Understanding Diffusion Behavior of Helium Diffusion in BCC Tungsten

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Background

- *Helium is the important product in structural materials in fusion reactor, either generated by (n,α) transmutation reaction, or injected from high-energetic plasma.*
- *Helium is highly insoluble in metals, clustering and form bubble in the sinks, -> high temperature embrittlement.*
- *Diffusion is the first stage in helium kinetics: occurred at extremely low temperature: ~50K*

Non-Arrhenius Diffusion of He in W

- *Atomistic simulation to model the Helium diffusion: Many-body dynamical simulation*

$$H=\sum_{i=1}^{N}\frac{\boldsymbol{p}_i^2}{2m_i}+U\left(\boldsymbol{r}_i\right)+H_{\text{env}}\Rightarrow\begin{cases}\dot{\boldsymbol{r}}_i=\boldsymbol{p}_i/m_i\\ \dot{\boldsymbol{p}}_i=-\nabla U\left(\boldsymbol{r}_i\right)-\gamma_i\boldsymbol{p}_i+\sigma_i\xi_i\left(t\right)\end{cases}\Rightarrow D=\frac{\left\langle\left[\boldsymbol{r}\left(t+\tau\right)-\boldsymbol{r}\left(t\right)\right]^2\right\rangle}{6\tau}$$

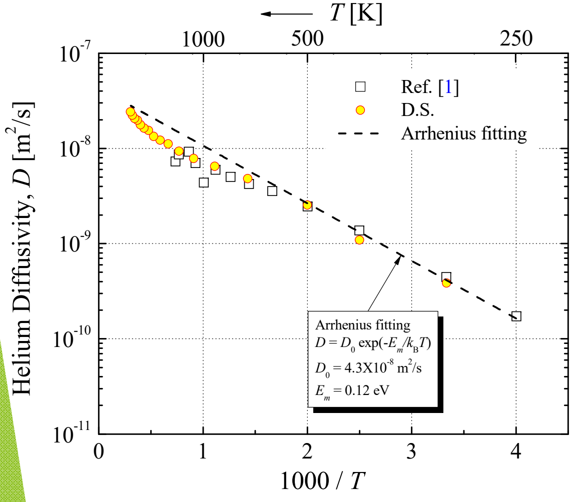
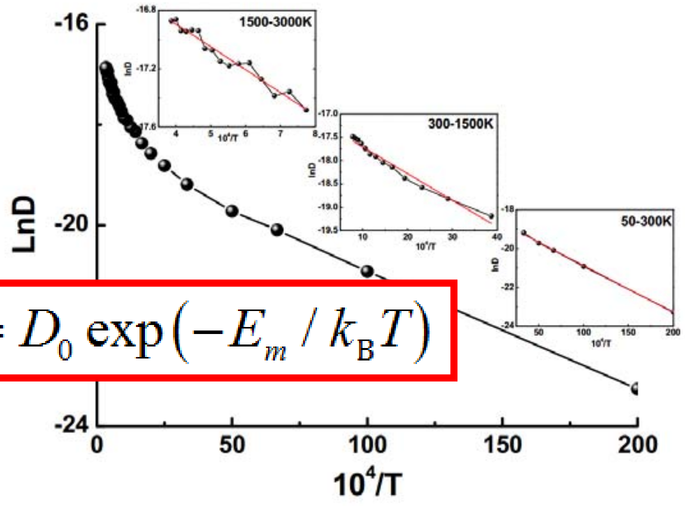
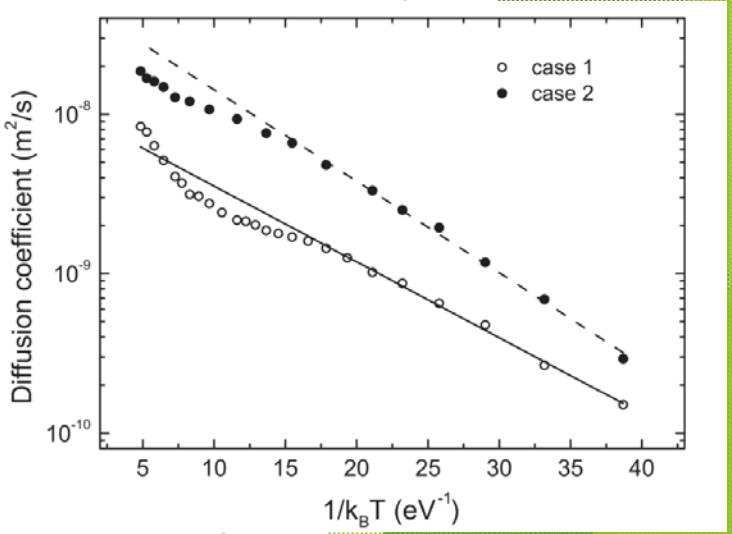


