Molecular Dynamics Simulations of Hydrogen Diffusion in Aluminum and Palladium

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ABSTRACT

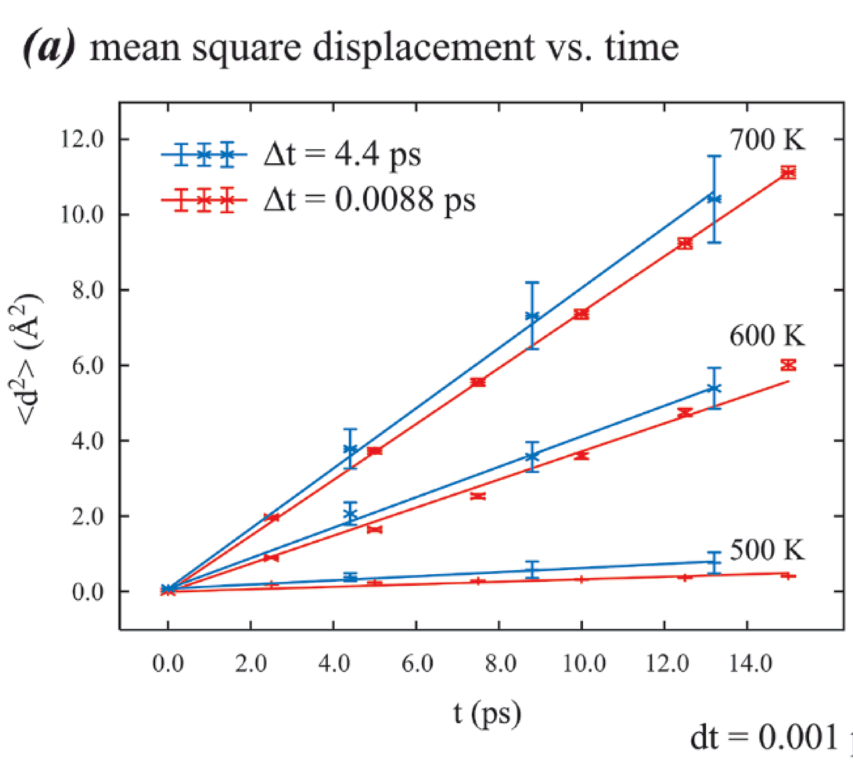
Hydrogen diffusion rates are important for hydrogen storage applications. In atomistic simulations, diffusion energy barriers are usually calculated for each atomic jump path using a nudged elastic band method. Practical materials often involve thousands of atomic jump paths not known a priori. It is also unclear how thousands of energy barriers relate to an overall diffusion behavior seen in experiments. Here we demonstrate that the overall diffusion energy barrier and pre-exponential factor can be accurately determined from Arrhenius equation constructed through molecular dynamics simulations of mean square diffusion distances at different temperatures. This progress will enable complex diffusion problems to be readily and reliably studied in the future. Preliminary application of this method has already begin the elucidate the experimental hydrogen diffusion data in aluminum and palladium.

