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# Low temperature diffusivity of self-interstitial clusters in tungsten

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The low temperature diffusivity of nanoscale crystal defects, where quantum mechanical fluctuations are known to play a crucial role, are essential to interpret measurements of irradiated microstructures conducted at cryogenic temperatures. Using density functional theory calculations, quantum heat bath molecular dynamics and open quantum systems theory, we provide a first evaluation of the low temperature diffusivity of self interstitial atom clusters in tungsten. Due to an exceptionally low defect migration barrier, our results show that interstitial defects exhibit very high diffusivity of order  $10^3 \mu\text{m}^2\text{s}^{-1}$  down to temperatures of 1K.

The microstructure of an irradiated crystal is a highly complex, correlated ensemble of intrinsic and extrinsic lattice defects, evolving via elastic interactions and stochastic thermal agitations on multiple timescales[1]. A popular strategy to reduce the spectrum of timescales present when analyzing irradiated microstructures is to perform experiments at low temperature, where processes with large migration barriers are frozen out, allowing individual migration or transformation processes to be identified through analysis of the time dependent electrical resistivity following irradiation[2–4]. In addition, transmission electron microscopy studies have used cryogenic temperatures to retard microstructure evolution, allowing direct access to the initial stages of irradiation damage which can be directly compared with atomistic simulations[5, 6].

In order to interpret experiments conducted at cryogenic temperatures it is essential to construct accurate models of defect migration rates in the presence of non-classical thermal fluctuations, which can be broadly classified into three regimes with decreasing temperature[7, 8]. Below the Debye temperature  $T_D$ , zero point motion causes thermal vibrations to be of far greater magnitude than their classical expectation value[9], leading to an effective renormalisation of the classical system temperature. Below some lower crossover temperature  $T_{cross}$ , incoherent ‘shallow-tunneling’ phenomena emerges, where non-classical trajectories at the peak of the migration barrier contribute significantly to the barrier crossing rate[7]. Finally, below some very small decoherence temperature  $T_{coh} \ll T_{cross}$ [10] the system can in principle coherently tunnel between vibrational ground states[11], which becomes the dominant migration mechanism as the system approaches absolute zero.

In this paper we produce an expression for the diffusivity of  $1/2\langle 111 \rangle$  self-interstitial atom (SIA) clusters in body centered cubic tungsten[12–20] valid for all temperatures above approximately 1K. Using density functional theory (DFT) calculations of the single SIA migration barrier we show that  $T_{cross} \simeq 0.6\text{K} \gg T_{coh}$ , meaning that we can ignore all tunneling phenomena above 1K and consider only the effect of zero point fluctuations through the use of quantum heat bath molecular dynamics[21]. The results of our simulations are well captured by a theoretic-

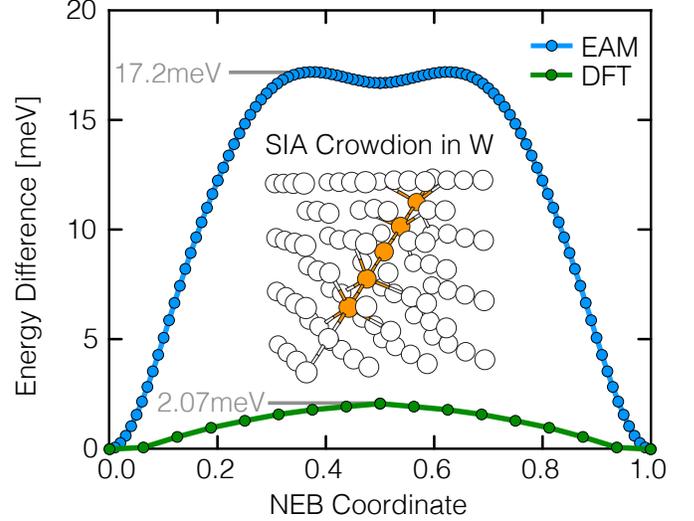


FIG. 1. (Color online) Nudged elastic band (NEB) calculations of the migration barrier for a crowdion defect in tungsten (inset), evaluated with an empirical EAM potential[22] and in DFT calculations.

cal expression derived through the use of open quantum systems theory[11] and previous work by two of us on the coupling of defects and thermal vibrations[13]. Using the DFT migration barrier in our theoretical expression generalized for larger SIA clusters then yields our main result for the low temperature defect diffusivity, which resembles a classical law but for a  $\hbar$  dependent effective temperature that captures all quantum mechanical effects.

