

A first-principles approach to transition states of diffusion

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2012 J. Phys.: Condens. Matter 24 305402

(<http://iopscience.iop.org/0953-8984/24/30/305402>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 146.186.211.66

The article was downloaded on 01/04/2013 at 21:21

Please note that [terms and conditions apply](#).

A first-principles approach to transition states of diffusion

M Mantina¹, Y Wang¹, R Arroyave², S L Shang¹, L Q Chen¹ and Z K Liu¹

¹ Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA

² Department of Mechanical Engineering and Materials Program, Texas A&M University, College Station, TX 77843, USA

E-mail: yuw3@psu.edu

Received 1 May 2012, in final form 19 June 2012

Published 6 July 2012

Online at stacks.iop.org/JPhysCM/24/305402

Abstract

We propose a first-principles approach for treating the unstable vibrational mode of transition states in solid-state diffusion. It allows one to determine a number of fundamental quantities associated with the transition state, in particular the enthalpy and entropy of migration and the characteristic vibrational frequency, along with their temperature dependences. Application to pure face centered cubic Al shows good agreement with available experimental measurements and previous theoretical calculations. The procedure is further applied in calculations of the migration properties of Mg, Si and Cu impurities in Al, and the differences among Mg, Si and Cu are discussed.

(Some figures may appear in colour only in the online journal)

Atomic diffusion is a common and important non-equilibrium process in solids that takes place at finite temperatures. It is the primary mechanism for mass transfer involved in processes ranging from precipitation reactions in alloys to incorporation of dopants in semiconductors. Several previous works [1–5], including our work [3, 4, 6, 7], have been focused on predicting self-diffusion and impurity diffusion coefficients using the transition state theory and first-principles calculations. In this work, we present the microscopic diffusion parameters such as enthalpy and entropy of migration and characteristic vibrational frequency from first-principles in comparison to other theories and experiments. An attempt is made to understand the effect of solute atom on diffusion properties.

According to the atomic theory [8] of diffusion, the magnitude of tracer/impurity diffusion coefficients, D , in a solid through the vacancy mechanism is determined by two fundamental microscopic parameters: C_v —the vacancy concentration adjacent to a tracer/impurity atom and w —the tracer/impurity atom jump frequency, with $D = 1/6fr^2ZC_vw$, where f is a correlation factor, r the jump distance and Z the number of nearest neighboring sites. Prediction of C_v or w as a function of temperature has been carried out through

first-principles calculations [3, 4, 6, 7]. Specifically in our previous works [3, 4, 6, 7], atom jump frequency w has been determined in a straightforward manner from transition state theory [3, 4, 6, 7]. However, computing the constituent dynamic properties, such as the entropy of migration and characteristic vibrational frequency, that are important for understanding the fundamental physics of the atomic jump, is more challenging.

The jump frequency is typically written as [9]

$$w = \nu^* \exp\left(-\frac{\Delta H_m^*}{k_B T}\right), \quad (1)$$

where ν^* is an effective frequency and ΔH_m^* is the enthalpy of migration. ν^* can be calculated as the quotient of the product of the vibrational frequencies of the initial state (IS) to that of the frequencies of transition state, excluding all imaginary frequencies of the transition state (TS) [4, 10].

The present work focuses on the long outstanding physical concept of entropy of migration ΔS_m by Vineyard [10], noticed by many previous works [1, 5, 11–17], to a lesser extent on ΔH_m . According to Vineyard [10], $\nu^* = \tilde{\nu} \exp(\Delta S_m/k_B)$ with $\tilde{\nu}$ representing the characteristic vibrational frequency of the migration atom in the system.

We notice that the calculations of $\tilde{\nu}$, ΔS_m , and ΔH_m in equation (1) have been difficult due to the fact that they are associated with TS which is an unstable state with the migrating atom at the saddle point. Previously, classical/*ab initio* dynamical simulations have been used [5, 12, 13, 16] to obtain their values, while few other studies involved simple approximations [1, 11, 17–19].

Directly computing microscopic diffusion parameters involving an unstable transition state is fundamentally challenging. In defining the thermodynamic properties of migration resulting from reversibly taking a system in initial state to transition state, a constant number of degrees of freedom needs to be maintained [20]. Due to the instability of the transition state the thermodynamic properties of this state are defined with one fewer degree of freedom (DOF) compared to the initial state.