Method

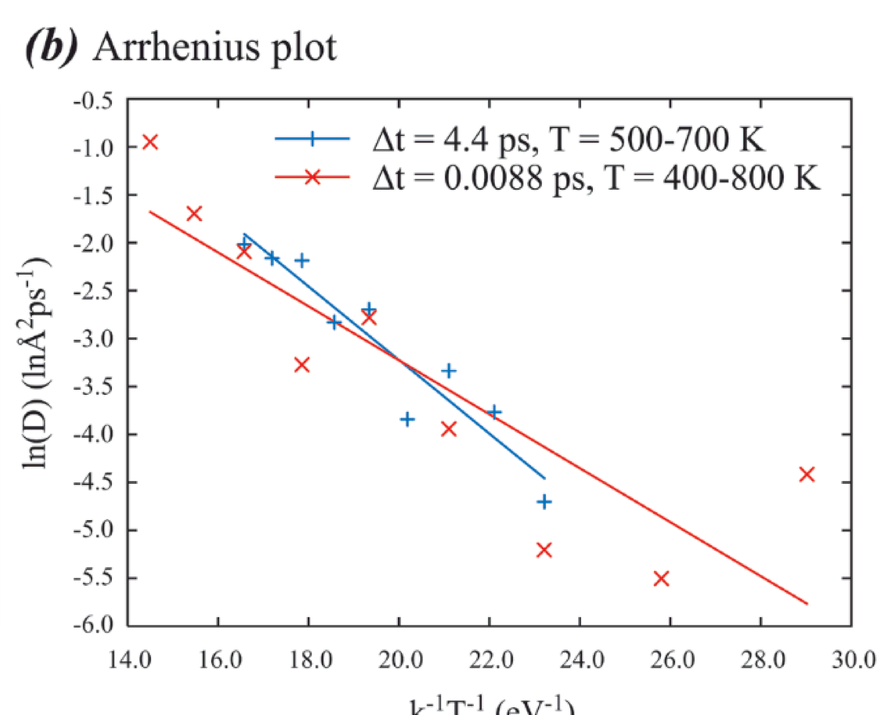
1. Molecular dynamics simulations are performed for 0.88 ns;
2. Hydrogen positions are recorded every 0.0088 ps;
3. Recorded positions are used to calculate mean square displacement;
4. Mean square displacement is converted to diffusivity;
5. Diffusivities at different temperatures are fitted to Arrhenius equation;
6. Arrhenius equation gives diffusion barrier and pre-exponential factor.

