Energetics and kinetics of vacancy diffusion and aggregation in shocked aluminium \textit{via} orbital-free density functional theory

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A possible mechanism for shock-induced failure in aluminium involves atomic vacancies diffusing through the crystal lattice and agglomerating to form voids, which continue to grow, ultimately resulting in ductile fracture. We employ orbital-free density functional theory, a linear-scaling first-principles quantum mechanics method, to study vacancy formation, diffusion, and aggregation in aluminium under shock loading conditions of compression and tension. We calculate vacancy formation and migration energies, and find that while nearest-neighbor vacancy pairs are unstable, next-nearest-neighbor vacancy pairs are stable. As the number of nearby vacancies increases, we predict that vacancy clusters preferentially grow through next-nearest-neighbor vacancies. The energetics are found to be greatly affected by expansion and compression, leading to insight as to how vacancies behave under shock conditions.

1. Introduction

Ductile fracture is the dominant failure mode for metals under shock conditions. For example, bridges, automobiles, and aircraft subjected to high-explosive detonations experience significant mechanical stress. Subsequent ductile fracture is often the cause of failure in such systems.\textsuperscript{1} Improving understanding of the mechanisms of ductile fracture may help design better, more durable components. A number of recent studies, both experimental and theoretical, have focused on characterizing shock-induced ductile fracture. Laser ablation and gas gun setups can produce shocked samples similar to those found in high-explosive detonations,\textsuperscript{2,3} with post-mortem

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{Image description.}
\end{figure}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
Column 1 & Column 2 \\
\hline
Data 1 & Data 2 \\
\hline
\end{tabular}
\caption{Table description.}
\end{table}

\begin{equation}
E = \frac{1}{2}mv^2 + U
\end{equation}

...continued...
The simplest defects are atomic vacancies, which affect mechanical, thermodynamic, electrical, and optical properties of metals and are thought to play a critical role in ductile fracture via their migration to form small vacancy clusters as nucleation sites for void formation and growth. Vacancies may also affect the mechanism of fracture in other, more subtle ways as well. For instance, vacancies affect dislocation mobility. For example, Benoit and coworkers discovered that ultra-high-purity aluminium cold-worked at low temperatures decreased the elastic modulus of the metal, suggesting that vacancies lubricate dislocation motion.\(^8\)\(^\text{–}\)\(^1\)\(^0\)\(^\text{–}\)\(^1\)\(^2\) Theoretical studies recently provided evidence supporting this result.\(^1\)\(^3\)\(^\text{–}\)\(^1\)\(^4\)\(^\text{–}\)\(^1\)\(^5\)\(^\text{–}\)\(^1\)\(^6\)\(^\text{–}\)\(^1\)\(^7\)\(^\text{–}\)\(^1\)\(^8\)\(^\text{–}\)\(^1\)\(^9\)\(^\text{–}\)\(^2\)\(^0\)\(^\text{–}\)\(^2\)\(^1\)\(^\text{–}\)\(^2\)\(^2\)\(^\text{–}\)\(^2\)\(^3\)\(^\text{–}\)\(^2\)\(^4\)\(^\text{–}\)\(^2\)\(^5\)\(^\text{–}\)\(^2\)\(^6\)\(^\text{–}\)\(^2\)\(^7\)\(^\text{–}\)\(^2\)\(^8\)\(^\text{–}\)\(^2\)\(^9\)\(^\text{–}\)\(^3\)\(^0\)\(^\text{–}\)\(^3\)\(^1\)\(^\text{–}\)\(^3\)\(^2\)\(^\text{–}\)\(^3\)\(^3\)\(^\text{–}\)\(^3\)\(^4\)\(^\text{–}\)\(^3\)\(^5\)\(^\text{–}\)\(^3\)\(^6\)\(^\text{–}\)\(^3\)\(^7\)\(^\text{–}\)\(^3\)\(^8\)\(^\text{–}\)\(^3\)\(^9\)\(^\text{–}\)\(^4\)\(^0\)\(^\text{–}\)\(^4\)\(^1\)\(^\text{–}\)\(^4\)\(^2\)\(^\text{–}\)\(^4\)\(^3\)\(^\text{–}\)\(^4\)\(^4\)\(^\text{–}\)\(^4\)\(^5\)\(^\text{–}\)\(^4\)\(^6\)\(^\text{–}\)\(^4\)\(^7\)\(^\text{–}\)\(^4\)\(^8\)\(^\text{–}\)\(^4\)\(^9\)\(^\text{–}\)\(^5\)\(^0\)\(^\text{–}\)\(^5\)\(^1\)\(^\text{–}\)\(^5\)\(^2\)\(^\text{–}\)\(^5\)\(^3\)\(^\text{–}\)\(^5\)\(^4\)\(^\text{–}\)\(^5\)\(^5\)\(^\text{–}\)\(^5\)\(^6\)\(^\text{–}\)\(^5\)\(^7\)\(^\text{–}\)\(^5\)\(^8\)\(^\text{–}\)\(^5\)\(^9\)\(^\text{–}\)\(^6\)\(^0\)\(^\text{–}\)\(^6\)\(^1\)\(^\text{–}\)\(^6\)\(^2\)\(^\text{–}\)\(^6\)\(^3\)\(^\text{–}\)\(^6\)\(^4\)\(^\text{–}\)\(^6\)\(^5\)\(^\text{–}\)\(^6\)\(^6\)\(^\text{–}\)\(^6\)\(^7\)\(^\text{–}\)\(^6\)\(^8\)\(^\text{–}\)\(^6\)\(^9\)\(^\text{–}\)\(^7\)\(^0\)\(^\text{–}\)\(^7\)\(^1\)\(^\text{–}\)\(^7\)\(^2\)\(^\text{–}\)\(^7\)\(^3\)\(^\text{–}\)\(^7\)\(^4\)\(^\text{–}\)\(^7\)\(^5\)\(^\text{–}\)\(^7\)\(^6\)\(^\text{–}\)\(^7\)\(^7\)\(^\text{–}\)\(^7\)\(^8\)\(^\text{–}\)\(^7\)\(^9\)\(^\text{–}\)\(^8\)\(^0\)\(^\text{–}\)\(^8\)\(^1\)\(^\text{–}\)\(^8\)\(^2\)\(^\text{–}\)\(^8\)\(^3\)\(^\text{–}\)\(^8\)\(^4\)\(^\text{–}\)\(^8\)\(^5\)\(^\text{–}\)\(^8\)\(^6\)\(^\text{–}\)\(^8\)\(^7\)\(^\text{–}\)\(^8\)\(^8\)\(^\text{–}\)\(^8\)\(^9\)\(^\text{–}\)\(^9\)\(^0\)\(^\text{–}\)\(^9\)\(^1\)\(^\text{–}\)\(^9\)\(^2\)\(^\text{–}\)\(^9\)\(^3\)\(^\text{–}\)\(^9\)\(^4\)\(^\text{–}\)\(^9\)\(^5\)\(^\text{–}\)\(^9\)\(^6\)\(^\text{–}\)\(^9\)\(^7\)\(^\text{–}\)\(^9\)\(^8\)\(^\text{–}\)\(^9\)\(^9\)
binding energies, as well as the mobility of vacancies in the presence of another vacancy. Conclusions are drawn at the end.

