Phonon density of states for solid uranium: Accuracy of the embedded atom model classical interatomic potential

A S Antropov\textsuperscript{1,2}, K S Fidanyan\textsuperscript{1,2} and V V Stegailov\textsuperscript{1}

\textsuperscript{1} Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13 Bldg 2, Moscow 125412, Russia
\textsuperscript{2} Moscow Institute of Physics and Technology, Institutskiy Pereulok 9, Dolgoprudny, Moscow Region 141700, Russia

E-mail: antropov@phystech.edu

Abstract. An accurate computation of the vibrational properties of a crystal lattice, such as phonon density of states and dispersion curves, is necessary for the description of thermodynamic properties of the solid state as well as defect migration rates. In this work, we use a simple embedded atom model classical interatomic potential. The phonon density of states for the $\alpha$ and $\gamma$ phases of uranium at different temperatures was calculated by three methods: the lattice dynamics approach, the Fourier transformation of the velocity autocorrelation function and the Green’s function method for lattice dynamics.

1. Introduction
Dynamics of defects in a crystal lattice determines the wide range of mechanical properties of solids. Research in this direction is especially important for nuclear material science. However, experimental study of the defects motion and interaction is rather difficult due to complicated observation techniques, especially in the case of point defects. Growing computer power opens a way to the computer simulation of diffusion processes. The diffusion of defects is a relatively slow process, so kinetic methods with enhanced performance should be used. Probabilities of defect jumps in different directions are needed for this approach. Several works show the connection between the diffusion rate and vibration properties of a crystal lattice. Vineyard showed in 1957 that the rate of activated processes in the solid can be represented via the normal vibrational modes of the system \cite{1}. Later Herzig with colleagues revealed the correlation between the high self-diffusion coefficient in the $\langle 111 \rangle$ direction and low frequency phonons with appropriate wave vector in the bcc metals \cite{2}. One can also derive thermodynamic properties of the solid state from the phonon density of states, for example vibrational entropy and melting temperature \cite{3, 4}.

Several x-ray scattering experiments with $\alpha$-uranium were carried out to find out dispersion curves at room temperature \cite{5, 6}. The phonon density of states was measured in a range of temperatures from 50 up to 1213 K (including $\alpha$, $\beta$ and $\gamma$ phases) \cite{7}. These results can be used as a reference for molecular dynamics calculations.

Quantum models based on the electron density functional theory can be considered as the most accurate, however very computationally demanding \cite{8}. Moreover, ab initio calculations
of uranium are difficult due to its complex electron structure [9]. In particular, one should pay attention on the core size in pseudopotential models [10].

In the last decade researchers developed a set of empirical interatomic potentials for U [11–13]. The comparison between potentials helps to improve them and to choose the most suitable one for a particular purpose [14, 15].

There are different methods how to obtain vibrational properties of crystal. The dynamical matrix of the ideal lattice gives a set of discrete normal modes [16]. However, it cannot describe the peculiarities of high temperature spectra, which are important for the uranium due to the $\alpha$–$\beta$–$\gamma$ phase transitions. The velocity autocorrelation function gives the phonon density at finite temperatures [17,18]. Another method proposed by Ling Ti Kong consists in the reconstruction of the dynamical matrix of the crystal via the Green’s function [19, 20]. Comparing the results of different methods helps to find most suitable one for the particular problem and conditions, under which accurate quantum computations can be later performed.

In this paper, the phonon density of states of pure uranium in $\alpha$ and $\gamma$ phases is calculated using the EAM (embedded atom model) potential and different methods described above.

2. phDOS calculation methods

2.1. Dynamical matrix

Direct method of the phonon density of states (phDOS) computation is to displace any atom of the system and find $(3N)^2$ second derivatives of the potential energy (the dynamical matrix). If one considers $\Delta x_i = a \cos(\omega t + \phi)$, then a set of differential equations describing the motion of each atom looks like

$$
\begin{align*}
\omega^2 \begin{pmatrix} x_1 \\ \vdots \\ x_{3N} \end{pmatrix} &= \begin{pmatrix} \frac{1}{m_1} \frac{\partial^2 U}{\partial x_1^2} & \cdots & \frac{1}{\sqrt{m_1 m_{3N}}} \frac{\partial^2 U}{\partial x_1 \partial x_{3N}} \\ \vdots & \ddots & \vdots \\ \frac{1}{\sqrt{m_{3N} m_1}} \frac{\partial^2 U}{\partial x_{3N} \partial x_1} & \cdots & \frac{1}{m_{3N}} \frac{\partial^2 U}{\partial x_{3N}^2} \end{pmatrix} \end{align*}
$$

The eigenvalues of the matrix in the right part of the equation are the squares of normal mode frequencies [16]. The distribution of these frequencies gives the estimate for the phonon density of states [21]. However the principle disadvantage of this method is that the harmonic approach works only at zero temperature. Anharmonic effects could not be considered directly and they apply a “quasi-harmonic” correction to account finite temperature, but it is difficult and sometimes impractical.