Vineyard [10], in defining the entropy of migration, maintained the initial and transition states to have the equal number of DOF by imposing a constraint whereby both states are prevented from oscillating along the direction (in momentum space) parallel to the diffusion direction. Van Vechten [21] followed another approach through the ballistic model (BM) of atom migration in which the diffusing atom hopping across the saddle point is considered to move ballistically, with the vibrational modes of the hopping atom at the saddle point replaced by translational modes. Attempts had also been made to estimate the values of entropy of migration using the ballistic model, by Dobson *et al* [22] and Wager [23] who considered only modes related to the migrating atom, neglecting any change in the vibrational behavior of atoms neighboring the activated atom–vacancy pair. This can be problematic when trying to extend the formalism to impurity-containing systems, as in such cases, differences between the radii of the migrating and host atoms can lead to significant vibrational effects.

In this work, we propose to explicitly treat the vibrational mode in the diffusion direction as the integral component of both initial and transition states. The free energy contribution of this particular vibration mode, \tilde{F} , is defined from statistical mechanics as

$$\tilde{F} = -k_B T \ln \tilde{Z}, \quad (2)$$

where \tilde{Z} is the partition function from the energy states accessible to the diffusing atom in the diffusion direction. In order to obtain \tilde{Z} , we construct a double-well potential by projecting the potential energy landscape along the diffusion direction as the migrating atom hops from its initial position to a neighboring vacancy. The lost DOF at the transition state is then recovered by adding the free energy contribution due to the vibrational mode in the diffusion direction back to the system. We therefore treat, $\tilde{\nu}$, the characteristic vibrational frequency of the migration atom as [6]:

$$\tilde{\nu} = k_B T / h \tilde{Z}. \quad (3)$$

The atom migration properties are determined after including the vibrational contributions from all the atoms in the system. Hence our procedure can be directly extended to systems containing impurities, with the temperature dependences of

these individual quantities computed. As far as we are aware, this work represents the first attempt to accurately determine atom jump frequencies as well as temperature-dependent migration properties directly from first-principles. We here illustrate the procedure for the well-studied case of fcc Al.

For our first-principles calculations, we use the projector augmented wave (PAW) potentials [24, 25]. Both the local density approximation (LDA) [26] and the generalized gradient approximation (GGA) [27] are examined for pure Al. Tests indicated that a Monkhorst–Pack k -point mesh of $11 \times 11 \times 11$ and an energy cutoff of 300 eV are sufficient to yield converged migration barriers within 0.01 eV for these systems. We obtain similar convergence of the energetics calculated using supercells with 32 and 64 atoms. Hence, a supercell with 32 lattice sites ($2 \times 2 \times 2$ conventional fcc cells) is employed. All configurations are completely relaxed with respect to internal coordinates, volume and shape. To quantitatively determine the transition state, we use the nudged elastic band (NEB) method [28] as implemented in the highly efficient Vienna *ab initio* simulation package (VASP) [29].

The phonon frequencies are calculated using the supercell approach [30], as implemented in the alloy theoretic automated toolkit (ATAT) [31] package. The total free energy is calculated using the equation:

$$F(T, V) = E_c(V) + k_B T \sum_q \sum_j \ln \left\{ 2 \sinh \left[\frac{h \nu_j(q, V)}{2 k_B T} \right] \right\}, \quad (4)$$

where $E_c(V)$ stands for the 0 K static energy, and $\nu_j(q, V)$ represents the frequency of the j th phonon mode at wavevector q and volume V . The summation j is over the stable vibrational modes of the system, excluding the unstable modes [6, 32]. The entropy and enthalpy are computed from the free energy through the standard thermodynamic relations. In the harmonic approximation (HA), the free energies are calculated at the fixed 0 K equilibrium volume, while in the quasi-harmonic approximation (QHA), the free energies are determined by finding the minima along curves of free energy as a function of volume by means of interpolation at given temperatures.