2. Theoretical method

Aside from benchmark tests using Kohn–Sham (KS) DFT to assess errors, we use OF-DFT throughout this work. Unlike traditional $O(N^3)$ scaling KS-DFT, OF-DFT is a near linear-scaling $[O(N \ln N) \text{ via fast Fourier transforms}]$ quantum mechanics method that minimizes an energy functional based solely on the electron density.\(^{20}\) As a result, large quantum mechanical simulation cells containing hundreds to thousands of atoms can be utilized, which allows us to predict vacancy behavior in the limit of very low concentrations not affordable with KS-DFT. While this density-only approach greatly speeds up calculations by several orders of magnitude, such efficiency does not come for free. Some accuracy is sacrificed, on two fronts, each of which we now briefly review.

Unlike the orbital-based kinetic energy expression in KS-DFT, which is exact for non-interacting electrons, approximate kinetic energy density functionals (KEDFs) must be used instead in OF-DFT, since no orbitals are available. At present, the most accurate linear scaling KEDFs for condensed matter are those constructed to produce the correct linear response behavior for the non-interacting electron gas, as given by the Lindhard response function.\(^{21}\) This class of KEDFs may be written as\(^{20}\)

$$T_s[\rho] = T_{TF}[\rho] + T_{VW}[\rho] + T_X[\rho]$$

(1)

where $T_{TF}$ is the Thomas–Fermi functional (exact for the uniform electron gas),\(^{22}\) $T_{VW}$ is the von Weizsäcker functional (exact for a single orbital),\(^{23}\) and $T_X$ is a term introduced to recover the correct linear response behavior.\(^{24,25}\) These linear-response-type functionals are most accurate when the density within the system is slowly-varying, such as in bulk, nearly-free-electron-like metals, such as aluminium. We will show that the error due to our choice of KEDF\(^{26}\) is negligible, with the remaining error due to the second approximation, discussed next.

The pseudopotentials (potentials replacing the nucleus plus core electrons) that must be used within OF-DFT tend to be less accurate and transferable than ones usually employed in KS-DFT. Typically, KS-DFT uses nonlocal pseudopotentials, where different potentials act on electrons of different angular momentum, via orbital-based projection operators. As a result of their flexibility, nonlocal pseudopotentials tend to be more accurate than single-$l$-channel local pseudopotentials that only depend on the distance of the electron from the nucleus. However, only local pseudopotentials can be used within OF-DFT, due to the lack of orbitals on which to project nonlocal pseudopotentials. Errors incurred by this approximation for relative energetics are $\sim 0.1$–$0.2$ eV. A systematic means of improving local pseudopotentials via inversion of the Kohn–Sham equations for bulk crystals was recently reported;\(^{27}\) this technique was not employed here, but could be in future work to reduce this level of error further.

Given the approximations described above, it is natural to suggest using KS-DFT to avoid the OF-DFT errors. However, use of KS-DFT is very expensive for metals, due to both the cubic scaling of the algorithm and its prefactor, which is determined by the number of Brillouin zone sampling points required [generally very large ($\sim 10^3$) for metals]. This expense of KS-DFT becomes even more prohibitive once structural optimization of minima and transition states are considered, both of which require many energy and force evaluations, making it difficult to use more than tens of metal atoms with KS-DFT. Furthermore, since OF-DFT using state-of-the-art KEDFs describes nearly-free-electron-like metals with accuracy resembling conventional KS-DFT,\(^{26,28,29}\) OF-DFT is an ideal choice. Particularly relevant to the present work, Wang et al.\(^{30}\) showed that OF-DFT employing a KEDF with a density-dependent response kernel (the Wang–Govind–Carter or WGC KEDF) predicts relative stabilities and structures of various phases of Al, as well as the Al $E_{\text{c1}}$ to within 10 meV/atom of KS-DFT.\(^{26}\) More benchmarks presented here confirm the accuracy of the WGC KEDF, as well as extend the range of agreement to non-equilibrium conditions. We therefore use conventional KS-DFT only for benchmarking on smaller cells.

We will also compare KS-DFT and OF-DFT using the Perdew-Zunger local density approximation (LDA)\(^{30}\) versus the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA)\(^{31}\) for electron exchange and correlation. KS-DFT was performed within CASTEP version 2.0,\(^{32}\) using CASTEP’s default ultrasoft nonlocal LDA and GGA pseudopotentials for Al (cutoff radii $r_{\text{c}} = r_{\text{g}} = 2.0$ bohr).\(^{33,34}\) In addition, the Al local pseudopotential of Goodwin, et al.\(^{35}\) was used in both KS-DFT and OF-DFT, in order to assess its quality and errors due to its use. While the ultrasoft pseudopotentials could be used with a smaller plane wave basis (kinetic energy cutoff of 300 eV for LDA and 400 eV for GGA), the local pseudopotential required a kinetic energy cutoff of 600 eV to converge the KS-DFT total energies to within 1 meV/atom. A $k$-point spacing of 0.031 Å\(^{-1}\) on a Monkhorst–Pack grid\(^{36}\) was used, which converged the total energies to within 5 meV atom\(^{-1}\).

OF-DFT was executed within a new FORTRAN90-based code developed in our group.\(^{37}\) Throughout this work, we used the WGC KEDF mentioned above\(^{26}\) (parameters $(\alpha, \beta) = (5/3, -3/2)$). A plane wave kinetic energy cutoff of 1200 (or sometimes 1400) eV was used for all OF-DFT calculations to converge the total energy to $10^{-5}$ meV/atom. Since these OF-DFT calculations involve up to $\sim 1000$ atoms, we required very precise convergence of the actual total energy (i.e., not just on a per atom basis).

The linear and quadratic synchronous transit method (LST/ QST) included within CASTEP was employed to find transition states within KS-DFT, with a maximum force threshold of 50 meV Å\(^{-1}\).\(^{38}\) In OF-DFT, the climbing-image nudged elastic band (CINEB) transition state search algorithm\(^{39,40}\) was employed, with nine images (interpolated structures) found to be sufficient for convergence to a maximum force threshold of 10 meV Å\(^{-1}\).

In order to verify the nature of critical points as either minima or saddle points, we evaluate vibrational frequencies via

$$\nu_i = \frac{1}{2\pi} \sqrt{k_i}$$

(2)
where $k_i$ is an eigenvalue obtained from the mass-scaled force constant (Hessian or energy second derivative) matrix. The Hessian is constructed from numerical finite differences of analytic force components, each of which are calculated by evaluating the forces engendered due to small $x$, $y$, and $z$ central ($\pm 0.02$ Å) displacements of the diffusing atom and a number of nearest neighbors. Next, each component of the Hessian is scaled by the inverse geometric mean of the atomic masses involved

\[ h_{ij} = \frac{f_{ij}^{0.02}}{\sqrt{m_i m_j}} \]  

(3)

where $f_{ij}$ is the force on an atom $i$ in the $x$, $y$, or $z$ direction due to a displacement of atom $j$ in the $x$, $y$, or $z$ direction, and $m_i$ and $m_j$ correspond to the masses of the atoms. Since all masses are identical in our case, each Hessian matrix element is simply divided by the atomic mass of Al.

Although the resulting Hessian should be symmetric, numerical noise prevents full symmetry. Therefore, the Hessian matrix is then symmetrized via

\[ h_{ij} = \frac{h_{ij} + h_{ji}}{2} \]  

(4)

and finally diagonalized to find the eigenvalues.