2.2. Velocity autocorrelation function

A quite different technique is to obtain information about vibrational properties from the molecular dynamics trajectory of the crystal lattice [17,18]. Let us consider the set of harmonic oscillators. The velocity of each atom is given by

$$
v = \sum_i A_i \omega_i \sin(-\omega_i t + \phi_i). \tag{2}
$$

The velocity autocorrelation function is by definition

$$
\gamma(t) = \frac{\langle v(t) \cdot v(0) \rangle}{\langle v(0)^2 \rangle}, \tag{3}
$$

where angle brackets mean the average over all atoms and different initial times. Substitution of equation (2) to equation (3) gives

$$
\gamma(t) = \frac{\langle \sum_i A_i \omega_i \sin(-\omega_i t + \phi_i) \cdot \sum_j A_j \omega_j \sin(\phi_j) \rangle}{\langle \sum_i A_i \omega_i \sin(\phi_i) \rangle^2}. \tag{4}
$$
Taking into account that the averaging is performed over an ensemble with random phases $\phi_i$,

$$
\gamma(t) = \frac{\langle \sum_i A_i^2 \omega_i^2 \sin(-\omega_i t + \phi_i) \cdot \sin(\phi_i) \rangle}{\langle \sum_i A_i^2 \omega_i^2 \sin^2(\phi_i) \rangle} = \frac{\sum_i A_i^2 \omega_i^2 (\sin(-\omega_i t + \phi_i) \cdot \sin(\phi_i))}{\sum_i A_i^2 \omega_i^2 (\sin^2(\phi_i))} = \frac{\sum_i A_i^2 \omega_i^2 \cos(-\omega_i t)}{\frac{1}{2} \sum_i A_i^2 \omega_i^2}.
$$

Replacing the summation by the integral and accounting that $E_\omega = A^2 \omega^2/(2M)$ one can see that the phonon density of states, which is proportional to $E_\omega$, can be obtained from the velocity autocorrelation function by the Fourier transformation. This method can be applied in a wide range of temperatures. One should keep in mind that a phonon lifetime is finite at non-zero temperature. Due to interaction between phonons, the velocity autocorrelation function is damping and therefore we should take into account thermal broadening.

### 2.3. Elastic Green’s function method

The way to avoid several aforementioned problems was described by Ling Ti Kong [20]. In this method, the dynamical matrix is calculated directly from the molecular dynamics simulation [19]. In the case of one-dimensional harmonic oscillator with the force constant $k$ we have

$$
\frac{1}{2} k \langle x^2 \rangle = \frac{1}{2} k_B T, \quad k = \frac{k_B T}{\langle x^2 \rangle}.
$$

Similarly to the one-dimensional case, one can analyse $3N$-dimensional case, $l$-atom displacement in the $\alpha$ direction is denoted as $u_{l\alpha}$. Let us introduce a lattice Green’s function as

$$
G_{l\alpha, l'\alpha'} = \langle u_{l\alpha} u_{l'\beta} \rangle.
$$

In terms of the Green’s function the force constants $\Phi_{l\alpha, l'\beta}$ can be expressed:

$$
\Phi_{l\alpha, l'\beta} = k_B T [G^{-1}]_{l\alpha, l'\beta}.
$$

It is more convenient to access the Green’s function and the force coefficients in the reciprocal space for consideration of the phonons with particular wave vectors. It allows to find a dispersion curve and pHDOs in particular direction. The coefficients of the dynamical matrix in the reciprocal space are

$$
D_{l\alpha, l'\beta} = \frac{1}{\sqrt{m_l m_{l'}}} \tilde{\Phi}_{l\alpha, l'\beta},
$$

$$
\tilde{\Phi}_{l\alpha, l'\beta} = \sum_{l', \beta} \Phi_{l\alpha, l'\beta} \exp[iq(r_l - r_{l'})].
$$

The eigenvalues of the $D$ matrix give the squared frequencies of lattice vibrations. The eigenvectors are the phonon wave vectors in the first Brillouin zone.

### 3. Interatomic potential EAM

Plenty of models of the interaction between atoms can be chosen to perform molecular dynamics simulations for a particular system. The choice of a classical empirical potential, describing vibrational properties in the best possible way, is an important question.