Initial Calculation of Hydrogen Diffusion in Aluminum

Mean Square Displacement



Arrhenius Plots

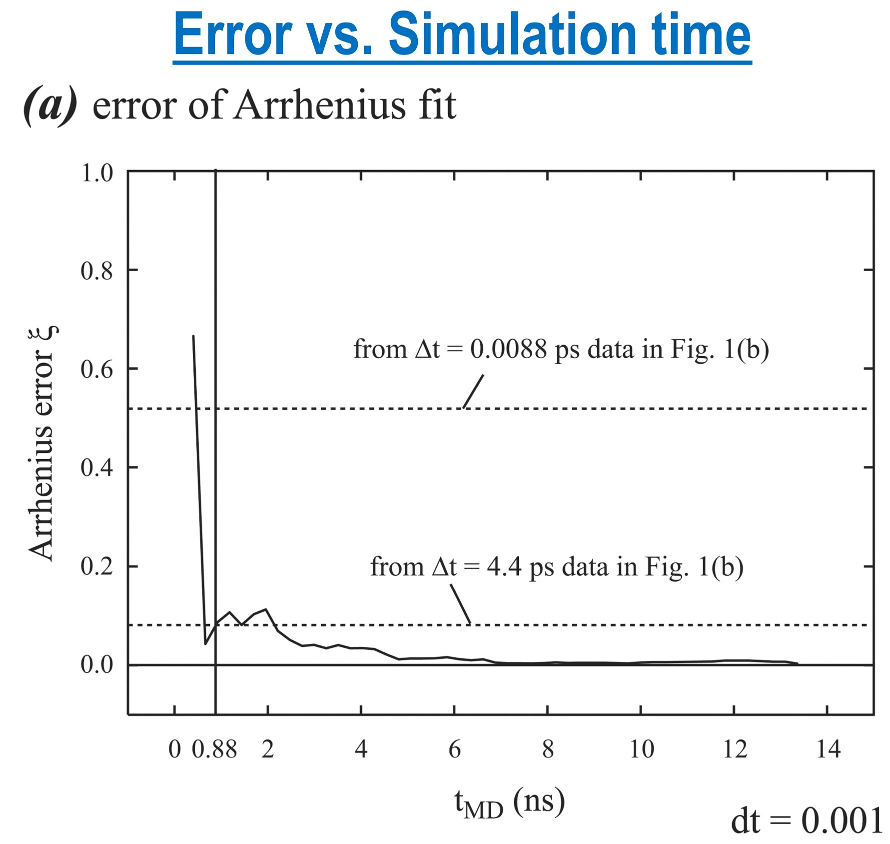


dt = 0.001 ps, t_{MD} = 0.88 ns

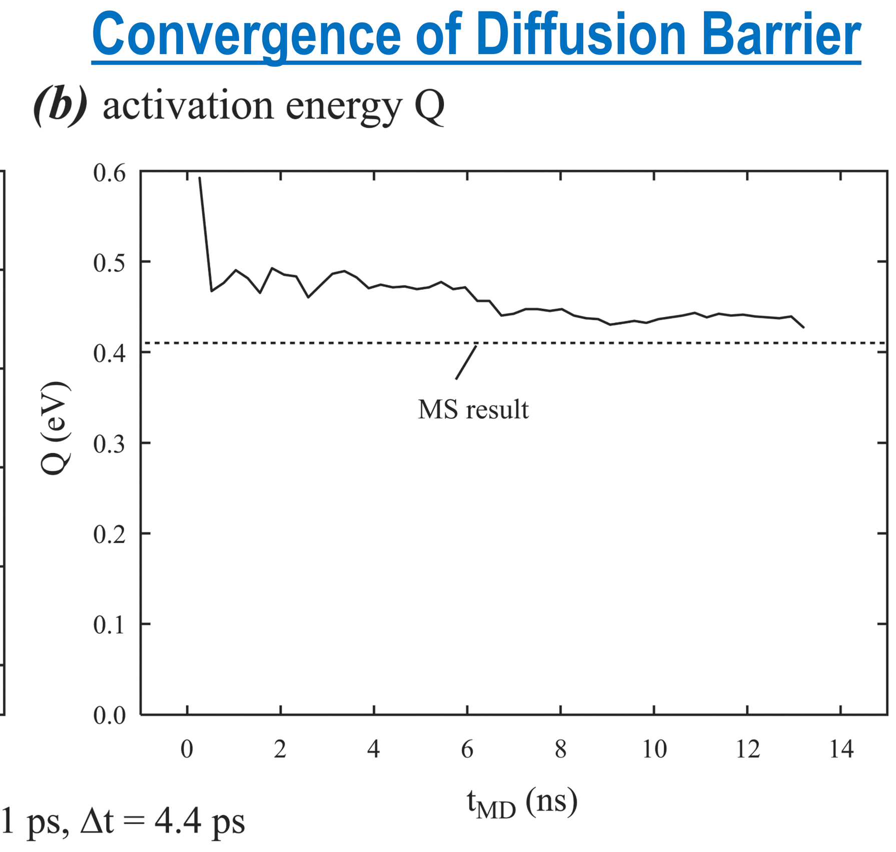
Statistical errors are too large for the results to be useful.