3. Results

A. Vacancy formation energy, $E_v$

Definitions. The vacancy formation energy $E_v$ quantifies the stability of a vacancy in the bulk crystal and determines, to some extent, the likelihood of its formation and persistence. Considerable effort has been spent measuring vacancy concentrations in metals, mainly through differential dilatometry, positron annihilation techniques, and the measurement of residual electrical resistance after rapid thermal quenching. Though $E_v$ in aluminum has been calculated many times over the last few decades, we study it again for two reasons. First, a variety of different pseudopotentials, exchange–correlation functionals, cell sizes, and codes have been used in past DFT calculations. For a fair comparison against energies presented later, we recalculate them here. Second, we predict vacancy formation energies over a wide range of volumes and pressures not considered previously but relevant to formation of vacancies under non-equilibrium (shock) conditions.

$E_v$ is the energy required to remove an atom from the bulk. In the limit of an infinitely large system, $E_v$ at constant volume is given by

\[ E_v(V) = E(N - 1, 1, V) - \frac{N-1}{N} E(N, 0, V) \]  

(5)

where the notation $E(N,n,V)$ is used to describe a periodic cell of $N + n$ lattice sites, $N$ of which are occupied, in a volume $V$.

The ratio in front of $E(N,0,V)$ accounts for difference in the number of atoms between the initial bulk state and the final state containing a vacancy.

However, for finite-size systems, Gillan\textsuperscript{46} showed that the following definition

\[ E_v(V) = E\left(N - 1, 1, \frac{N-1}{N} V\right) - \frac{N-1}{N} E(N, 0, V) \]  

(6)

gives the most rapid convergence of $E_v$ to the thermodynamic limit with increasing system size. Note that this definition also has the satisfying property of conserving both number of atoms and volume in the initial and final states. Thus, eqn (6) is the equation we will use for $E_v$ at constant volume.

Under constant pressure, $E_v$ is simply defined as

\[ E_v(P) = E(N - 1, 1, P) - \frac{N-1}{N} E(N, 0, P) \]  

(7)

Here, the notation $E(N,n,P)$ is used to describe the energy of a system of $N$ atoms in $N + n$ lattice sites under a pressure $P$. Since pressure is an intensive quantity, there is no need to conserve (and thus scale) the pressure in the first term.

One may switch between the constant volume and constant pressure definitions by first fitting to Murnaghan’s equation of state\textsuperscript{44}

\[ E(V) = \frac{V B_0}{B_p} \left( \frac{V_0/V}{B_p - 1} + 1 \right) - B_0 V_0 \frac{P}{B_p - 1} \]  

(8)

where $B_0$ is the bulk modulus and $B_p$ is its pressure derivative. Then, a relationship between $P$ and $V$ for both the bulk and the vacancy systems may be obtained by taking the derivative of the Murnaghan fit, $dE/dV$, which is related to the pressure as $P = -(dE/dV)$ and solving for $V(P)$

\[ V(P) = V_0 \left( 1 + \frac{B_p P}{B_0} \right)^{-1/B_p} \]  

(9)

By combining these two equations, the energy as a function of pressure is obtained. However, the thermodynamically relevant quantity under constant pressure is the enthalpy, which we calculate via

\[ H(P) = E(P) + PdV \]  

(10)

where $dV$ is the change in volume from the pristine bulk to the vacancy-containing system under pressure $P$\textsuperscript{55}

\[ dV = V(N - 1, 1, P) - \frac{N-1}{N} V(N, 0, P) \]  

(11)

All calculations below begin with the ground state of the perfect Al bulk crystal, namely the fcc phase at the equilibrium lattice constant, which is predicted to be 4.032 Å by both OF-LDA (with the WGC KEDF) and KS-LDA, when the same local pseudopotential is employed. This value compares very well to the experimental value of 4.050 Å at 298 K.\textsuperscript{56} In all local pseudopotential calculations that follow, we adopt 4.032 Å as our bulk lattice constant. However, the ultrasoft nonlocal pseudopotential yields different equilibrium lattice constants: 3.963 Å within KS-LDA and 4.045 Å within KS-GGA. All predictions based on nonlocal pseudopotential KS-DFT used the appropriate equilibrium lattice constant (i.e. 3.963 Å for KS-LDA and 4.045 Å for KS-GGA).

Effect of periodic cell size. Since we perform calculations with periodic boundary conditions, the cell needs to be large
OF-DFT, 256 lattice sites, GGA 0.387 — OF-DFT, 256 lattice sites, LDA 0.475

OF-DFT, 32 lattice sites, LDA 0.515 0.396
KS-DFT, Local PSP, LDA, 32 lattice sites 0.506 0.402

Lattice site cells or smaller in DFT predictions of 32 lattice site periodic cell. Previous authors have used 32 of KS-DFT, all comparisons of KS-DFT and OF-DFT use a 256 lattice sites.

energies at both extremes are well-converged (to within 3 meV) faster under compression, we find that the vacancy formation energy is converged to within 3 meV by 256 lattice sites.

Although the energy converges faster under compression than under expansion, we find that the vacancy formation energies at both extremes are well-converged (to within 3 meV) by 256 lattice sites.

Comparison of OF-DFT with KS-DFT. Due to the expense of KS-DFT, all comparisons of KS-DFT and OF-DFT use a 32 lattice site periodic cell. Previous authors have used 32 lattice site cells or smaller in DFT predictions of \( E_{\text{vf}} \), obtaining results ranging from 0.59 to 0.83 eV.\textsuperscript{46–49} Based on our results above, use of a 32 lattice site cell engenders only an 0.04 eV error in the \( E_{\text{vf}} \). Alternatively, an 0.04 eV repulsion exists between vacancies at this concentration (since \( E_{\text{vf}} \) decreases as the cell size increases). In any case, a comparison between KS-DFT and OF-DFT at this small cell size still provides a valid means to assess the severity of the approximations used in OF-DFT.

Since KS-DFT and OF-DFT differ in their treatment of only two terms (the pseudopotential and the KEDF), we can determine readily which is the limiting approximation for Al by examining the data summarized in Table 1. First, we assess the accuracy of the WGC KEDF. Use of the same local pseudopotential in KS-LDA and OF-LDA yields very similar structurally relaxed \( E_{\text{eq}} \) of 0.506 and 0.515 eV, respectively. This confirms the accuracy of the WGC KEDF for Al, with errors of less than 0.01 eV expected due to the KEDF. Next, to assess the accuracy of the pseudopotential, we compare KS-LDA using the Goodwin, et al. local pseudopotential to CASTEP’s default nonlocal ultrasoft LDA pseudopotential for Al. The latter produces a structurally relaxed \( E_{\text{eq}} \) of 0.73 eV, in line with what has been reported previously for cells of this size.\textsuperscript{51}

Thus, the majority of error in OF-DFT relative to KS-DFT with a nonlocal pseudopotential originates from use of this local pseudopotential, not from the WGC KEDF. Note, however, that the 0.17 eV discrepancy between the local and nonlocal pseudopotential predictions is within the level of discrepancy often found between different nonlocal pseudopotentials. So it is simply a level of uncertainty associated with using the pseudopotential approximation, whether in OF-DFT or KS-DFT. Nevertheless, we see that OF-DFT with the WGC KEDF yields results as accurate as KS-DFT when the same pseudopotential is used, at least at the equilibrium volume \( V_{\text{eq}} \) of fcc Al.

