

## First-Principles Calculation of Self-Diffusion Coefficients

M. Mantina, Y. Wang, R. Arroyave,\* L. Q. Chen, and Z. K. Liu

*Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, USA*

C. Wolverton

*Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, USA*

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We demonstrate a first-principles method to compute all factors entering the vacancy-mediated self-diffusion coefficient. Using density functional theory calculations of fcc Al as an illustrative case, we determine the energetic and entropic contributions to vacancy formation and atomic migration. These results yield a quantitative description of the migration energy and vibrational prefactor via transition state theory. The calculated diffusion parameters and coefficients show remarkably good agreement with experiments. We provide a simple physical picture for the positive entropic contributions.

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Diffusion is responsible for many different materials processes. While accurate first-principles calculations have been possible for the energetics of crystalline solids at zero temperature (for recent reviews, see [1–3]), it is considerably more challenging to predict kinetic coefficients such as atomic mobility or diffusivity at finite temperatures, which involve unstable transition states. In this Letter, we demonstrate a quantitatively accurate method to predict atomic diffusivity as a function of temperature via first-principles calculations within the framework of transition state theory.

One of the most common means of atomic diffusion in crystalline solids is via the vacancy mechanism. Conceptually, it can be broken down into two separate processes: (i) vacancy formation and (ii) vacancy-atom exchange. The macroscopic diffusion coefficient can then be written in terms of microscopic parameters, i.e., the atomic jump distance and jump frequency. For example, for a cubic crystal [4],

$$D = a_0^2 C_v \Gamma, \quad (1)$$

where  $a_0$  is the lattice parameter,  $\Gamma$  is the successful atom jump frequency, and  $C_v$  is the vacancy concentration. The equilibrium  $C_v$  at a given temperature  $T$  is given by

$$C_v = \exp(\Delta S_f^{\text{vib}}/k_B) \exp(-\Delta H_f/k_B T), \quad (2)$$

where  $\Delta H_f$  and  $\Delta S_f^{\text{vib}}$  are the enthalpy and vibrational entropy of vacancy formation.

According to transition state theory (TST) [5,6], the jump frequency  $\Gamma$  in Eq. (1) may be written in terms of enthalpy of migration  $\Delta H_m$  and an effective frequency  $\nu^*$  as  $\Gamma = \nu^* \exp(-\Delta H_m/k_B T)$ , where

$$\nu^* = \prod_{i=1}^{3N-3} \nu_i / \prod_{j=1}^{3N-4} \nu'_j. \quad (3)$$

In Eq. (3),  $\nu_i$  and  $\nu'_j$  are the normal vibrational frequencies

at the equilibrium and transition states, respectively, for a system of  $N$  atoms and one vacancy. The product in the denominator specifically excludes the frequency corresponding to the unstable mode at the transition state.

From Eqs. (1)–(3), we see that an entirely first-principles calculation of self-diffusion coefficient  $D$  would require the computation of the equilibrium lattice parameter  $a_0$ , the enthalpy of vacancy formation and atom migration, and the vibrational entropy of vacancy formation as well as the effective frequency  $\nu^*$ . Previous work on the calculation of temperature-dependent self-diffusion coefficients has either adopted (semi)empirical approaches [7–10] or computationally demanding classical and *ab initio* molecular dynamics simulation techniques [11–13].

Here we describe a first-principles procedure to calculate all the quantities entering the self-diffusion coefficient. We illustrate this approach for the well-studied case of self-diffusion in Al. We calculate the enthalpy and entropy of vacancy formation, the energetics of atomic migration, and the vibrational properties of atomic configurations along the migration path. In addition, via the quasiharmonic approximation, we also consider the role of thermal expansion. We show that an entirely first-principles calculated self-diffusion coefficient for fcc Al matches well with experimental and computational data available in the literature in terms of activation energy, diffusion prefactor, and the thermodynamics of vacancy formation.

For our first-principles calculations, we use the projector augmented wave potentials [14,15] as implemented in the highly efficient Vienna *ab initio* simulation package (VASP) [16]. Results using both the local density approximation (LDA) [17] and the generalized gradient approximation (GGA) [18] for the exchange correlation are examined and compared. Tests indicate that a Monkhorst-Pack  $k$ -point mesh of  $11 \times 11 \times 11$ , an energy cutoff of 300 eV, and 32-atom supercells are sufficient to yield converged migration barriers within 0.01 eV for this system. To quantitatively

determine the transition state, we use the nudged elastic band method [19].