Due to the very small defect migration barrier, we find that the low temperature diffusivity remains very high (of the order of  $10^2 \mu\text{m}^2\text{s}$ ) and is effectively constant below 50K. This very high diffusivity is consistent with experimental observations down to 4.2K[2, 3] which find that such clusters remain mobile at all observation temperatures.

## STATIC CALCULATION OF THE CROWDION MIGRATION BARRIER

To accurately determine the migration barrier for a crowdion defect in Tungsten, we performed *ab initio* calculations using the VASP package[23, 24], using the AM05[25] pseudopotential with 12 valence electrons. The simulation supercell contained 129 atoms, with 5x5x5 gamma-point centred k-point grid and a plane-wave energy cutoff of 450 eV. The ion positions and simulation box shape of the 111 crowdion and 111 dumbbell structures were fully relaxed with energy and force convergence at 1e-7 eV and 1e-4 eV/Å. Identifying the start and end point as the crowdion and dumbbell structures, nudged elastic band[26] (NEB) calculations are performed using seven images, with the box shapes fixed and determined via interpolation of the start and end points. We set the energy convergence and force convergence at 1e-7eV and 5e-3eV/Å. After finishing all the calculations, we performed the elastic correction as implemented by Varvenne *et al.*[27] to eliminate the effect of elastic image interactions on the system energy. The results of these calculations are shown in figure 1, along with identical calculations using an embedded atom method (EAM) interatomic potential[28] developed by Marinica *et al.*[22], which we also use for our molecular dynamics simulations. The EAM calculations, in good agreement with other available interatomic potentials[12], gives a very small crowdion migration barrier of 17.2meV. This is consistent with classical molecular dynamics simulations, performed in this work and elsewhere[12, 13], that find crowdions execute free Brownian motion above 150K, as the migration barrier is overwhelmed by thermal agitations. However, as can be seen in figure 1, our DFT calculations yield an even smaller migration barrier of 2.07meV, in agreement with previous *ab initio* based approaches to model this defect[29].

As mentioned above, below a crossover temperature  $T_{cross}$ , non-classical shallow tunneling trajectories emerge as stationary action solutions in an imaginary time path integral evaluation of the defect density matrix[7].  $T_{cross}$  is given by  $T_{cross} \simeq \hbar|\omega_0^s|/2\pi k_B$ , where  $\omega_0^s$  is the unstable frequency at the top of the migration barrier. Using  $\omega_0^s$  extracted from our EAM calculations for a crowdion in tungsten gives  $T_{cross}=1.8K$ , whilst using the migration barrier found in DFT calculations gives  $T_{cross}=0.6K$ . This very low crossover temperature allows us to neglect all tunneling phenomena above  $\sim 1K$  and focus only on the effect of quantum zero point fluctuations on the thermally activated defect motion. In the supplementary material we also provide an estimate of the decoherence temperature, finding  $T_{coh} \simeq 10^{-8}K$ , as expected due to tungsten's large atomic mass. As existing empirical potentials cannot capture the extremely low crowdion migration barrier found in our DFT simulations, the observed defect diffusivities found in our molecular dynamics simulations

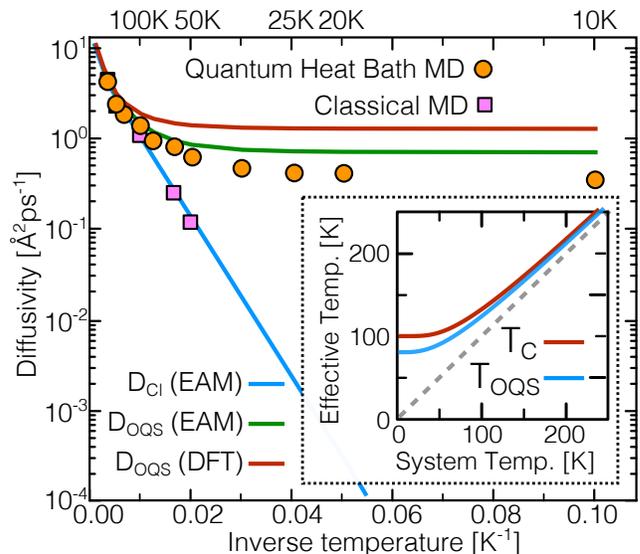


FIG. 2. (Color online) The results from classical and quantum heat bath simulations of crowdion diffusion in tungsten, along with theoretical predictions using our diffusivity  $D_{OQS}$  derived from open quantum systems theory, using the migration barrier found using the EAM potential and in DFT calculations. We also plot the classical diffusivity  $D_{Cl}$  calculated using equation (5) but setting  $T_{OQS} \rightarrow T$ .

must be modified to account for the discrepancy. We return to this point in section XXX, when developing our theoretical treatment of the low temperature diffusion.