We next consider whether the OF-DFT approximations cause trouble under severe expansion and compression. Fig. 2 displays the dependence of \( E_{\text{vf}} \) on volume, where a range of ±20% from \( V_{\text{eq}} \) is considered. Again, these calculations compared local pseudopotential KS-LDA and OF-LDA within a 32 lattice site cell. Also shown is the effect of cell size for \( E_{\text{vf}} \) under compression and expansion, by comparing the OF-DFT results for 32 and 256 lattice site cells. We see that OF-DFT and KS-DFT agree extremely well under compression, with a maximum deviation of only 0.1 eV at 120% of \( V_{\text{eq}} \). The maximum deviation in \( E_{\text{vf}} \) between 32 and 256 lattice site cells is 0.04 eV, in line with what has been reported previously for cells of this size.\textsuperscript{51}

### Table 1

<table>
<thead>
<tr>
<th>Method</th>
<th>Vacancy formation energy, ( E_{\text{vf}} )</th>
<th>Vacancy migration energy, ( E_{\text{m}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td>0.67 ± 0.03,\textsuperscript{57} 0.67\textsuperscript{57}, 0.66 ± 0.02\textsuperscript{58}</td>
<td>0.61 ± 0.03,\textsuperscript{57} 0.62,\textsuperscript{59} 0.65 ± 0.06\textsuperscript{60}</td>
</tr>
<tr>
<td>KS-DFT, Nonlocal PSP, LDA, 32 lattice sites</td>
<td>0.73</td>
<td>0.626</td>
</tr>
<tr>
<td>KS-DFT, Nonlocal PSP, GGA, 32 lattice sites</td>
<td>0.54\textsuperscript{a}</td>
<td>0.599</td>
</tr>
<tr>
<td>KS-DFT, Local PSP, LDA, 32 lattice sites</td>
<td>0.506</td>
<td>0.402</td>
</tr>
<tr>
<td>OF-DFT, 32 lattice sites, LDA</td>
<td>0.515</td>
<td>0.396</td>
</tr>
<tr>
<td>OF-DFT, 256 lattice sites, LDA</td>
<td>0.475</td>
<td>0.416</td>
</tr>
<tr>
<td>OF-DFT, 256 lattice sites, GGA</td>
<td>0.387</td>
<td>—</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Data from ref. 52; a 64 lattice site cell and an ultrasoft pseudopotential were employed.
cells is even smaller (0.056 eV). From these tests, we conclude that OF-DFT with a state-of-the-art KEDF can be relied upon to produce results close to Kohn-Sham DFT at all volumes under consideration, and is thus a useful tool with which to study the behavior of vacancies in shocked aluminum.

**Effect of exchange–correlation functional.** As demonstrated above, a 256 lattice site cell converges the OF-DFT $E_{\text{vf}}$ relative to a 500 lattice site cell to within 2 meV at $V_{\text{eq}}$. We therefore employed a 256 lattice site cell to examine the sensitivity of $E_{\text{vf}}$ to the choice of exchange–correlation functional. Fig. 2 shows that the GGA systematically yields a lower $E_{\text{vf}}$ than the LDA. At $V_{\text{eq}}$, the OF-LDA $E_{\text{vf}} = 0.475$ eV while the OF-GGA $E_{\text{vf}} = 0.387$ eV. The consistently lower values obtained with the GGA functional has precedent in earlier KS-DFT calculations. Deviations from recent KS-DFT calculations, ranging from 0.66 to 0.72 eV using LDA and 0.53 to 0.59 eV using GGA, can be attributed to our use of a local pseudopotential, which appears to systematically underestimate $E_{\text{vf}}$ by $\sim 0.2$ eV.

The GGA $E_{\text{vf}}$ are consistently lower by $\sim 0.075$–0.1 eV than those from the LDA, but follow the same trend of $E_{\text{vf}}$ decreasing with lattice expansion and increasing under compression. Carling, et al. argued that vacancies can be regarded as having an internal surface, for which a surface energy correction should be added to $E_{\text{vf}}$. For a single vacancy under zero pressure, this correction was estimated to be 0.15 eV for GGA and only 0.06 eV for LDA. Since GGA underestimates the magnitude of the surface energy more than LDA, the uncorrected LDA results should be considered the more accurate values.

**Vacancy formation enthalpy as a function of pressure.** Experiments measure vacancy formation enthalpies under constant pressure, not vacancy formation energies at constant volume. Transformation of the 256 lattice site OF-DFT constant $V$ data to constant $P$ data by the procedure described earlier produces $E_{\text{vf}}$ at zero external pressure and 0 K of 0.5 and 0.4 eV using OF-LDA and OF-GGA, respectively. The small deviations from $V_{\text{eq}}$ $E_{\text{vf}}$ in Table 1 are due to uncertainties in the Murnaghan equation of state fit; hence we report the $E_{\text{vf}}$ only to an accuracy of 0.1 eV. Differential dilatometry and positron annihilation measurements produce values of 0.67 and 0.66 $\pm 0.02$ eV, respectively. The OF-DFT values appear low by $\sim 0.2$ eV due to the local pseudopotential. However, the experiments are typically performed at high temperatures to have a measurable concentration of vacancies, while the quantum mechanics corresponds to 0 K. Empirical potential molecular dynamics simulations indicate that the vacancy formation enthalpy decreases by $\sim 0.08$ eV as the temperature decreases from the melting point to 0 K. Thus, the “measured” vacancy formation enthalpy at 0 K may be estimated roughly as 0.58 eV, suggesting the error due to the local pseudopotential is $\sim 0.1$ eV.

Fig. 3 compares OF-DFT versus KS-DFT and LDA versus GGA vacancy formation enthalpies as a function of pressure. Regardless of the specific data set used, these data (Fig. 2 and Fig. 3) consistently suggest that vacancies become more stable under expansion, even to the point of becoming thermodynamically favorable at $\sim 12\%$ expansion. Conversely, vacancies are unstable under compression. This result is intuitive: as bulk aluminum is pulled apart and all of the metallic bonds are stretched, in order to preserve favorable bond lengths and lattice structure over as much of the structure as possible, atoms reconfigure themselves so that one occupied lattice site is sacrificed to create a vacancy.

**B. Vacancy mobility in bulk aluminium**

As mentioned above, the timescales and feasibility of nano-void formation in bulk metals may be dominated by vacancy mobility in the bulk as the rate limiting step. We now discuss predicted activation energies, pre-exponential factors, and diffusion coefficients for vacancy diffusion in bulk fcc Al at various volumes and pressures, as well as activation energies for vacancy diffusion under non-uniform deformation. Given
that the LDA has been shown above and previously by others to produce more accurate results for Al, in what follows we only discuss DFT-LDA predictions in detail. Table 1 does contain vacancy migration energy ($E_a$) predictions for DFT-GGA, where we see once again by comparison to experiment that the LDA results are more reliable. Hence we do not consider GGA results further.

Nearest-neighbor vacancy migration energy. The vacancy migration energy $E_a$ is determined by a transition state search, where the initial and final states are relaxed structures with one vacancy in sites $a$ and $b$, respectively. We first consider the case where $a$ and $b$ are nearest neighbors. An atom moves from site $b$ to site $a$, during which a vacancy “diffuses” from site $a$ to site $b$ (see Fig. 4).