Upon creating a vacancy, a small amount of effective “internal surface” is created in the material. The commonly used GGA and LDA functionals underestimate this surface energy, and a method was recently proposed [1,20,21] to compute the corresponding correction terms. For Al, within GGA (LDA), we incorporated the surface correction terms of 0.15 eV (0.06 eV) for the vacancy formation energy and 0.05 eV (0.02 eV) for the migration energy [12,20].

The normal phonon frequencies are calculated using the direct force-constant approach [22], as implemented in the Alloy Theoretic Automated Toolkit (ATAT) [23] package. The same energy cutoff and  $k$ -point mesh sizes as for the total energy calculations are used for the vibrational calculations. The contributions to the free energy from the normal phonon frequencies are obtained through conventional harmonic equations [24]. The electronic contributions to enthalpy and entropy are found to be negligible for Al at the temperatures of interest.

To elucidate the effects of thermal expansion on the various factors entering the diffusion coefficient, we calculated results for both harmonic and quasiharmonic approximations (HA and QHA). In the QHA we calculated the free energies for three different volumes, with lattice parameters differing by 2%. The free energy and the equilibrium volume at a given temperature were determined by finding the minimum along the free energy curve as a function of volume by means of interpolation.

In Table I we compare our first-principles results for vacancy formation enthalpy and entropy, migration barrier, and vibrational prefactor, with previous calculations and experimental measurements. In all cases, our first-principles results are in excellent agreement with experimental data. We also note that our first-principles vibrational prefactor calculated from Eq. (3) is in excellent agreement with the calculation of Sandberg, Magyari-Kope, and Mattsson [12], who used molecular dynamics and a density functional theory fitted embedded atom potential.

To examine the physics of the vacancy formation entropy in more detail, we use the following approximate decomposition of the formation entropy, motivated by previous attempts [32,33], to understand the formation entropy of impurities in Al (in this case, “impurity” is either a vacancy or a migrating atom in the transition state):

$$\Delta S = \Delta S_{\text{imp}}^e + \Delta S_{\text{NN}} + \Delta S_{\text{vol}} \quad (4)$$

where  $\Delta S_{\text{imp}}^e$  is an “Einstein-like” contribution due to the vibration of the impurity atom. For the present case, the impurity is the vacancy, and so this term is zero.  $\Delta S_{\text{NN}}$  is the effect on the vibrations of the surrounding Al atoms caused by the breaking of Al—Al bonds to introduce the vacancy. It yields a positive contribution since the Al atoms surrounding a vacancy feel “softening” of their bonds to the vacancy compared to the Al—Al bond. These atoms will have lower vibrational frequencies for modes in the direction of the vacancy.  $\Delta S_{\text{vol}}$  is a “volumelike” effect on the vibrations of the surrounding Al atoms, which is negative due to contraction of the Al—Al bonds near a vacancy. However, this volume term is overwhelmed by  $\Delta S_{\text{NN}}$  and leads to a positive vacancy formation entropy. This can be seen in Fig. 1 from the increased density of lower frequency modes and a decreased density of high frequency modes for Al with vacancy compared to pure Al.

Next, we turn to the phonon density of states (DOS) for the transition state (TS). An atom in the TS allows for much “empty space” for several of the surrounding Al atoms, and hence will lead to a lowering of the frequencies of most of these modes. On the other hand, the atom in the TS is very close to some neighboring Al atoms and will cause high vibrational frequencies associated with the modes involving these closely spaced Al—Al pairs. Note that in Fig. 1 the phonon DOS for the TS bears out these qualitative arguments: The main low-frequency portion of the DOS is shifted to lower frequencies than either pure Al or the Al vacancy (corresponding to the “open space” associated with the TS), whereas there is a small peak at very high frequencies (corresponding to the closely spaced Al—Al vibrations). But, the first of these two effects

TABLE I. First-principles calculated quantities entering calculation of self-diffusion coefficient. We give HA results from current work, using GGA and LDA (with “surface” corrections), and compare to other calculated and experimental data. Data for  $\Delta H_m$  in “experimental” column are deduced from experimental values for  $Q$  from [25–29] using  $\Delta H_f = 0.67$  eV.