## QUANTUM HEAT BATH MOLECULAR DYNAMICS

As tunnelling phenomena can be neglected for system temperatures above  $\simeq 1K$  for the SIA clusters considered here, semi-classical simulations which only retain quantum zero-point motion are adequate to model the low temperature diffusion. To this end, we have implemented the colored noise quantum heat bath proposed by Barrat and Rodney[21] (see supplementary material) in the MD and spin-lattice dynamics program SPILADY[30]. The simulation supercell contained 16001 atoms, with supercell vectors of  $20a[001]$ ,  $20a[010]$  and  $20a[001]$ . The crowdion configuration was structurally relaxed with a conjugate gradients minimization and then thermalized with either a quantum or classical heat bath for 0.1ns. Simulation trajectories were obtained at ten temperatures between 10K and 200K, at intervals of 10K between 10K and 80K, with longer trajectories broken into four independent segments with an independent thermalization process. The quantum heat bath trajectories were all 1ns in length, whilst the classical heat bath trajectories were up to 4ns in length at the lowest temperatures, yielding robust statistical data on the defect diffusivity. The de-

fect position was extracted by first time-averaging over a period of  $\sim 50$ fs, applying a high-pass energy filter to reveal the defect core, then taking the center of mass of the remaining atoms. At lower temperatures, the defect trajectory is characterized by isolated stochastic jumps; in this case, the diffusivity is given by  $D = b^2 N_{\text{jump}} / 2t_{\text{sim}}$ , where  $N_{\text{jump}}$  is the number of defect jumps,  $t_{\text{sim}}$  the total simulation time and  $b$  the jump length between potential minima. At higher temperatures, typically above 150K for the simulations presented here, the defect trajectory exhibits a continuous stochastic motion and the diffusivity  $D = \langle (\delta x)^2 \rangle / 2\delta t$  is calculated through analysis of the mean squared displacement[13].

The simulated defect diffusivities are displayed on Arrhenius plots ( $1/k_B T, \ln D$ ) in figure 2. The diffusivity  $D_{\text{cl}}(T)$  extracted from classical heat bath molecular dynamics clearly exhibit the classical Arrhenius relationship  $\ln |D_{\text{cl}}(T)| = \ln |D_0| - \Delta V / k_B T$  below 100K, with an activation energies  $\Delta V$  of 0.018eV, in very good agreement with the value 0.0172 extracted from static calculations. From previous studies of crowdion motion in bcc metals, it is known that the Arrhenius behavior is known to break down at temperatures above 150K; at high temperature the diffusivity is that of a freely diffusing particle,  $D = k_B T / \gamma$ , where  $\gamma$  is the frictional coupling between the defect and thermal vibrations[12, 13, 20]. However, in contrast to purely classical simulations, the diffusivities  $D_{\text{qu}}(T)$  extracted from quantum heat bath molecular dynamics deviate significantly from the classical law at low temperature, indicating the influence of quantum zero point motion on defect migration.

## THEORETICAL TREATMENT OF LOW TEMPERATURE DEFECT DIFFUSION

We have seen that due to the very low migration barriers found in static calculations, for system temperatures above 10K we are able to neglect all tunneling phenomena, and der In previous work a theoretical and numerical scheme was developed to analyze the thermal vibrations surrounding migrating crystal defects, initially applied to study the phonon drag force[13, 20]. The method uses a defect migration pathway as calculated from a barrier climbing calculations, defining the defect position coordinate  $r$  to be the reaction coordinate along this pathway. By considering possible structural variations along the migration pathway ( $\delta r \in \mathbb{R}$ ) and perpendicular to the migration pathway ( $\mathbf{x} \in \mathbb{R}^{3N-1}$ ) one can show the crystal's potential energy  $V$  can be expanded as

$$V(r + \delta r, \mathbf{x}) = V_0(r + \delta r) + \sum c_k x_k \delta r + \sum_k m \omega_k^2 \frac{x_k^2}{2}, \quad (1)$$

where  $V_0(r)$  is the periodic migration potential shown in figure 1. The vibrational frequencies  $\{\omega_k\}$  and coupling constants  $\{c_k\}$  are related to the Hessian matrix of

second derivatives[13, 20]. The coupling constants  $\{c_k\}$  allow the defect system to be thermalized through interaction with the surrounding thermal vibrations, giving rise (in a classical picture) to a dissipative drag force  $-\gamma \dot{r}$  and a fluctuating thermal force of strength  $\gamma k_B T$ , where the dissipative strength  $\gamma$  can be expressed[13, 20] as a function of the  $\{\omega_k\}$  and  $\{c_k\}$ . We have evaluated the  $c_k$  for a various defects in bcc metals[13, 20], including the crowdion defect considered here; explicit expressions for  $\{\omega_k\}$ ,  $\{c_k\}$  and  $\gamma$  are given supplementary material.