We first determine the effect of periodic cell size on the migration activation energy at $V_{eq}$. Fig. 5 shows the OF-LDA WGC KEDF vacancy migration energy ($E_a$) for 32, 108, 256, and 500 lattice site cells. The nearest-neighbor migration energies at these sizes were 0.396, 0.414, 0.416, and 0.415 eV, respectively. We therefore conclude that a 108 lattice site cell is sufficient for convergence of $E_a$ to the infinitely dilute limit.

Earlier we assessed errors in $E_{vf}$ due to using OF-DFT; we now assess errors in the same manner for $E_a$. Again, due to the expense of KS-DFT, we employ a 32 lattice site periodic cell. Judging by the results above, we expect that this small cell will produce finite size effect errors of $\sim 0.02$ eV. At $V_{eq}$, the $E_a$s predicted by local pseudopotential OF-LDA and KS-LDA are in excellent agreement: 0.396 and 0.402 eV, respectively. However, KS-LDA using the nonlocal pseudopotential yields $E_a = 0.626$ eV at $V_{eq}$. An earlier KS-LDA calculation with a different nonlocal pseudopotential predicted 0.57 eV, illustrating the degree of uncertainty engendered by different nonlocal pseudopotentials. Nonlocal pseudopotential KS-LDA results are closest to the measured value of $0.61 \pm 0.03$ eV (see Table 1). The close agreement between KS and OF DFT results using the same local pseudopotential, and the discrepancy between nonlocal and local pseudopotential KS-DFT values, again demonstrates that the main source of error ($\sim 0.2$ eV) is due to the local pseudopotential, and not our choice of KEDF.

Given these benchmarks, we conclude that migration energy calculations using OF-LDA with the WGC KEDF on 108 lattice site cells will converge the migration energies in terms of the model but may systematically underestimate $E_a$ by $\sim 0.2$ eV. These conclusions guide what is reported below.

Beyond isolated vacancy mobility, we also examined how $E_a$ changes in the presence of nearby vacancies. OF-LDA in a 500 lattice site cell (fully converged cell size for two vacancies) predicts that a nearby vacancy (a third nearest-neighbor) enhances the mobility of a vacancy by consistently lowering $E_a$ by $\sim 0.05$ eV over the entire volume range we consider above. This suggests that once vacancies start to aggregate, the rate of aggregation may be autocatalytic.

As in the case of $E_{vf}s$, we also recast $E_a$ in terms of constant pressure. At zero external pressure and 0 K, we predict migration enthalpies of 0.40 and 0.41 eV, respectively, from local pseudopotential OF-LDA and KS-LDA, again confirming the quality of the WGC KEDF. The trend followed for OF and KS LDA is the same: tensile loads (negative pressures) lower the vacancy migration barrier, while compressive loads (positive pressures) raise it. These data lend themselves to a simple interpretation. As the lattice expands, the reaction path becomes less crowded, decreasing the activation energy, and vice versa.

Next-nearest-neighbor vacancy migration energy. We also considered the possibility of next-nearest-neighbor (nnn) vacancy migration within OF-LDA. At $V_{eq}$, the nnn vacancy
$E_a$ is predicted to be 1.38 eV in a 32 lattice site cell and 1.57 eV in both 108 and 256 lattice site cells, suggesting a converged nnn $E_a$ of ~1.6 eV. Since this barrier is much higher than the barrier for nearest-neighbor vacancy migration, nnn vacancy migration is not likely to occur at appreciable rates and therefore the effect of expansion and compression on nnn vacancy migration was not investigated.

**Uniaxial expansion and compression.** So far we have only considered uniform deformations (hydrostatic pressure). However, metals under shock loading conditions are likely to undergo non-uniform deformations, and in particular, uniaxial deformations may be of specific relevance.

To investigate the effect of uniaxial loading on vacancy diffusion, we consider how $E_a$ changes under expansion and compression along the [001] direction ($z$-axis in Fig. 7). Since uniaxial loading breaks the crystalline symmetry, $E_a$ will no longer be equal in all directions. For example, diffusion within the (001) plane, such as in the [110] direction, will differ from other nearest-neighbor directions. Fig. 8 displays the effect of uniaxial compression and expansion on $E_a$, where a 256 lattice site periodic cell is sufficient for $E_a$ convergence to within ~0.05 eV.

Upon compression along [001], we predict that it becomes more difficult to diffuse along the [110] direction, but easier to diffuse along [101]. This makes sense physically, since compression along [001] brings lattice sites in the [101] direction closer together, so exchange of atoms (or vacancies) becomes easier. At the same time, atoms from layers above and below squeeze the empty spaces between lattice sites in the [110] direction, and the exchange of atoms between these lattice sites become very difficult. Diffusion in both directions become easier as we expand along the [001] direction, with preference given to the [110] direction as steric effects from atomic layers above and below are removed.

**The diffusion coefficient.** We now turn our attention to calculating the diffusion coefficient for vacancies in bulk aluminium, given by

$$D = D_0 \exp \left( -\frac{E_a}{k_B T} \right)$$

(12)
where $D_0$ is the pre-exponential factor, $E_a$ is the vacancy migration energy, $k_B$ is the Boltzmann constant and $T$ is the temperature. $D_0$ can be obtained from

$$D_0 = \frac{d^2}{6 \pi \eta \nu_0 \exp \left( \frac{S^M}{k_B} \right)} \quad (13)$$

Here $d$ is the jump distance (the nearest-neighbor distance), $z$ is the number of nearest-neighbor sites, $\nu_0$ is the jump frequency, and $S^M$ is the migration entropy. Generally, $S^M$ is so small that the exponential is often taken to be unity, as we will do here. The jump frequency, the frequency of an atom successfully diffusing into a vacancy, may be calculated via the following harmonic transition state theory approximation

$$\nu_0 = \frac{3N}{2 \pi \lambda^2} \prod_i \nu_i^{\text{GS}}$$

$$\times \prod_i \nu_i^{\text{TS}}$$

which is the product of all vibrational frequencies of the ground state divided by the product of the real vibrational frequencies of the transition state.

Jump frequency $\nu_0$ and pre-exponential factor $D_0$. We again benchmark OF-LDA against local pseudopotential KS-LDA for jump frequency predictions. Due to the expense of including many nearest neighbors in the Hessian matrix, we first include only the moving atom (later we discuss results obtained with more moving atoms). Using the 32 lattice site periodic cell, we again find excellent agreement between KS and OF DFT, where jump frequencies at $V_{eq}$ are predicted to be $3.93 \times 10^{12}$ s$^{-1}$ and $3.89 \times 10^{12}$ s$^{-1}$ for OF-LDA and KS-LDA, respectively. These values are close to a previous estimate by Sandberg et al., who predicted a jump frequency of $2.69 \times 10^{12}$ s$^{-1}$ using an embedded atom method potential.

The jump distance, $d$, is calculated as the distance between the relaxed endpoints of the vacancy migration minimum energy path. Then, using the jump frequency in eqn (13), we obtain the pre-exponential factor, $D_0$. For a 32 lattice site periodic cell at $V_{eq}$, we obtain $D_0 = 5.93 \times 10^{-3}$ cm$^2$ s$^{-1}$ from KS-LDA and $D_0 = 5.87 \times 10^{-3}$ cm$^2$ s$^{-1}$ from OF-LDA, suggesting once again that the OF-DFT predictions are reliable.

