Quantifying the anomalous self-diffusion in molybdenum with first-principles simulations

T. R. Mattsson  
HEDP Theory, Sandia National Laboratories, Albuquerque, New Mexico 87185-1189, USA

N. Sandberg  
Department of Physics, Royal Institute of Technology, Stockholm SE-100 44, Sweden

R. Armiento  
Theoretische Physik, Universität Bayreuth, D-95440 Bayreuth, Germany

A. E. Mattsson  
Multiscale Dynamic Materials Modeling, Sandia National Laboratories, Albuquerque, New Mexico 87185-1322, USA

I. INTRODUCTION

Metals in body-centered cubic (bcc) crystal structure, e.g., Mo, Ta, and W, have long posed a serious challenge for computational materials science. Thermophysical properties such as the specific heat show unusually large anharmonic contributions, and until recently, electronic-structure calculations were in stark qualitative and quantitative disagreement with experiments, e.g., concerning the relative stability between competing phases. Even when considering the simplest lattice defect, the vacancy, very large uncertainties persist. Since vacancies, among others, govern substitutional diffusion in crystals, the lack of quantitative understanding of their properties impedes the development of a theory of diffusion in bcc metals and alloys similar to the one that has been established in face-centered cubic systems such as Al.

In this paper, we focus on vacancy formation and migration in Mo. Experimentally, although the self-diffusion rate is a geometrical factor $c_v$ and enthalpy $H_v^f$ of vacancy formation, the corresponding quantities governing vacancy migration, $S_v^m$ and $H_v^m$, since both these processes are thermally activated, 

$$D = \frac{1}{6} \sqrt{f f c_v \Gamma_v},$$

where $f$ is a geometrical factor (the correlation factor, $f = 0.73$ in a bcc crystal) and $l$ is the jump length in the crystal.

A microscopic model of diffusion in bcc metals needs to provide $c_v$ and $\Gamma_v$ as a function of temperature. Alternatively, the model can instead yield the entropy $S_v^f$ and enthalpy $H_v^f$ of vacancy formation, and the corresponding quantities governing vacancy migration, $S_v^m$ and $H_v^m$, since both these processes are thermally activated, 

$$c_v = \exp(S_v^f/k_B - H_v^f/k_B T)$$

$$\Gamma_v = \Gamma_0 \exp(S_v^m/k_B - H_v^m/k_B T).$$

Here, $\Gamma_0$ is a trivial prefactor within the transition-state theory (TST) (Ref. 11) and $k_BT$ is Boltzmann’s constant times
temperature. The temperature variation in $q$ therefore corresponds to temperature variation in $H^f_v$ and/or in $H^{0\nu}$, both possibilities have been suggested in the literature.\textsuperscript{12,13}

In order to resolve the origin of the anomalous self-diffusion rate in bcc metals, we employ extensive DFT (Refs. 14 and 15) MD simulations to calculate (i) the temperature variation in $H^f_v$ and (ii) the absolute jump rate $\Gamma_v$ of vacancies at high temperature. In combination with established methods for calculating the limiting low-temperature (classical) values of $H^f_v$, $S^f_v$, $H^{0\nu}$, and $S^m$, this allows for a full microscopic description of vacancy formation and self-diffusion in Mo.

III. APPLYING DENSITY-FUNCTIONAL THEORY TO CALCULATE DEFECT ENERGIES

The accuracy of a DFT calculation is determined by the exchange-correlation term used.\textsuperscript{16} We choose the recently developed AM05 functional.\textsuperscript{9,17} It has demonstrated high fidelity for transition metals, refractory metals, semiconductors, and oxides.\textsuperscript{15} For Mo, application of the AM05 functional yields a 0 K lattice constant of 3.134 \AA\ and a bulk modulus of 283 GPa. Particularly important for studies of defects, AM05 includes the intrinsic surface error.\textsuperscript{9,20} Earlier functionals require postprocessing corrections to be made when analyzing vacancy energies,\textsuperscript{19,20} corrections that cannot be made during a DFT-MD simulation. Taken together, the beneficial properties of AM05 make it meaningful to attempt the computationally demanding DFT-MD runs required for the current problem.