To derive an effective migration rate in the temperature regime of interest, we note that equation (1) is the widely studied 'oscillator bath' Hamiltonian used in the theory of open quantum systems[11], which aims to integrate away the vibrational degrees of freedom  $\mathbf{x}$  to leave an *effective* distribution function for the defect density matrix, which then yields a Fokker-Planck equation for the Wigner quasi-probability function  $W(\delta r, p_r)$ [7, 31]. Expanding the potential around  $r = 0$  to obtain  $V(\delta r) = V(0) + m\omega_0^2(\delta r)^2/2$ , a standard result is that  $W(\delta r, p_r)$  follows the approximate evolution equation[11, 32]

$$\frac{\partial W}{\partial t} = \left( \frac{\partial}{\partial p_r} (m\omega_0^2 \delta r + \gamma p_r) - \frac{p_r}{m} \frac{\partial}{\partial r} + D \frac{\partial^2}{\partial p_r^2} \right) W, \quad (2)$$

where explicit expressions for  $D, \gamma$  are given in the supplementary material. The evolution equation (2) has a steady state distribution  $W_\infty(\delta r, p_r) = Z^{-1} \exp(-[V(\delta r) + p_r^2/2m] \gamma/D)$ , that clearly resembles a classical Gibbs distribution with an effective temperature (see supplementary material)

$$T_{\text{OQS}} \equiv \frac{D}{k_B \gamma} = \frac{\hbar \sum_k c_k^2 \omega_k^{-2} \sin(\omega_k \tau_C) \coth\left(\frac{\hbar \omega_k}{2k_B T}\right)}{2k_B \sum_k c_k^2 \omega_k^{-3} \sin(\omega_k \tau_C)}, \quad (3)$$

where  $\tau_C = 0.05$ ps is the calculated correlation time of the defect force[13]. It is straightforward to show that  $T_{\text{OQS}} \rightarrow T$  at high temperature, but at low temperature  $T_{\text{OQS}}$  tends to a constant value due to zero-point fluctuations. In the inset of figure 2 we compare  $T_{\text{OQS}}$  to the effective 'classical' temperature of a solid state system with normal modes  $\{\omega_k\}$ [9]

$$T_C = \frac{1}{3(N-1)k_B} \sum_{k=1}^{3N-3} \frac{\hbar \omega_k}{2} \coth\left(\frac{\hbar \omega_k}{2k_B T}\right), \quad (4)$$

which can also be evaluated numerically through analysis of the atomic velocities  $T_C = m \langle V^2 \rangle / 3N$ . We see that both effective temperatures show a very similar behavior, with  $T_{\text{OQS}}$  tending to a slightly lower temperature than  $T_C$ . Equations (2) and (3) show that, in the approximation of a harmonic potential well, the coupling of a crystal defect to the surrounding vibrational modes results in an effectively *classical* Fokker-Planck equation (2), with all quantum mechanical effects contained in the  $\hbar$  dependent effective system temperature  $T_{\text{OQS}}$ . Although no

exact result exists for the general non-linear migration potential in the open quantum systems theory setting, an approximate diffusivity  $D_{OQS}$  that accounts for quantum zero point motion can be produced by using the effective temperature  $T_{OQS}$  in the *classical* expression for one dimensional motion in a periodic potential[33, 34]

$$D_{OQS} = \frac{kTb^2/\gamma}{\int_0^b \exp\left(-\frac{F(r)}{k_B T_{OQS}}\right) dr \int_0^b \exp\left(\frac{F(r)}{k_B T_{OQS}}\right) dr} \quad (5)$$

where  $F(r)$  is the free energy of migration, given in the harmonic approximation by

$$F(r) = V_0(r) + k_B T_{OQS} \sum_k \ln |\omega_k| + F_0, \quad (6)$$

where  $F_0$  is a constant term that does not affect our results. When  $k_B T_{OQS}$  is much smaller than the free energy barrier  $\Delta F$ ,  $D_{OQS}$  is given by the well known expression from Kramers transition state theory[33]