Diffusion parameter	Computational		Experimental
	GGA	LDA	
$\Delta H_f$ (eV)	0.70	0.77	0.67 [30]
	0.69 [20]	0.76 [20]	$0.67 \pm 0.03$ [31]
$\Delta S_f$ ( $k_B$ )	1.18	1.21	1.1 [30]
	1.1 [20]	1.2 [20]	0.7 [31]
$\Delta H_m$ (eV)	0.57	0.60	0.81, 0.64, 0.61,
	$0.60 \pm 0.02$ [12]		$0.66, 0.58 \pm 0.03$
$\nu^*$ (THz)	19.3	16.6	
	22.6 MP/EA [12]		

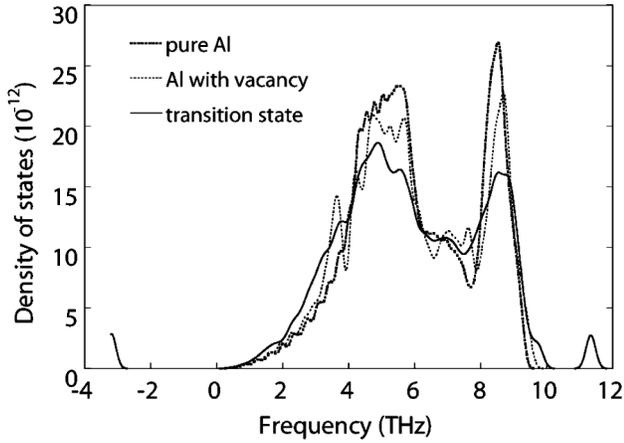


FIG. 1. First-principles (GGA) calculated phonon DOS of defect-free fcc Al, Al with a single vacancy, and Al with the diffusing atom in the transition state. The negative frequencies in phonon DOS of TS are due to the unstable mode.

dominates, as evidenced by the fact that the value of  $\nu^*$  is large compared to the frequency of any other mode of the initial state. From this one can conclude that  $\nu^*$  effectively gives a positive “entropiclike” contribution to migration.

Using the calculated enthalpy and entropy of vacancy formation, we compare the first-principles calculated equilibrium vacancy concentration versus experiment as a function of temperature in Fig. 2. The agreement is excellent, particularly for the GGA calculations. We note that inclusion of the entropic contribution to vacancy formation (which increases the vacancy concentration by a factor of  $\sim 3$ ) is crucial towards obtaining this quantitative agreement with experiment.

To compare with the experimental results of tracer diffusion, we have multiplied the self-diffusion coefficients obtained from Eq. (1) by a correlation factor  $f$ , equal to 0.7815 [34] for fcc lattice. These results from the HA and QHA plotted as a function of temperature are illustrated in

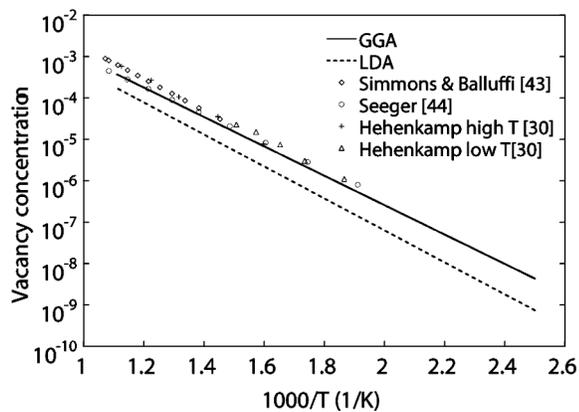


FIG. 2. Equilibrium vacancy concentration from first-principles (LDA and GGA quasiharmonic calculations) plotted in comparison with experimental data [30,43,44]. The experimental results of Seeger [44] are from monovacancies only.