We next tested the sensitivity of jump frequency to periodic cell size and Hessian dimension within OF-LDA. We find that a 108 site cell is sufficient, exhibiting no change in jump frequency with respect to a 256 site cell. However, since the atomic masses are all equivalent in bulk aluminium, the atoms are strongly coupled. We observe a qualitative difference (a factor of $\sim 1.6$) when the jump frequency is obtained from a Hessian based only on the diffusing atom compared to a Hessian constructed from the diffusing atom and its nearest neighbors. Tests at $V_{eq}$ suggest that jump frequencies from a 12-atom force constant matrix (the moving atom and 11 nearest neighbors) is well-converged compared to including second and third nearest neighbors, and remains converged with respect to cell size. Using OF-LDA with a 108 site cell and displacements of 12 atoms to define the force constant matrix, we obtain $\nu_0 = 6.11 \times 10^{12}$ s$^{-1}$ and $D_0 = 9.0 \times 10^{-3}$ cm$^2$ s$^{-1}$.

Fig. 9 exhibits how uniform expansion and compression affects the jump frequency $\nu_0$ and the pre-exponential factor $D_0$, calculated with OF-LDA in a 108 lattice site cell, using 12 moving atoms to define the Hessian. $\nu_0$ increases with compression and decreases slightly with expansion. Again, this is intuitive: as the lattice expands, the force constants at both the transition state and the minimum decrease due to anharmonicity. However, since the atoms are forced to be closer together in the transition state, the force constants decrease more slowly than for the energy minimum as the lattice expands. This leads to an overall decrease (increase) in $\nu_0$ as the lattice expands (compresses). Also shown is the effect of compression and expansion on $D_0$, which has an additional dependence on the jump distance, $d$, which increases with expansion and decreases with compression, leading to a change in curvature of the dependence of $D_0$ on volume.

The diffusion coefficient $D$. Fig. 10 displays the overall diffusion coefficient $D$ as a function of the expansion and compression, accounting for the effect of deformation on both $D_0$ and $E_a$. Additionally, since we determined a systematic error of 0.2 eV in the predicted $E_a$ due to the local pseudopotential, we present a best estimate of $D$ as it varies under compression and expansion and as a function of temperature, by adding a 0.2 eV correction to each OF-LDA $E_a$. At room temperature, the corrected room temperature diffusion coefficient predicted by OF-LDA varies from $4.61 \times 10^{-17}$ to $1.76 \times 10^{-11}$ cm$^2$ s$^{-1}$.

Fig. 9 Jump frequency and pre-exponential factor as a function of uniform expansion and compression from OF-LDA with the WGC KEDF in a 108 lattice site periodic cell.
under 20% compression to 10% expansion, respectively, with a value of 3.83 \( /C2 \cdot 10 /C0 \cdot 13 \text{cm}^2 \cdot s /C0 \cdot 13 \) predicted at \( V_{eq} \) and room temperature. Thus, the overall diffusion is greatly enhanced by expansion.

We also display (lower panels) diffusion coefficients calculated with an activation energy defined as \( Q = E_{vf} + E_a \), which is appropriate in the case where vacancy formation is coupled directly to the diffusion event. Both the uncorrected OF-LDA (WGC KEDF) values are given, as well as values for \( Q \) corrected upward by 0.2 eV for the error in \( E_a \) noted above and upward by 0.1 eV for the error in \( E_{vf} \). It is clear from these contour plots that vacancy diffusion is facilitated by temperature and expansion, and that vacancy diffusion drops rapidly with temperature and compression.

C. Vacancy–vacancy interactions

Now that we have quantified the stability and mobility of isolated vacancies in bulk aluminium and verified that OF-DFT performs as well as KS-DFT provided a high quality KEDF is used, we next use OF-DFT to examine how vacancies may aggregate to form nanovoid nuclei under shock conditions.

Divacancy formation energies. We first examine nearest-neighbor (nn) and next-nearest-neighbor (nnn) divacancy clusters, which are likely the first species to form in nucleation of a nanovoid. Similar to the definition of the monovacancy formation energy (eqn (6)), the divacancy formation energy \( E_{vf2} \) can be expressed as

\[
E_{vf2} = E(N - 2, 2, \frac{N - 2}{N} V) - \frac{N - 2}{N} E(N, 0, V) \tag{15}
\]

Table 2 displays structurally relaxed divacancy formation energies in a 256 site periodic cell within OF-LDA (GGA) at \( V_{eq} \). nn divacancies cost 1.043 (0.875) eV to form, while nnn divacancies are easier to form, at a cost of 0.895 (0.720) eV. These values are converged with respect to cell size to within \( \pm 0.02 \text{ eV} \), as the \( E_{vf2} \)s in an 864 site cell were 1.029 (0.858) eV for nn and 0.883 (0.705) eV for nnn, respectively, within LDA (GGA). Generally, under uniform expansion and compression, \( E_{vf2} \) follows the same trends as \( E_{vf} \) (Fig. 11). Regardless of which exchange–correlation functional is employed, nn \( E_{vf2} \)s are consistently higher than nnn \( E_{vf2} \)s, consistent with divacancy binding energies discussed next.

Divacancy binding energies. The divacancy binding energy \( E_b \) allows us to assess the feasibility of the first step of vacancy aggregation. We define it as the energy to form a divacancy from two isolated monovacancies, under constant volume conditions.

\[
E_b = 2E(N - 1, 1, V) - (E(N - 2, 2, V) + E(N, 0, V)) \tag{16}
\]

In contrast to vacancy formation energies, it is not necessary here to scale the volume in vacancy-containing terms, since both the volume and the number of atoms in the initial state
(a bound divacancy) and the final state (two isolated vacancies) remain constant.

A positive $E_b$ means that forming a divacancy from two monovacancies is energetically favorable; i.e., it costs energy to separate the vacancies. At $V_{207}^{\infty}$, OF-DFT (WGC KEDF) $E_{b}$s are predicted to be negative for nn’s, $-0.086$ eV ($-0.091$ eV), but positive for nnn’s, $0.062$ eV ($0.063$ eV) within the LDA (GGA). These binding energies calculated for 256 lattice site cells are converged to within $0.003$ eV with respect to a 864 site cell. Thus, we predict that nn divacancies are unstable relative to two isolated monovacancies, but nnn divacancies are (barely) stable. This result is consistent with previous KS-DFT predictions by Carling and Kaxiras, $12$ all of which found an unstable nn divacancy (divacancy binding enthalpies ranging from $-0.05$ to $-0.07$ eV with LDA and $-0.07$ to $-0.08$ eV with GGA) using cell sizes of 80–108 sites. Our OF-DFT nnn $E_{b}$s agree with the KS-DFT predictions of Uesugi et al., both of which are an order of magnitude larger than Carling et al.’s predictions.$^{52,53}$ The results of Uesugi, et al. are probably more accurate, since they used a larger number of $k$-points.$^{62}$

The curious prediction of an unstable nn divacancy was explained nicely by Carling et al. The negative $E_b$ can be understood in terms of the tendency of the atoms in the first shell around a vacancy to form directional bonds with each other. These localized bonds stabilize the monovacancy. Forming a nn divacancy requires the breaking of these bonds, which costs energy, while forming a nnn divacancy is less disruptive. This nn instability appears to be specific to the peculiar properties of aluminium, as it is not found, e.g., in magnesium. $^{62}$ It is encouraging that our OF-DFT recovers KS-DFT results so well, even for this special case.