The DFT-MD simulations were performed with a massively parallel version of the PAW core-potential code VASP 5.1.40 (Refs. 21–25) on Cray XT (Ref. 26) using stringent convergence settings.\textsuperscript{16} We used a plane-wave cutoff of 400 eV using the 6 electron Mo PAW PBE core function of 08Apr2002. Real-space projections are not applied, to maintain highest possible accuracy. All results presented are for the mean-value $k$ point (1/4,1/4,1/4). Convergence with respect to $k$ points was investigated by comparing energy differences between $\Gamma$ point (0,0,0), mean-value point (1/4,1/4,1/4), and Monkhorst-Pack grids (2$^3$ and 4$^3$). Using the mean-value point is a significant improvement upon the $\Gamma$ point, with little to no improvement when going to higher grids. The electronic states are distributed according to Mermin’s finite-temperature formulation of DFT.\textsuperscript{27}

Structural optimization was used to find the low-temperature limit of the vacancy-formation energy $H^f_v$ and the migration activation energy $H^{0\nu}$ in 128 atom supercells. The vacancy formation entropy $S^f_v$ and the migration prefactor $\Gamma_0 \exp(S^0_v/k_B T)$ were obtained by calculating force constant matrices\textsuperscript{5} via finite displacements,\textsuperscript{28} this was done by calculating the force-constant matrix via finite displacements\textsuperscript{5} in 54 atom unit cells. To verify that the size of the system is adequate, we performed separate model potential calculations from 54 to 800 atoms. We find that prefactors calculated via the force-constant matrix method are well represented in the 54-atoms supercells. The DFT-MD simulations, which are necessary for the study of the anharmonic contributions to the formation and migration free energy, are the most computationally demanding parts of the present work.

IV. VACANCY FORMATION ENERGY FROM MD SIMULATIONS

The vacancy-formation energy was obtained by comparing thermally averaged energies in a system containing a vacancy, with that in a bulk system, using DFT-MD. The simulations were done at fixed volumes $V$, corresponding to the relaxed volumes of the bulk and vacancy systems at zero kelvin, respectively. With increasing temperature the pressure therefore increases by $\Delta p(T)$. The corresponding increase in free energy is to lowest order $\Delta G(T) = V\Delta p(T)T^2/2K$. We subtract this term, calculated separately for the bulk and vacancy systems, by using the pressure from the DFT-MD calculations, and bulk moduli $K$ from static DFT calculations. The corresponding change in predicted vacancy concentration is relatively small, which can be understood in the following way. The increase with temperature, $\Delta p(T)$, is somewhat larger in the bulk system compared to the vacancy system, but it is weighted by a factor 127\,128 in the calculation of the change in free energy per vacancy. The net effect is that the predicted vacancy concentration is changed by less than 20%. The bulk modulus of the vacancy system is lower than that of the bulk system by approximately 2.5%, which is roughly in line with the expectation that $K$ varies as the square of the electronic density.\textsuperscript{29}

Figure 1 shows the considerable anharmonic increase in $H^f_v$ with temperature. The increase is well described by a quadratic polynomial in $T$. By using the thermodynamic relation $T\delta S^{0\nu}/\delta T$, $S^f_v$ can be obtained, with the reference formation entropy $S^0_v(T=0)$ taken from phonon calculations. Table I presents the calculated vacancy-formation parameters, and
TABLE I. Calculated vacancy formation and migration parameters compared with experimental data.

Static DFT means classical quantities at 0 K. DFT-MD includes thermal effects of vibrational and electronic origin. For each experimental value, we have compared with DFT-MD results for the same temperature (interval) as indicated below.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$H_f^v$ (eV)</th>
<th>$H_m^v$ (eV)</th>
<th>$Q$ (eV)</th>
<th>$S_f^v(k_B)$ (Hz)</th>
<th>$\Gamma_{eff}^{SD}/h$ (10^{-3} s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000, ... , 2500</td>
<td>3.10</td>
<td>1.30</td>
<td>4.40</td>
<td>0.7</td>
<td>1.5 x 10^{13}</td>
</tr>
<tr>
<td>2500, ... , 3000</td>
<td>3.90</td>
<td>1.32</td>
<td>5.04</td>
<td>2.30</td>
<td>0.18</td>
</tr>
<tr>
<td>Experiments</td>
<td>3.0 ± 0.2 (\text{Ref. 4.})</td>
<td>1.30(\text{Ref. 8.})</td>
<td>4.78(\text{Ref. 8.})</td>
<td>1.5(\text{Ref. 8.})</td>
<td>10^{-3} , ... , 10 (\text{Ref. 8.})</td>
</tr>
<tr>
<td>2890</td>
<td>3.6 ± 0.2 (\text{Ref. 7.})</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

\(\text{Ref. 7.}\) (positron lifetime spectroscopy data).