To calculate \tilde{Z} , we first determine the double-well potential, as illustrated in figure 1, describing motion of the diffusing atom along the diffusion direction over the entire diffusion path. System geometries with the diffusing atom at intermediate positions along the diffusion path are relaxed with respect to volume and shape (atomic positions are not relaxed in order to avoid the displacements of the atoms to equilibrium positions). The potential thus obtained is scaled to the barrier height resulting from NEB calculations to compensate for incomplete relaxations. The resulting double-well potential is identical to the potential diagram from NEB for the path between the two equilibrium positions, as can be seen in figure 1. The Hamiltonian of this double-well potential is numerically solved to get the eigen-energies, ε_i , a procedure described in a previous work for treating phonon instabilities in bcc Zr [33]. From these eigen-energies we

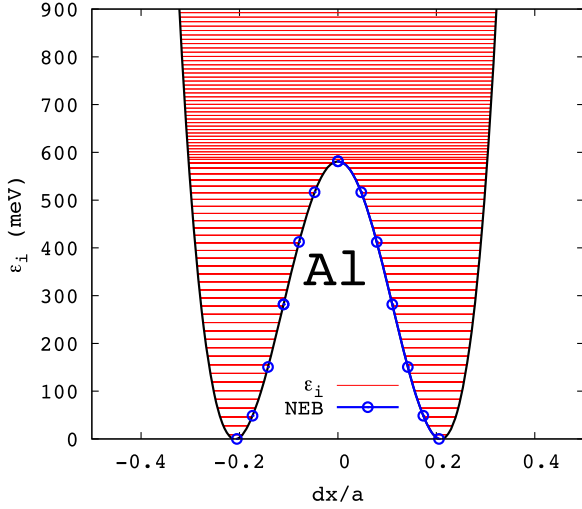


Figure 1. First-principles calculated double-well potential representing the motion of the diffusing atom from its equilibrium lattice position to adjacent equilibrium position that is vacant. The discrete energy states of this potential are also illustrated in the figure. The minimum energy path between the two equilibrium positions obtained from NEB method is also plotted.

obtain \tilde{Z} as a function of temperature from the equation:

$$\tilde{Z} = \sum_i \exp\left(\frac{-\varepsilon_i}{k_B T}\right). \quad (5)$$

Enthalpy and entropy of the vibrational mode in the diffusion direction, \tilde{H} and \tilde{S} , can be obtained from this partition function. Consequently, the enthalpy and entropy of migration are calculated by the following equations:

$$\begin{aligned} \Delta H_m &= H_{TS}^* - H_{IS} + \tilde{H} = \Delta H_m^* + \tilde{H} \\ \Delta S_m &= S_{TS}^* - S_{IS} + \tilde{S} = \Delta S_m^* + \tilde{S}, \end{aligned} \quad (6)$$

where H_{TS}^* and S_{TS}^* represent the enthalpy and entropy calculated at the transition state from equation (4) with the unstable model excluded, and H_{IS} and S_{IS} are the enthalpy and entropy calculated at the initial state under the HA. The net DOF on the right-hand side of equation (6) is thus zero, providing a solution to the problem that the HA cannot numerically handle the contribution of the unstable phonon mode to any required thermodynamic quantities. The jump frequency in equation (1) can thus be re-written as

$$w = \tilde{\nu} \exp\left(-\frac{\Delta H_m - T \Delta S_m}{k_B T}\right). \quad (7)$$

For impurity migration properties, the present calculations are only conducted within LDA without considering surface correction [34]. Surface-correction values have been estimated for few pure elements [35], but are not available for systems with impurities. Unlike GGA, fortunately, energetics from LDA have small error associated [36].

Our results of migration properties obtained from the harmonic approximation for pure Al are tabulated in table 1 in comparison with other values reported in the literature. We see that our results, in terms of the enthalpy of migration, and the

Table 1. Results from the harmonic approximation of the current work on fcc Al in comparison with other calculated and critically analyzed experimental data with ν^* deduced from the diffusion prefactor D_0 .