Experiments measure a positive divacancy binding energy (see Table 2) although it is not known if this is a nn or nnn divacancy. The experiments typically extract the binding energy of a divacancy by assuming that the enthalpy of formation of a divacancy is not temperature-dependent, leading to a positive $E_b$. $^{44,45,66}$ Carling et al.$^{53}$ showed that if the temperature dependence of the formation enthalpy (due to anharmonicity of the lattice vibrations) is accounted for, the experimental data cannot rule out a negative divacancy binding free energy, even at the melting point. Another interpretation of the experimental data has been proposed by Lu and Kaxiras, $^{12}$ whose KS-DFT calculations suggest that if hydrogen is trapped within aluminium vacancies, the bonding around the monovacancy is sufficiently disrupted that nn divacancy formation in aluminium becomes energetically favorable. Thus, either hydrogen impurities or a temperature-dependent formation enthalpy (positive at high temperatures, negative at low temperatures) could reconcile the experimental data with the seemingly contradictory theoretical predictions at 0 K. On the other hand, it could simply be that the experiments are detecting nnn divacancy clusters rather than nn, with the difference in magnitude of $E_b$ attributable to the temperature dependence noted above.

Recently, Gavini et al. considered $E_{b}$s in Al with a new quasi-continuum OF-DFT code.$^{67}$ After calculating the relaxed $E_b$ for effective system sizes of $n = 4$, 32, 256, 2048, 16348, and one million effective lattice sites, they obtained negative nn $E_{b}$s for $n = 4$ and 32, but positive nn $E_{b}$s (indicating a bound divacancy) for cells containing 256 lattice sites and greater. They concluded that the negative nn $E_b$ was a finite-size effect, providing a potential niche for their approach to obtaining results at large cell sizes. However, instead of using the WGC KEDF, they used a Thomas–Fermi + 1/6 von Weizsacker (TF + 1/6 VW) KEDF. This functional does not recover any known physical limits, such as that of the linear

---

**Table 2.** Divacancy formation and binding energies (eV) at the equilibrium bulk volume determined by KS-DFT, OF-DFT, and experiment. OF-DFT data utilized the WGC KEDF and a 256 lattice site periodic cell. ref.$^{52}$ used a 80 lattice site cell, while refs.$^{12}$ and 62 used a 108 lattice site cell; all literature values used nonlocal pseudopotentials

<table>
<thead>
<tr>
<th>Exchange-correlation</th>
<th>Nearest-neighbor divacancy</th>
<th>Next-nearest-neighbor divacancy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KS-DFT</td>
<td>OF-DFT</td>
</tr>
<tr>
<td>Formation energy</td>
<td>LDA</td>
<td>+1.48$^{,53}$ +1.49$^{62,u}$</td>
</tr>
<tr>
<td></td>
<td>GGA</td>
<td>+1.19$^{,33}$</td>
</tr>
<tr>
<td>Binding energy</td>
<td>LDA</td>
<td>−0.07$^{52}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>−0.06$^{12}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>−0.05$^{62}$</td>
</tr>
<tr>
<td></td>
<td>GGA</td>
<td>−0.08$^{52}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>−0.07$^{12}$</td>
</tr>
</tbody>
</table>

$^a$ Derived from data presented in ref. 62.

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**Fig. 11.** OF-DFT divacancy formation energy as a function of uniform expansion and compression in a 256 lattice site periodic cell.
response of the electron gas either at the low-q or the high-q limit.\textsuperscript{68}

The question therefore arises: is the turnover in the sign of the $E_b$ in their computations truly due to size dependence, and therefore a model artifact, or simply a side effect of using a poor KEDF? In order to determine this, we performed calculations of the relaxed $E_b$ within OF-LDA using both the TF + $1/6$ VW and the WGC KEDFs for $n = 4, 32, 128, 256, 500,$ and $864$ lattice sites (see Fig. 12). It is clear from the figure that while the sign of $E_b$ flips for the TF + $1/6$ VW KEDF and converges rather quickly to a positive value as the system size increases, the $E_b$ determined with the more accurate and physically well-founded WGC KEDF\textsuperscript{26} converges to the expected negative value as the system size increases (small differences up to $\sim 0.08$ eV between Fig. 12 and the graph in ref. 67 are due to differences in calculation details, but the comparison remains valid). The positive $E_b$ found by Gavini et al. was due to their poor choice of KEDF and not a size effect. Indeed, the sign change occurs simply going from 4 to 32 lattice sites, with only small changes occurring for cells larger than 32 sites. This is not surprising either, because studying a divacancy in a 4 site cell is grossly unphysical, given that this corresponds to a state of matter with 50% vacancies. Indeed, contrary to ref. 67’s conclusions it is evident from Fig. 12 that the size-converged solution is obtained very quickly, once the vacancy concentration is reduced to $\sim 5\%$ (32 site cell), thereby obviating the need for such large cell sizes as claimed in ref. 67. This is also not surprising, given that both the electronic and structural perturbations due to a divacancy die off very quickly (one to a few lattice sites away). Therefore, although their concept of coarse-graining OF-DFT is certainly worthy of pursuit, meaningful results must await the implementation of a more reliable KEDF and suggestions of a significant size dependence to the divacancy binding energy are incorrect.

Lastly, a look at the behavior of $E_b$ under expansion and compression of a size-converged 256 site cell (Fig. 13) shows that nn divacancies are predicted to be stable at all volumes, whereas nn divacancies are unstable at 0 K except perhaps at very extreme expansions and compressions. Further, both types of divacancies gain stability under both expansion and compression at low temperatures, suggesting that shock waves will indeed promote vacancy aggregation.

**Trivacancies.** If nn divacancies are unstable, yet nnn divacancies are stable, what will be the preferred structure of trivacancies formed from a nnn divacancy? Fig. 14 depicts the eight possible types of trivacancies. These trivacancy clusters were carved out of 500 lattice site periodic cells ($5 \times 5 \times 5$ 4-atom cubic unit cells of fcc Al). The energies discussed below are converged with respect to an 864 lattice site ($6 \times 6 \times 6$ cubic unit cells of fcc Al) periodic cell to within 0.05 eV throughout the range of compression and expansions studied. At $V_{eq}$, the trivacancy formation energies (defined analogously to the divacancy formation energies) show that type H is the most stable, followed in order by types G, F, E, C, B, D, A (see Table 3). This ordering is as one might expect, given that nn divacancies are unstable: as the number of nn divacancy pair interactions within the trivacancy cluster increases, the stability of the trivacancy decreases. Thus, the instability of the nn divacancy appears to hold for larger vacancy clusters as well.

The relative stability of these trivacancy clusters as function of expansion and compression is shown in Fig. 15. Clearly, the most stable trivacancy throughout much of the volume range is type H, where vacancies are lined up in a linear chain of nnns (see Fig. 14H). Type G, also comprised of only nnns, is also quite stable, consistent with the favored pairwise binding

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig12.png}
\caption{Nearest-neighbor divacancy binding energies for the TF + $1/6$ VW and WGC KEDFs as a function of cell size in periodic OF-LDA calculations.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig13.png}
\caption{OF-LDA (WGC KEDF) divacancy binding energies using a 256 lattice site periodic cell, as a function of uniform expansion and compression. Left: Nearest-neighbor divacancies. Right: Next-nearest-neighbor divacancies.}
\end{figure}
of nnn divacancies. Type C (2 nn + 1 nnn) trivacancies are predicted to be favored under high compression.

