrive back at the first method.

Using these methods, we have deduced values for $\lambda$. These results are presented in figure 7, where we compare them with recommended experimental values due to Brandt *et al* (1967). We stress that our calculations only account for the lattice contribution to $\lambda$, and completely omit the contribution from the electronic mechanism, which is expected to be important at high temperatures. Recently Harding and Martin (1989) have calculated the electronic contribution to $\lambda$ using the experimental values for the thermal band gap and the migration energy of electrons and holes. In order to estimate the total thermal conductivity of UO$_2$, we have added their prediction for the electronic contribution to our simulation values. The resulting estimates, shown in the figure, are in excellent agreement with the experimental values.

## 4. Discussion

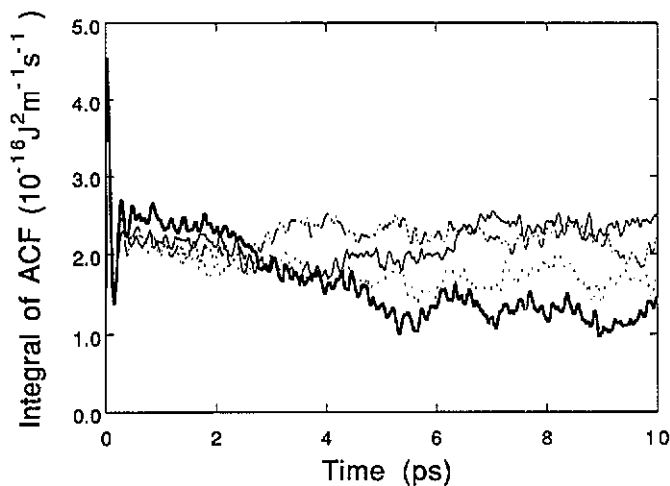The approach we have taken in this work is designed to show that we can now model

**Figure 6.** Time integrals of the correlation functions $C_{xx}(t)$ from 50 000 time-step sub-sections of the simulation run for UO$_2$ at 3007 K.
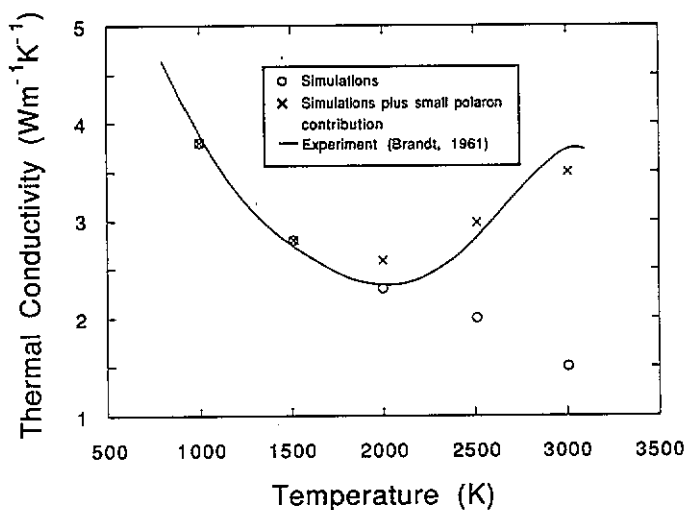


**Figure 7.** Simulated thermal conductivity of UO$_2$ as a function of temperature (open circles) compared with experimental results (Brandt *et al* 1967) (full curve). Crosses show the result of adding Harding and Martin's (1989) small-polaron contribution to the present calculations.

ionic materials like CaF$_2$ and UO$_2$ well enough to produce fairly reliable predictions for transport coefficients such as the thermal conductivity. This assumes two things: firstly, that our modelling of the potential energy function is good enough, and secondly that the Green–Kubo method for calculating transport coefficients is under adequate technical control. The results we have obtained confirm that these assumptions are justified.

For CaF$_2$, our potential model has, of course, been extensively tested in previous work. Although experimental results for $\lambda$ are rather limited in range, we have shown

here that the simulation values are in reasonable agreement (to within 30%) with an interpolation of the available measurements in the low-temperature range, where a direct comparison can be made. To put this comparison in context it should be noticed that the individual contributions to this interpolation are at considerable variance with each other. For high temperatures, our values are consistent with what would be expected from an extrapolation of the experimental results. This agreement provides useful support for the simulations of $UO_2$, which are the main object of the present work.

$UO_2$ is a considerably more difficult material to model. It is therefore very gratifying that our results for $\lambda$ are in such close agreement (to within 5%) with experiment over the temperature range 1000–2000 K. Given the somewhat poorer agreement for $CaF_2$, there may be an element of luck in this, but it does suggest that our results for the range between 2000 K and the melting point give reliable values for the lattice contribution to $\lambda$. As expected, the values for $\lambda$ from simulation and experiment differ greatly in this range, the difference being more than a factor of two at the melting point. As we noted in the introduction, the anomalous increase in the experimental conductivity is believed to be due to electronic contributions to $\lambda$. The excellent agreement with experiment obtained when we add to our simulation results the electronic contribution calculated by Harding and Martin (1989) provides useful support for their theory of this contribution.

A significant technical point that emerges from this work concerns the contribution to $\lambda$ from ionic diffusion. We have found that if one uses equation (2) to calculate $\lambda$, there is a substantial cancellation between the terms $L_{ee}$ and $L_{ez}^2/L_{zz}$ in the high-temperature superionic region. Special attention therefore needs to be paid to the reduction of statistical errors. We have shown how the statistical accuracy can be improved by exploiting the freedom to express $\lambda$ in different ways in terms of the integrals of correlation functions, through equation (5). This procedure should be of more general use in calculating $\lambda$ for ionic conductors, including molten salts.

In the present work, we have not addressed the question of the behaviour of $\lambda$ in non-stoichiometric $UO_2$, which is of considerable practical importance. The electronic contribution should be strongly suppressed in the hyperstoichiometric material ($UO_{2+x}$), in a way that appears to conflict with experiment (Harding and Martin 1989). We expect that molecular dynamics simulations of $\lambda$ for this situation will provide useful information, and we plan to undertake such calculations in the near future.

## Acknowledgments

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