Method	ΔH_m (eV)	ΔS_m (k_B)	$\tilde{\nu}$ (THz)	ν^* (THz)
Current GGA	0.52	2.53	2.10	26.5
Current LDA	0.58	2.28	2.26	22.1
BM [23]	0.72	2.68	8.3	121.5
cB Ω [37]	0.71	2.99	6.8	135
EAM/MP [5]	0.61			22.6
Exp [40]	0.61 ± 0.03			26.0

effective frequency ν^* obtained using double-well potential, are in very good agreement with the data from experiments and dynamical simulations. We would like to draw attention towards our prediction of entropy of migration, that matches well with the prediction from other computational works in the literature [23, 37] (discussed earlier). To our knowledge there is no existing study that attempted to determine the value of characteristic vibrational frequency $\tilde{\nu}$, although existing predictions for ν^* and ΔS_m confirm the prediction for $\tilde{\nu}$ from the current work.

Within HA the thermodynamics of atom migration processes are found to be nearly constant with temperature. Within QHA, due to the varying thermal expansion coefficients of the initial and transition states, the enthalpies and entropies of migration vary with temperature. In the case of Al these temperature dependences are seen to be small, about 3% from the Debye temperature to close to the melting temperature, and the resulting tracer jump frequencies found to be similar to the harmonic case. Therefore for calculating migration properties of impurities in Al only harmonic approximation is adopted.

Predicted migration properties for impurities Mg, Si and Cu in Al along with data deduced from solute diffusion measurements are tabulated in table 2. It can be seen that the predicted data is in the same range as experimental data. Existing discrepancies could be due to comparison to experimental data coming from measurements over small temperature range at high temperatures. The value of ν^* calculated using Vineyard's theory is compared to the prediction from double-well approach in table 3. Inaccurate result of ν^* from Vineyard's theory is because it involves two approximations: (i) high temperature limit with constant vibrational frequencies and (ii) considering only the phonons at wavevector equal to zero to obtain individual vibrational frequencies in the supercell. From Wert and Zener [9], the more accurate definition of the effective frequency is based on the comparison of the partition function of the system in initial state without restraint on the solute atom and the partition function of the system in transition state with the solute atom constrained from moving along the diffusion direction (one degree of freedom less) [6]. We note that the partition functions should be calculated using the all phonon frequencies along all wavevector direction. Our calculated effective frequencies are supported (see table 1) by the work of Sandberg *et al* [5].

Table 2. Migration properties of impurity atoms in fcc Al, calculated from the harmonic approximation using LDA potential in comparison with experimental ΔH_m deduced from the activation energy Q , and ν^* deduced from diffusion prefactor D_0 using the vacancy–solute binding enthalpy and entropy from critically analyzed experimental data [41], assuming negligible effects of correlation.

Diffusion parameter	Tracer	ΔH_m (eV)	ΔS_m (k_B)	$\tilde{\nu}$ (THz)	ν^* (THz)
Current (LDA)	Mg	0.42	2.74	1.54	23.85
	Si	0.55	2.59	1.41	18.8
	Cu	0.57	1.90	0.94	6.29
Experimental	Mg	0.67 ± 0.12 [42],			18.4 [42],
		0.61 ± 0.09 [43]			$12.1^{+13}_{-6.7}$ [43]
	Si	0.69 ± 0.03 [44],			0.85 [44],
		0.64 ± 0.03 [45]			$0.96^{+0.14}_{-0.14}$ [45]
	Cu	0.73 ± 0.16 [46],			13.2^{+46}_{-10} [46],
		0.68 ± 0.22 [47]			$5.88^{+20.5}_{-4.6}$ [47]

Table 3. Effective frequency ν^* (THz) using LDA from double-well approach compared to Vineyard’s transition state theory [9].

Migrating atom	Double-well		Vineyard’s TST
	$T = 400$ K	$T = 900$ K	
Al (HA)	22.06	22.2	16.6
Al (QHA)	20.47	21.4	14.4
Mg (HA)	23.85	24.9	18.6
Si (HA)	18.8	18.2	15.7
Cu (HA)	6.32	6.25	4.03