$$\lim_{k_B T_{OQS} \ll \Delta F} D_{OQS} = \frac{m\omega_0^g |\omega_0^s|}{\gamma} \left( \prod_{k=1}^{3N-4} \frac{\omega_k^g}{\omega_k^s} \right) \times \exp\left(-\frac{\Delta V}{k_B T_{OQS}}\right), \quad (7)$$

where  $\omega_0^g$ ,  $|\omega_0^s|$  are the frequencies at the ground and saddle point of the static migration potential  $V(x)$ , taken here either from EAM or DFT calculations, whilst the  $\{\omega_k^{o,s}\}_1^{3N-4}$  are the eigenfrequencies at the ground state and saddle state[33], which here we take only from EAM calculations. At effective temperatures such that  $k_B T_{OQS} \gg \Delta F$  we obtain the free diffusion result

$$\lim_{k_B T_{OQS} \gg \Delta F} D_{OQS} = \frac{k_B T_{OQS}}{\gamma}. \quad (8)$$

Equation (5) constitutes our main theoretical result, an expression for the migration rate of a crowdion in a heavy atom system, valid down to temperatures of at least 10K. In figure 2 equation (5) is shown using the migration potential  $V_0(x)$  found using the empirical potential used for the molecular dynamics simulations and DFT calculations. We see that using the migration barrier 17.2meV of the empirical potential,  $D_{OQS}$  is in good agreement with the diffusivity extracted from our quantum heat bath molecular dynamics simulations. When using the much lower migration barrier of 2.07meV from our DFT calculations we find that, as such a small migration barrier is easily overcome by all effective classical temperatures, the diffusivity is essentially identical at all system temperatures to the free diffusion limiting form (8).

### GENERALIZATION TO LARGER SIA CLUSTERS

Whilst we have calculated an accurate diffusion model for single SIA crowdions, irradiated materials will in prac-

tice have a large distribution of SIA cluster sizes[6]. Migration barriers of larger SIA loops have not yet been calculated in DFT calculations due to computational restrictions on the system size; however, from previous classical heat bath molecular dynamics studies of SIA cluster motion in bcc metals, it is known that for larger SIA clusters the migration barrier is to be approximately constant[16, 19], with a prefactor that scales as  $\sqrt{N}$  the square root of the cluster size[19]. In addition, above around 200K the cluster motion exhibits free Brownian motion[20], where  $D = k_B T/\gamma$ , with a friction coefficient  $\gamma$  that also scales as  $\sqrt{N}$ . We have performed classical molecular dynamics simulations of a 7-SIA cluster, using trajectories of upto 94ns at low temperature to obtain statistically robust measurements of the diffusion. We find a migration barrier of around 70meV at low temperature and a friction coefficient of 13meV/Å<sup>2</sup> ps at high temperature. However, as our DFT calculations revealed that the crowdion migration barrier was around 12 of the EAM value; accounting for this discrepancy yields an SIA migration barrier of around 8meV. The effects of such a small migration barrier will be overcome at effective classical temperatures of 50K, allowing us to use the high temperature approximation (8) for the loop mobility. Collating the information from *ab initio* calculations and quantum heat bath molecular dynamics simulations thus gives our main result, the diffusivity of an N-SIA cluster in tungsten

$$D_{OQS}(N) = \frac{k_B T_{OQS}}{2\sqrt{\pi N} \gamma_0}, \quad (9)$$

where  $\gamma_0 = 1.38\text{meV}/\text{\AA}^2 \text{ps}$  and the effective temperature  $T_{OQS}$  is formally given in equation (3). However, for practical purposes we find that the total diffusivity is well approximated by  $D_{OQS}(N) \simeq 176\sqrt{85^2 + T^2}/\sqrt{N} \mu\text{m}^2\text{s}^{-1}$ .

### DISCUSSION

Our main result, equation (9), provides a first calculation of the diffusivity of self interstitial clusters in tungsten, valid down to the cryogenic temperatures used in a wide variety of experiments investigating post irradiation microstructure evolution. Due to the influence of zero point motion, we find that the diffusivity remains very high, of order  $10^3 \mu\text{m}^2\text{s}^{-1}$  for a 100-SIA cluster. This has clear implications for transmission microscopy experiments conducted on 1 – 3 $\mu\text{m}$  in thick foils at low temperatures[5]; using a diffusivity of  $10^3 \mu\text{m}^2\text{s}^{-1}$  we expect clusters to diffuse across the foil thickness in around 0.03s, leading to a likely depreciation in the cluster population even at cryogenic temperatures. Furthermore, the strongly non-Arrhenius behavior of the cluster diffusivity seen in our quantum heat bath simulations implies that attempts to fit classical Arrhenius expressions must be treated with caution, as only

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