Error Reduction

Error vs. Simulation time



Convergence of Diffusion Barrier

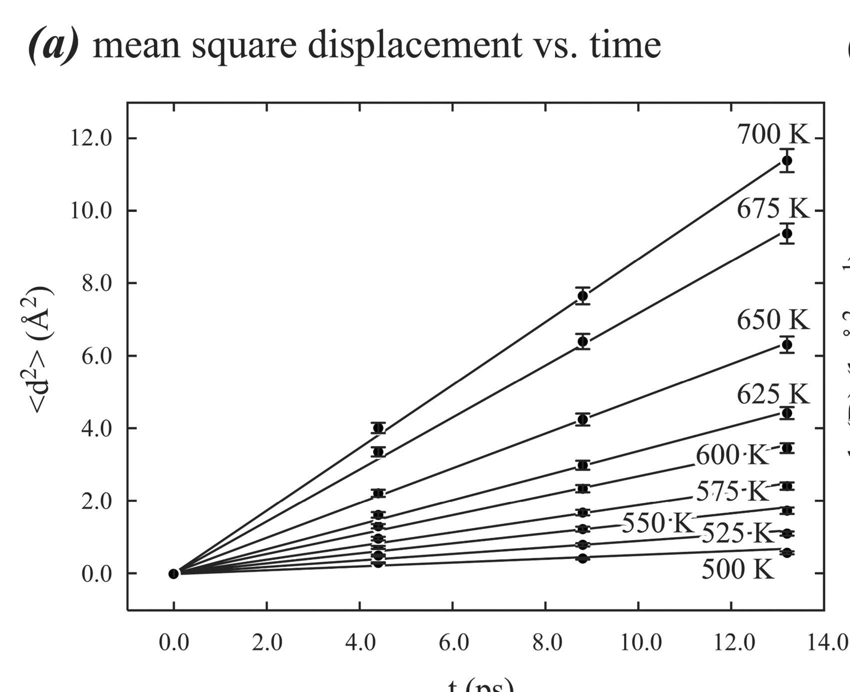


dt = 0.001 ps, Δt = 4.4 ps

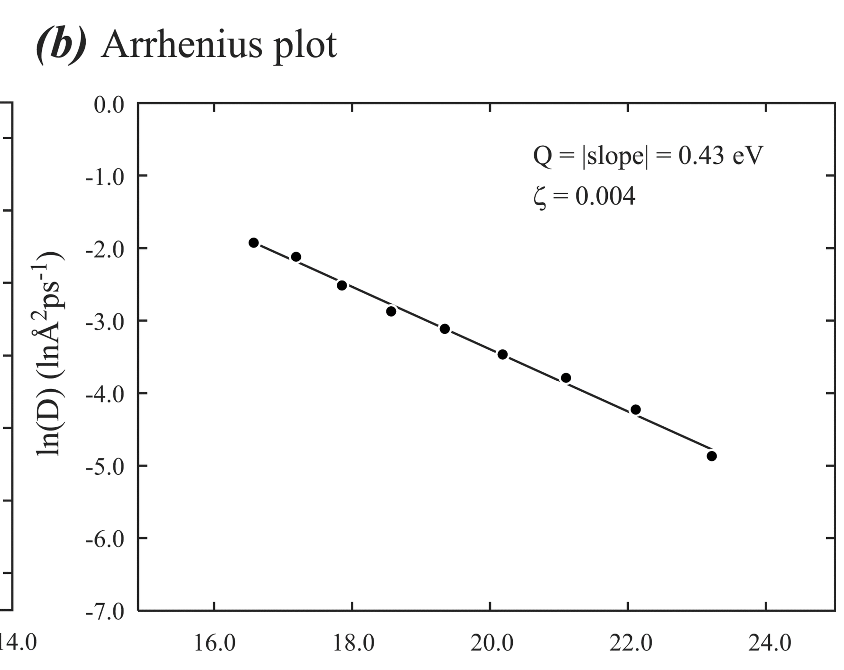
When simulation time is increased to 10 ns or above, error becomes negligible, and highly converged diffusion barrier can be achieved.