We attempt to understand the physical factors influencing the values of enthalpy and entropy of migration and characteristic vibrational frequency of different impurities in Al. Based on a previous first-principles work by Wang *et al* [38], the size of Mg, Si and Cu atoms in an fcc lattice is in the order of $r_{Mg}(1.6 \text{ \AA}) > r_{Si}(1.39 \text{ \AA}) > r_{Cu}(1.28 \text{ \AA})$. We see that the enthalpy of migration (listed in table 2) is smaller for impurity with a larger size and vice versa. To understand this behavior in the energetics, we study the relaxed configurations. Large Mg solute ($r_{Al} = 1.43 \text{ \AA}$) is seen to move towards the vacancy ($\sim 0.12 \text{ \AA}$) pushing apart its nearest neighboring Al atoms adjacent to vacancy in the initial state itself, resulting in lower barrier for migration. Si atom exhibits similar behavior, but to a smaller extent ($\sim 0.04 \text{ \AA}$), thus experiencing higher barrier for migration than Mg. Small Cu solute is seen to be pushed away from the vacancy ($\sim 0.03 \text{ \AA}$) with the nearest neighboring Al atoms adjacent to vacancy coming closer together, requiring much higher energy to migrate.

To understand the trend of the entropy of migration and characteristic vibrational frequency that are based on the vibrational frequencies in the system, we study the force constants in the transition and initial states. Force constants obtained in the present work, for the first and second nearest neighbors to the impurity, indicate greater (lesser) bond softening on movement of larger (smaller) solute atom to the saddle point. Change in vibrational frequency described by $\Delta\nu = \sqrt{\Delta k / \sqrt{m_{Al}m_{imp}}}$ [39] is seen to be of the same order as change in force constants (Δk): $\Delta\nu_{Mg} > \Delta\nu_{Si} > \Delta\nu_{Cu}$. Larger decrease in the vibrational frequency on migration causes higher positive entropy of migration. It is observed here that the larger the solute atom size, the greater is its

entropy of migration. But as the change in frequency involves effects of both mass (m_{imp}) and force constants (k) of the solute atom, this trend could alter in other cases. However, the newly developed ability to compute these fundamental microscopic quantities, as demonstrated in this work, allows one to understand the effects of various physical factors of a solute atom on its diffusivity in a given solvent.

In summary, we developed a first-principles approach to treat the unstable transition state of diffusion. Our proposed double-well approach allowed determination of enthalpy and entropy of migration and characteristic vibrational frequency as a function of temperature, for self-diffusion and impurity diffusion. This contributes towards accurate prediction of jump frequencies and thus diffusion coefficients. From the current study the insufficiency of Vineyard’s description of ν^* is also demonstrated.

Acknowledgments

This work was supported financially by the Office of Naval Research (ONR) under the contract number of N0014-07-1-0638 in the United States managed by Dr David Shifler, DOE Basic Sciences under Grant No. DOE DE-FG02-07ER46417 (Yi Wang and Chen), and in part supported by instrumentation funded by the National Science Foundation through grant OCI-0821527. Calculations were also conducted at the National Energy Research Scientific Computing Center, which is supported by the Office of Science of the US Department of Energy under Contract No. DE-AC02-05CH11231.

References

- [1] Blöchl P E, Van de Walle C G and Pantelides S T 1990 *Phys. Rev. Lett.* **64** 1401
- [2] Janotti A, Kremar M, Fu C L and Reed R C 2004 *Phys. Rev. Lett.* **92** 085901
- [3] Mantina M, Wang Y, Arroyave R, Wolverton C, Chen L Q and Liu Z K 2008 *Phys. Rev. Lett.* **100** 215901
- [4] Mantina M, Wang Y, Chen L Q, Liu Z K and Wolverton C 2009 *Acta Mater.* **57** 4102
- [5] Sandberg N, Magyari-Kope B and Mattsson T R 2002 *Phys. Rev. Lett.* **89** 065901
- [6] Mantina M, Chen L Q and Liu Z K 2009 *Defects and Diffusion, Theory and Simulation: An Annual Retrospective I* ed D J Fisher (Stafa-Zurich: Trans Tech Publications) p 1