One of the most widely used models of the atom interaction for metals and alloys is EAM [22]. According to this model the potential energy of an atom is represented as a sum of the pair
interactions energy and the embedding function that depends on the effective electron density at a given atom:

\[ U_i = U_i^{\text{pair}} + U_i^{\text{emb}}(\rho), \]

\[ \rho = \sum_{j \neq i} \rho_j(R_{ij}). \]

The functions \( U_i^{\text{pair}}, U_i^{\text{emb}} \) and \( \rho_j(R_{ij}) \) are fitted to experimental data or results of quantum calculations [23].

In this work computations are performed using EAM interatomic potential for uranium [11].

4. Details of computations

The phonon density of states is obtained for the pure uranium crystal lattice under zero pressure at several temperatures. The computations are made with the molecular dynamics code LAMMPS. The temperatures are chosen the same as in the experimental work [7]. This range of temperatures covers the phase transition between \( \alpha \)-uranium at temperatures lower than \( \approx 940 \) K and \( \gamma \)-uranium at temperatures upper than \( \approx 1050 \) K.

The equilibrium lattice parameters for zero pressure at considered temperatures are found. The dynamical matrix in the harmonic approach is calculated for the system with 10 unit cells in each direction for the \( \gamma \)-lattice (2000 atoms) and 8 unit cells in each direction for the \( \alpha \)-lattice (2048 atoms). The molecular dynamics simulation is performed with the integration step that equals 1 fs for the simulation box with 20 unit cells in each direction. After reaching
an equilibrium at required temperature, the velocity autocorrelation function and the lattice Green’s functions were being obtained every 10 ps during 200 ps.

Calculations for each temperature are performed using the lattice constant values that correspond to the zero pressure isobar. Figure 1 shows that thermal expansion has quite a weak influence on the lattice dynamics results.

It is worth noting that the dynamical matrix (built directly or through the Green’s functions) gives a set of frequencies as delta-functions. In contrast, we can say that the Fourier transform of the VACF gives a finite width peak for each frequency, due to limited phonon lifetimes. The most significant process defining the phonon lifetime is a three-phonon collision. The probability of the phonon decay is given by [24]:

$$\frac{dW}{dt} = wN_1(N_2 + 1)(N_3 + 1)\delta(\omega_1 - \omega_2 - \omega_3)\frac{d^3k_2}{8\pi^3},$$

(13)

$$w = w(k_1, \omega_1, k_2, \omega_2, k_3, \omega_3),$$

(14)

where $N_i, k_i, \omega_i$ are the phonon occupation numbers, wave vectors and frequencies of the decaying phonon ($i = 1$) and the appearing phonons ($i = 2, 3$). Taking into account that at high temperatures in the classical limit $N \approx N + 1 \sim kT$, and integrating over all $k_2$ one can get

$$\frac{dN_1}{dt} = -w'(T, k_1, \omega_1)N_1.$$

(15)
Figure 3. The phonon density of states of $\alpha$- and $\gamma$-uranium calculated via the lattice dynamics approach, the Fourier transformation of velocity autocorrelation function, the Lorentzian broadening of the phDOS obtained by the Green’s function method. The experimental data are shown as well.

The amplitude of vibrations, correlated with initial ones, decays exponentially:

$$A = A_0 \exp[-w'(T, k_1, \omega_1)t].$$

The Fourier transform of such a function is a Lorentz curve. The specific view of $w'(T, k_1, \omega_1)$ is quite complex and depends on many factors [25, 26]. To compare the two methods, every box in the frequency histogram of the Green’s function method is broadened to a Lorentz curve. For simplicity the function $w'(T, k_1, \omega_1)$ is supposed to be $w' = aT$. The parameter $a$ is chosen to fit the results of the VACF method in the best possible way. The example of the resulting curve is shown in figure 2.

5. Results
Normal vibration modes obtained by the lattice dynamics approach, from the spectrum of velocity autocorrelation function and from the Lorentzian broadened result of the Green’s function method together with experimental data are shown in figure 3. At low temperatures (50 K) the results of the VACF method coincide with the results of the lattice dynamics approach. The Green’s function method gives a different result at 50 K, the reason for such a discrepancy has not been resolved yet. At higher temperatures the spectra of the VACF method and the Green’s function method are close to each other (with taking into account effect of temperature
broadening). However, the anharmonic effects reveal themselves already at 300 K and we see a large discrepancy with the zero temperature lattice dynamics results. The comparison with the experimental data illustrates an adequate level of accuracy of the EAM model considered.

6. Conclusions
This work has been devoted to the accuracy evaluation of the EAM classical interatomic potential for solid uranium. It was considered with respect to the results of phDOS calculations for $\alpha$ and $\gamma$-uranium using the exiting experimental data as a reference. We have given special attention to the question of phDOS calculation for $\gamma$-uranium unstable at $T = 0$ that makes the harmonic approximation inapplicable. Two methods have been compared: one method based on VACF calculations and another method based on Green’s functions calculations. The convergence criteria for both methods have been found.

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