Interestingly, type A trivacancies (3 nn), are the most favorable states under compression. This is correlated with the energy discontinuity located at $V_{eq}$. This discontinuity was traced to a sudden shift of one of the atoms next to the trivacancy as the volume decreases. This atom moves into the middle of the void comprising the trivacancy, resulting in a sudden lowering of the energy (Fig. 16). A similar effect was predicted for Cu using empirical potentials, where it was speculated that this type of relaxation should occur in larger vacancy clusters on {111} planes whenever an atom finds itself above such a trivacancy configuration.69

Although this configuration may have a role in the mechanism of void formation in aluminium, it is hard to imagine how this state could be created without first accessing an unstable nn divacancy. To our knowledge, the only previous theoretical study of trivacancies in aluminium were done by Lu and Kaxiras,12 in which they studied type A vacancy clusters, and they also found these clusters to be unfavorable with respect to isolated single vacancies.

We henceforth concern ourselves primarily with trivacancies that can be created sequentially from a stable nnn divacancy.

The trivacancy binding energy at constant volume is

$$E_{3b} = (E(N - 2, 2, V) + E(N - 1, 1, V)) - (E(N - 3, 3, V) + E(N, 0, V))$$  (17)

Five of the eight possible trivacancies can be reached from a nnn divacancy: types C, E, F, G, and H. As Table 3 displays,
the binding energies at $V_{eq}$ follow the same trend as the formation energies, with the linear chain of nnn vacancies (type H) the most stable.

The binding energies for these trivacancies as a function of uniform expansion and compression are shown in Fig. 17. Again, this shows nnn vacancy pair interactions are preferred under most conditions (types G and H), except at very high compressions when the type C trivacancy ($2\text{ nn} + 1\text{ nnn}$) becomes stable.

**Higher vacancy clusters.** One may continue this strategy to study larger vacancy clusters. OF-LDA (WGC KEDF) on tetra-vacancy clusters at $V_{eq}$ indicate that the most favorable way to add another vacancy to the most stable trivacancy (type H) is by adding another nnn vacancy to the end of the linear chain. A nnn vacancy perpendicular to the chain is also favorable, though less so than the linear chain, just as in the trivacancy case. All tetra-vacancies that result from adding a nn vacancy to a type H trivacancy are unstable. We see every reason to conclude that this trend will continue to larger vacancy clusters, and that larger vacancy clusters will continue to grow through next-nearest neighbors. One may speculate that, when a certain saturation of nnn vacancies is reached, the energetics may change to allow a nanovoid (containing nn vacancies) to form. However, a plausible mechanism for this transformation awaits future simulations.

### 4. Summary

In this work, we employed a linear-scaling first principles quantum mechanics method to predict the energetics of vacancy cluster formation as well as vacancy diffusion kinetics in bulk aluminium, under compression and expansion to mimic shock conditions that may induce ductile fracture. We first benchmarked our technique, orbital-free density functional theory (OF-DFT) with a state-of-the-art kinetic energy density functional (KEDF) against the more accurate Kohn-Sham (KS) DFT, for prediction of vacancy formation and migration energies, as well as for prediction of the diffusion coefficient. Errors due to the local pseudopotential approximation were found to be $<0.2$ eV, while errors due to this choice of KEDF were negligible. Use of a local pseudopotential lowers both the vacancy formation energy $E_{vf}$ and the migration energy $E_a$ by $0.1–0.2$ eV. OF-DFT and KS-DFT predict the same trends for $E_{vf}$ under compression (increases) and expansion (decreases). We therefore conclude that OF-DFT yields reliable predictions provided an accurate KEDF is employed. We also confirmed that the LDA for electron exchange and correlation produces a better physical description of aluminium than does the GGA, which is not surprising given the nearly-free-electron-like nature of aluminium. In the end, measured values for the vacancy formation and migration energies ($\sim 0.67$ and $\sim 0.6$ eV, respectively) are reproduced to within $0.2$ eV for OF-LDA using the WGC KEDF in a 256 site periodic cell (0.48 eV and 0.42 eV, respectively).

Asymptotic values of all properties were obtained by examining their dependence on simulation cell size, thereby eliminating finite size artifacts. Such studies are only possible at this point using OF-DFT, due to its computational efficiency. As a general rule, single vacancy properties need only a 108 site periodic cell for convergence, while di- and tri-vacancy properties require 256 and 500 site cells, respectively. For single vacancy formation and migration energies, a 108 site cell is sufficient for convergence to $\sim 8$ and $\sim 1$ meV,
respectively. Divacancy formation and binding energies are converged to 20 and 3 meV, respectively, in a 256 site cell. Finally, trivacancy formation energies require a 500 site cell to converge to within 50 meV.

Given these verification studies, we then characterized [with OF-LDA, a state-of-the-art KEDF (the WGC KEDF), and converged periodic cell sizes] the energetics and kinetics of isolated vacancy formation and migration, as well as the beginning states of vacancy aggregation under shock loading conditions (compression and expansion). The activation energy for diffusion between nn sites decreases under uniform expansion and increases under uniform compression, signifying that both vacancy formation and mobility are enhanced under expansion that may occur in the wake of a shock. Vacancy migration between nnn sites was excluded due to the high activation barriers predicted. Uniaxial loading along the [001] direction produces preferred directions for nn vacancy migration: under compression, the preferred diffusion path is along [101], while under expansion, the preferred direction is along [110]. Calculated jump frequencies and pre-exponential factors show surprisingly little sensitivity to compression and expansion. The calculated diffusion coefficients illustrate that single vacancy diffusion occurs most easily under expansion and at high temperature.

Finally, we studied the stability of small vacancy clusters. Formation of both nn and nnn divacancy clusters is favorable under uniform expansion. However, throughout the range of ±20% expansion and compression, we find that nn divacancies are unstable with respect to two isolated vacancies, but that nnn divacancies are stable, consistent with earlier KS-DFT predictions. Trivacancies follow this trend, as only trivacancies made up of nnn divacancies are predicted to be stable. With the exception of one exotic trivacancy found under compression, where one atom moves into the center of a trivacancy made up of nn divacancies, the most stable trivacancy throughout most of the range of expansion and compression is a linear trivacancy made up of successive nn vacancies. This trend continues even to tetra-vacancies, and perhaps beyond.

As a result of these studies, we can propose a picture of how nanovoids form in shocked aluminium. Individual vacancies form exothermically in the wake of a shock (under expansion of the lattice). They diffuse via nearest-neighbor sites, with a speed exponentially dependent on the degree of lattice expansion and temperature (the larger the expansion and the hotter the sample, the faster the diffusion). Vacancy aggregation begins with next-nearest-neighbor divacancy formation, with a preference for higher vacancy clusters comprised only of nn vacancy pairs, either as linear chains or as chains bent at right angles. We speculate that such nn vacancy clusters will collapse at some point to form a nanovoid comprised of nn vacancies, perhaps under a successive compressive shock, since we have seen that only under high compression can nn vacancies be formed.

Of course, in reality, the presence of dislocations, grain boundaries, and other defects will add complexity to the picture of ductile fracture that ultimately emerges. This work represents only a modest step toward elucidating the mechanism of shock-induced nanovoid nucleation in simple metals.

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