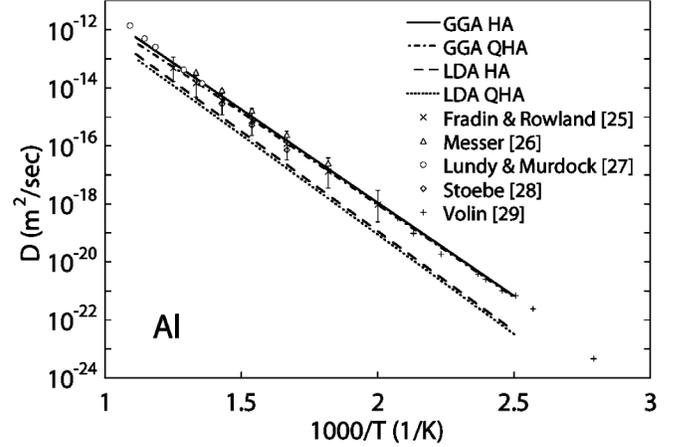


FIG. 3. Complete first-principles calculation results of self-diffusion coefficients for Al. Results are shown for both the HA and QHA using both LDA and GGA. Calculated results are compared with experimental results [25–29].

Fig. 3. From the figure we see that the self-diffusion coefficients from static first-principles calculations, specifically from GGA, have an excellent match with the experimental measurements. The tracer diffusion coefficient from Eq. (1) can be written in the form  $D = D_0 \exp(-Q/k_B T)$ , where  $D_0 = f a_0^2 \nu^* \exp(\Delta S_f^{ib}/k_B)$  and  $Q = \Delta H_f + \Delta H_m$ . In Table II, we compare the diffusion prefactor  $D_0$  and activation energy  $Q$  from the present work with experimental data. This result is quite encouraging when one considers that the calculations did not involve any adjustable parameters.

The diffusion coefficients from HA and QHA are very similar, indicating that the anharmonic effect of thermal expansion on diffusion for Al is negligible, at least within the confines of the quasiharmonic approximation. In the QHA, while we observe a slightly higher temperature dependence of enthalpies of vacancy formation and migration compared to HA, there are negligible anharmonic effects on the diffusion coefficients: the temperature dependences of the enthalpies and entropies are seen to al-

TABLE II. Comparison between first-principles and experimental diffusion prefactor  $D_0$  and activation energy  $Q$ . The temperatures represent the ranges over which diffusion coefficients were fit to extract  $D_0$  and  $Q$ . In this table we give the first-principles values for  $D_0$  and  $Q$  from harmonic approximation that are largely independent of temperature.

Studies	$D_0$ (m <sup>2</sup> /s)	$Q$ (eV)	$T$ (K)
Current GGA	$7.75 \times 10^{-6}$	1.27	
Current LDA	$6.6 \times 10^{-6}$	1.37	
Experimental [25]	$3.5 \times 10^{-6}$	1.25	500–800
Experimental [26]	$1.37 \times 10^{-5}$	1.28	550–750
Experimental [27]	$1.71 \times 10^{-4}$	1.48	720–920
Experimental [28]	$1 \times 10^{-5}$	1.33	600–700
Experimental [29]	$1.76 \times 10^{-5}$	1.31	360–480

most cancel each other. Moreover, the enthalpy of vacancy formation decreases by 3.2% ( $\sim 1\%$ ) as temperature increases from 400 to 900 K in GGA (LDA) while the corresponding enthalpy of migration increases by 2.5% ( $\sim 0.5\%$ ) in GGA (LDA). (The differing trend from that in [12] is mostly due to the explicit anharmonic effects not included in this work.) Therefore, in QHA also, like HA, the activation enthalpy ( $Q = \Delta H_f + \Delta H_m$ ) for diffusion is less sensitive to temperature. Such negligible anharmonic effects for closely packed crystals has been previously suggested by Franklin [35].

We note that the classical TST has been criticized in the past for the assumption of thermodynamic equilibrium between the equilibrium and activated states. Dynamical theories [36] were proposed to circumvent this assumption. However, Glyde [37] and others showed that the dynamic theories were essentially equivalent to TST as defined by Vineyard (TST-V). The accuracy of TST-V was recently confirmed by fully dynamical simulations [12,38,39]. Furthermore, predictions of diffusion parameters in crystalline phases (bulk [12,40,41] and surface [42]) using TST-V yielded results in good agreement with experiments. However, it is important to note that anharmonic contributions to vibrational DOF were not included in the original Vineyard theory. Nevertheless, due to near cancellation of anharmonic effects in most cases, we expect the predictions from TST-V to agree well with measured quantities, as also suggested by Harding [38].

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\*Current address: Department of Mechanical Engineering and Materials Program, Texas A&M University, College Station, TX 77843, USA.

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