V. DIRECT SIMULATION OF VACANCY MOBILITY

In the simulation of a single vacancy in a 128 lattice-point supercell at \(T=2600\) and 2800 K, the vacancy will migrate by thermal activation. This allows us to directly estimate the mean jump rate, \(\Gamma_m\), without the additional assumptions and approximations of TST. In order to unambiguously locate the vacancy at each time step, we use a model potential to quench a copy of each atomic configuration, and associate the empty lattice site with the position of the vacancy, thereby obtaining a trajectory in time of the vacancy migration. In the 2600 and 2800 K simulations, we logged 8 and 11 jumps, respectively, with the simulation at 2600 K being longer in real time. The resulting rate is shown in Fig. 2.

By comparing long model potential simulations in 127-, 1023-, and 3455-atom systems, we conclude that the jump rate in a 127-atom system is representative of that in larger systems to within 5%. We make the following observations: the major part of the temperature dependence in the diffusion activation energy \(Q\) can be attributed to vacancy formation, with a smaller but significant part associated with vacancy migration. The AM05 results can be considered in quantitative agreement with experimental data when considering the difficulties involved in accurate calculations of point defects and point-defect kinetics in transition metals. The 0 K vacancy-formation energy is 2.67 eV in PBE. Full DFT-MD simulations, using PBE, were performed to obtain the temperature dependence of the vacancy-formation energy.
formation enthalpy. For vacancy migration, the temperature
dependence was approximated with the one of AM05.

The effective activation energy $Q$ is 4.78 eV in experi-
ments from a low-temperature fit ($1350<T<2000$ K),
compared to 5.0 eV in our AM05 calculations. The corre-
sponding energies, at high $T$ ($T>2000$ K), are 5.50 eV in
experiments and 5.78 eV for AM05. Thus, there is a con-
sistent overestimation of $Q=H_f^v+H_t^m$ by 0.2–0.3 eV, or
only about 5%. It is important to note that the simulations have no
free parameters and hence can be repeated for materials and
conditions where experimental data is nonexistent, scarce,
expensive to obtain, or disputed. We conclude that the sys-
tematic high fidelity of AM05 for bulk properties translates
into accurate results also for self-diffusion, a significantly
more complex property.

We now discuss the current results for vacancies in the
light of available experimental information. Data on vacan-
cies in Mo are mainly from two types of experiments, resist-
vitively measurements after quenching, and positron annihi-
lations in Mo, but from the fit one obtains a value of
$\sigma$ in Mo, but from the fit one obtains a value of
$\sigma$ in Mo, but from the fit one obtains a value of
$\alpha(T_m)=0.001\%$, then, the experimental diffusion rate in combination with Eq.
(1) leads to a very high jump rate, $\Gamma(T_m)=22$ THz, which is
much higher than the cut-off frequency in the phonon
spectrum.

Positron annihilation experiments are done under equilib-
rium conditions, as opposed to resistivity measurements. In
such an experiment, either the Doppler-broadening, lifetime
(7), or positron lifetime spectrum (PLS) of annihilating pos-
itrons are measured. To distinguish trapped positrons from
free (bulk) positrons, a model of positron trapping is applied
in which assumptions are needed about the temperature de-
pendencies of lifetimes and/or trapping rates. From PLS data
one can derive the trapping rate $\alpha(T_m)$, where $\sigma$ is the trapping
rate per vacancy, without further assumptions about life-
times. We fitted data from Ref. 7 by using the quadratic
temperature dependence of $H_f^v$ to fit $\alpha(T_m)$, see Fig. 4. The
resulting 0 K formation energy $H_f^v(T=0)=2.85$ eV, which is
slightly below our calculated 3.10 eV. However, this result
assumes that the temperature variation in $\alpha$ can be neglected.

Absolute vacancy concentrations may now be obtained if
the specific trapping rate $\sigma$ is known. There are no estimates
of $\sigma$ in Mo, but from the fit one obtains a value of
$\exp(S_v/k_B)$, which in our case amounts to $0.5 \times 10^{14}$ Hz.
This value compares reasonably well with that in Al, where
the vacancy concentration has been independently measured.

VI. SUMMARY

We have presented and validated a microscopic modeling
approach based on DFT-MD that describes the anharmonic
behavior of Mo vacancy diffusion at high temperature and
can be applied to a wide range of materials. The simulations
provide a quantitative microscopic model of vacancy motion:
temperature dependence of the vacancy-formation energy,
absolute concentration, and vacancy jump rate. The success-
ful results for defects and diffusion in Mo opens for a type of
microscopic modeling that previously have been unavailable.
for bcc metals and alloys. We therefore expect the current results to stimulate further work on defects and diffusion in bcc systems.

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