Converged Calculation of Hydrogen Diffusion in Aluminum

Mean Square Displacement



Arrhenius Plots

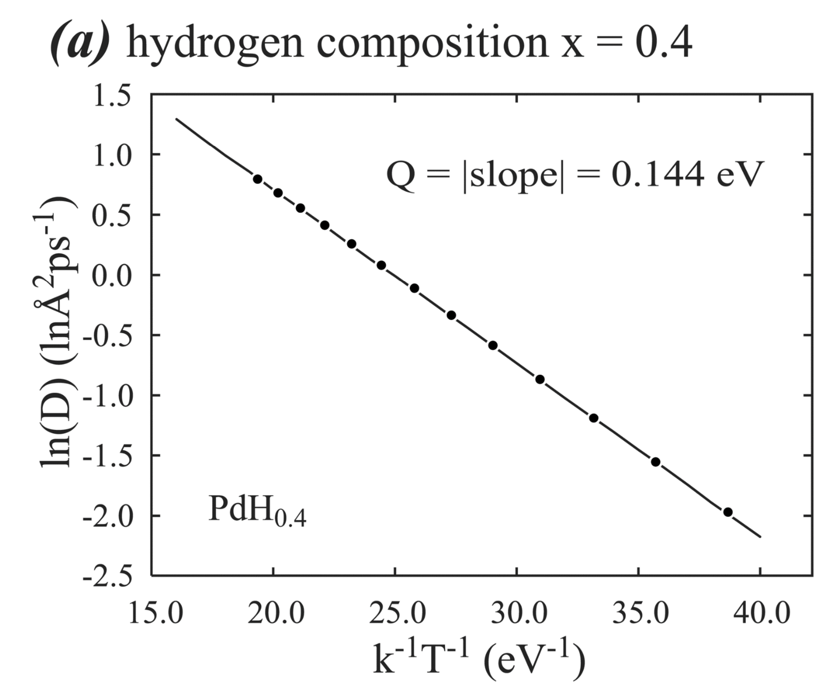


dt = 0.001 ps, Δt = 4.4 ps, t_{MD} = 13.2 ns

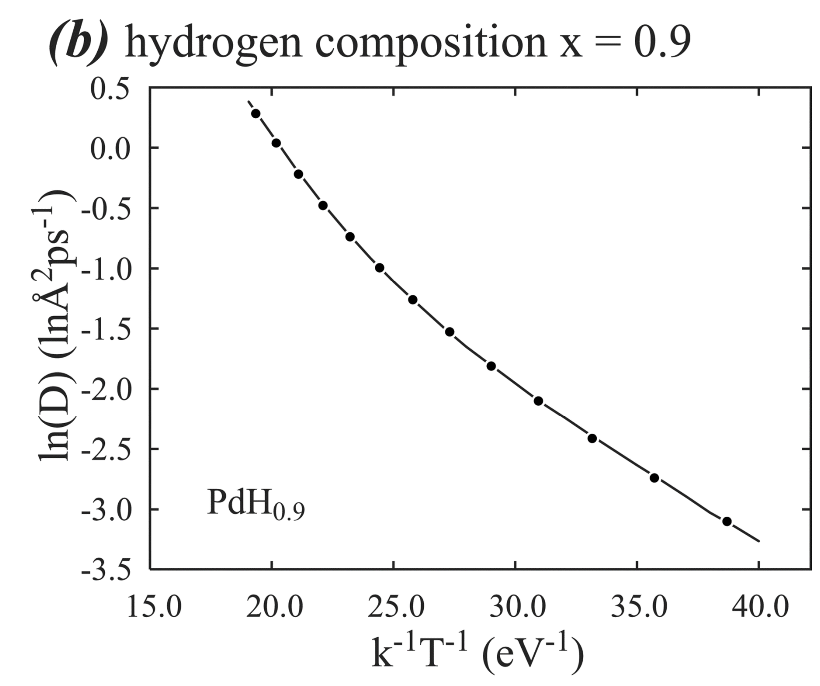
Highly converged molecular dynamics simulations convincingly indicate that the energy barrier for a single hydrogen atom diffusion in bulk aluminum is 0.43 eV.