- [7] Mantina M, Shang S L, Wang Y, Chen L Q and Liu Z K 2009 *Phys. Rev. B* **80** 184111
- [8] Peterson N L 1978 *J. Nucl. Mater.* **69/70** 3
- [9] Wert C and Zener C 1949 *Phys. Rev.* **76** 1169
- [10] Vineyard G H 1957 *J. Phys. Chem. Solids* **3** 121
- [11] Adams J B 1989 *J. Mater. Res.* **4** 102
- [12] Blöchl P E, Smargiassi E, Car R, Laks D B, Andreoni W and Pantelides S T 1993 *Phys. Rev. Lett.* **70** 2435
- [13] Boisvert G, Mousseau N and Lewis L J 1998 *Phys. Rev. B* **58** 12667
- [14] Frank W, Elsasser C and Fahnle M 1995 *Phys. Rev. Lett.* **74** 1791
- [15] Krcmar M, Fu C L, Janotti A and Reed R C 2005 *Acta Mater.* **53** 2369
- [16] Milman V, Payne M C, Heine V, Needs R J, Lin J S and Lee M H 1993 *Phys. Rev. Lett.* **70** 2928
- [17] Neumann G 1987 *Phys. Status Solidi b* **144** 329
- [18] Krcmar M, Fu C L, Janotti A and Reed R C 2005 *Acta Mater.* **53** 2369
- [19] Frank W, Breier U, Elsasser C and Fahnle M 1996 *Phys. Rev. Lett.* **77** 518
- [20] Rice S A 1958 *Phys. Rev.* **112** 804
- [21] Van Vechten J A 1975 *Phys. Rev. B* **12** 1247
- [22] Dobson T W, Wager J F and VanVechten J A 1989 *Phys. Rev. B* **40** 2962
- [23] Wager J F 1991 *Phil. Mag. A* **63** 1315
- [24] Blöchl P E 1994 *Phys. Rev. B* **50** 17953
- [25] Kresse G and Joubert D 1999 *Phys. Rev. B* **59** 1758
- [26] Ceperley D M and Alder B J 1980 *Phys. Rev. Lett.* **45** 566
- [27] Perdew J P, Burke K and Wang Y 1996 *Phys. Rev. B* **54** 16533
- [28] Henkelman G and Jonsson H 2000 *J. Chem. Phys.* **113** 9978
- [29] Kresse G and Furthmüller J 1996 *Phys. Rev. B* **54** 11169
- [30] Wei S and Chou M Y 1992 *Phys. Rev. Lett.* **69** 2799
- [31] Van de Walle A, Asta M and Ceder G 2002 *CALPHAD* **26** 539
- [32] Eyring H 1935 *J. Chem. Phys.* **3** 107
- [33] Wang Y, Ahuja R, Qian M C and Johansson B 2002 *J. Phys.: Condens. Matter* **14** L695
- [34] Mattsson A E, Schultz P A, Desjarlais M P, Mattsson T R and Leung K 2005 *Modelling Simul. Mater. Sci. Eng.* **13** R1
- [35] Carling K, Wahnstrom G, Mattsson T R, Mattsson A E, Sandberg N and Grimvall G 2000 *Phys. Rev. Lett.* **85** 3862
- [36] Mantina M 2008 *A First-Principles Methodology for Diffusion Coefficients in Metals and Dilute Alloys* (Dissertation: Pennsylvania State University)
- [37] Varotsos P A and Alexopoulos K D 1986 *Thermodynamics of Point Defects and Their Relation with Bulk Properties* vol 14 (Amsterdam: North-Holland)
- [38] Wang Y, Curtarolo S, Jiang C, Arroyave R, Wang T, Ceder G, Chen L Q and Liu Z K 2004 *CALPHAD* **28** 79
- [39] Van de Walle A and Ceder G 2002 *Rev. Mod. Phys.* **74** 11
- [40] Erhart P, Jung P, Schultz H and Ullmaier H 1991 *Atomic Defects in Metals* ed H Ullmaier (Berlin: Springer)
- [41] Balluffi R W and Ho P S 1973 *Diffusion* (Metals Park, OH: American Society for Metals) p 83
- [42] Moreau G, Cornet J A and Calais D 1971 *J. Nucl. Mater.* **38** 197
- [43] Verlinden J and Gijbels R 1980 *Adv. Mass Spectrom.* **8A** 485
- [44] Beerwald A H 1939 *Z. Elektrochem. Angew. Phys. Chem.* **45** 789
- [45] Bergner D 1984 *Neue Hutte* **29** 207
- [46] Peterson N L and Rothman S J 1970 *Phys. Rev. B* **1** 3264
- [47] Murphy J B 1961 *Acta Metall.* **9** 563