Converged Calculation of Hydrogen Diffusion in Palladium

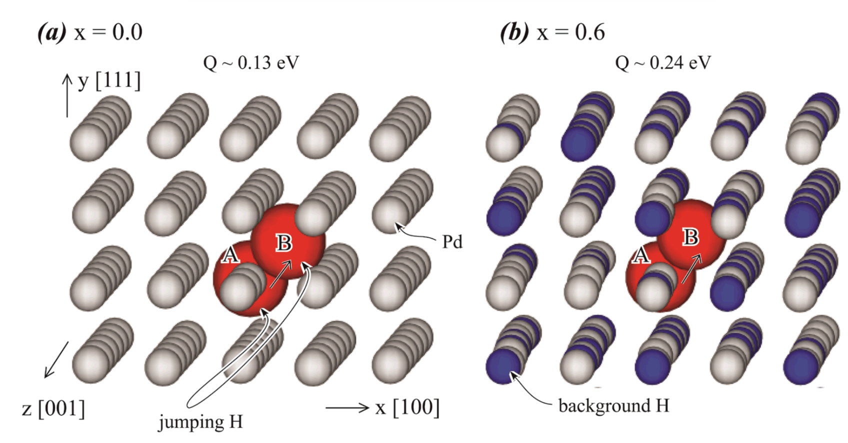
Arrhenius Plot at x = 0.4



Arrhenius Plot at x = 0.4



Two-Mechanism Model



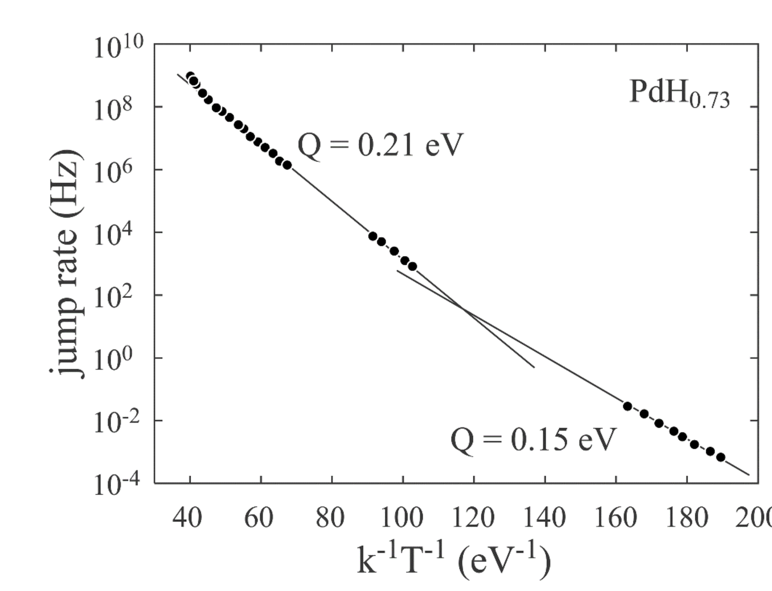
Highly converged molecular dynamics simulations convincingly predict that the Arrhenius plot is linear at low compositions and non-linear at high compositions.

Experimental Comparisons

H-in-Al Measurements[1]

feature explored	feature metric	D_0 (Å^2/ps)	Q (eV)	literature
grain size	> 25 mm	9.530×10^2	0.46	Ichimura et al[13,14]
	15 mm	4.580×10^2	0.38	
	4 mm	1.520×10^3	0.55	
	2 mm	2.110×10^4	0.69	
	3 mm	1.540×10^5	0.84	
	3 mm	4.220×10^6	1.11	
	4 mm	6.000×10^5	0.92	
Al purity	99.999 %	1.900×10^3	0.41	Papp et al[15,16]
	99.999 % + oxides (water-treated)	1.100×10^5	0.74	
	99.8 %	2.510×10^6	0.93	
unexplored	-----	1.100×10^3	0.42	Eichenauer et al[17,18]
	-----	2.100×10^3	0.47	
unexplored	-----	1.101×10^3	0.49	Outlaw et al[19]
unexplored	-----	2.000×10^2	0.52	Matsuo et al[20]
unexplored	-----	9.200×10^3	0.57	Ishikawa et al[21]
unexplored	-----	6.100×10^3	0.57	Saitoh et al[22]
unexplored	-----	2.600×10^3	0.61	Hashimoto et al[23]
unexplored	-----	1.300×10^5	0.69	Csanady et al[24]
unexplored	-----	1.750×10^0	0.17	Young et al[25]
unexplored	-----	1.200×10^9	1.45	Ransley et al[26]

H-in-Pd Measurements[2]



For PdH_x, experiments validated the non-linear Arrhenius plots at high compositions.

For aluminum, experiments validated that the hydrogen diffusion energy barrier is around 0.41-0.47 when the material is single crystalline and pure. The high barriers are associated with high pre-exponential factors, suggesting the possibility of trapping. Simulations begin to elucidate the inconsistent experimental data, especially the low barrier (0.17 eV) measured by Young et al.

1: X. W. Zhou, F. El. Gabaly, V. Stavila, and M. D. Allendorf, J. Phys. Chem. C, 120, 7500 (2016).

2: R. R. Arons, H. G. Bohn, and H. Lutgemier, Solid State Comm., 14, 1203 (1974).

Acknowledgements

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Conclusions

Robust molecular dynamics simulation methods allow confident determination of the overall diffusion energy barrier and pre-exponential factor from Arrhenius equation. Preliminary work has begun to elucidate the experimental data measured for aluminum and palladium.