Fig. 1 The Arrhenius plot of Diffusivity of He in W obtained from Dynamical simulation



$$D=D_0\exp\left(-E_m/k_BT\right)$$

X. Shu, P. Tao, X. Li, and Y. Yu (2014)



X. Shu, P. Tao, X. Li, and Y. Yu (2014)

Ref. 1: D. Perez, T. Vogel and B. P. Uberuaga, "Diffusion and transformation kinetics of small helium clusters in bulk tungsten", Phys. Rev. B **90**, (2014) 014102.

Non-Arrhenius Diffusion of He in W

- *Impurity diffusion is usually treated as a trapping-detrapping stochastic process:*

  Arrhenius Law $D = D_0 \exp\left(-E_m / k_B T\right)$

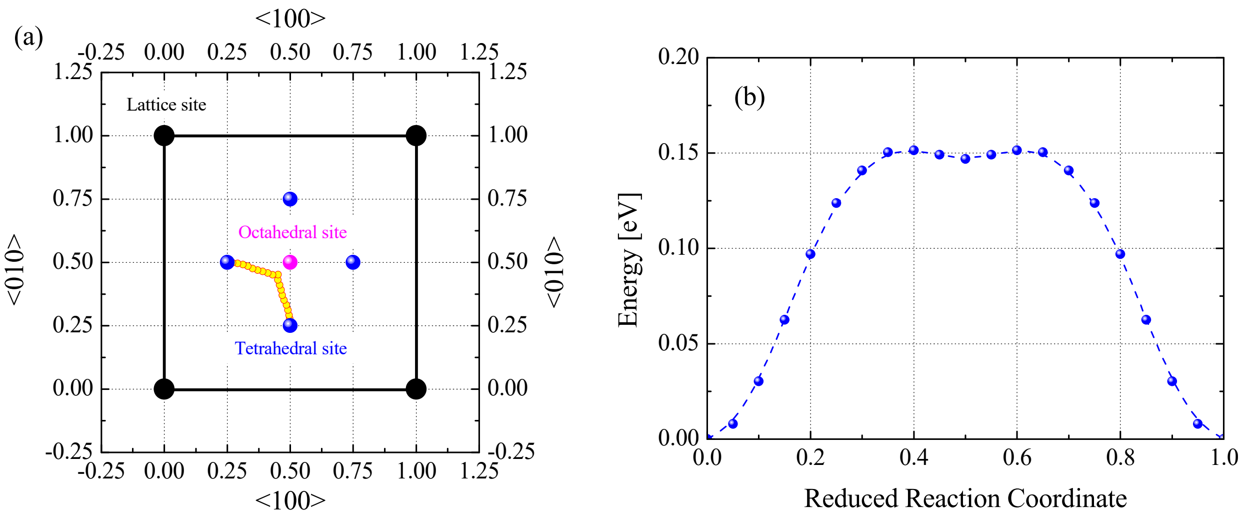
  - *Reversible: Quasi-Equilibrium*
  - *Deeply trapped* $E_m >> k_B T$
  - *Long relaxation time*

- *Sources of Non-Arrhenius diffusion:*
  - *temperature dependence of diffusion parameters: Anharmonicity*
  - *Multiple jump mechanism*
  - *Quantum statistics**

- *Helium Diffusion in W: Non-equilibrium* $E_m >> k_B T$??

Non-Equilibrium Nature of He Diffusion in W

$E_m >> k_{\mathrm{B}}T$ available at $T < 500\mathrm{K}$



	Method	Ref.
0.15	CG	Current work
0.06	*ab initio*	PRL **97** (2006) 196402
0.13	MD	MSMSE **22** (2014) 065010
0.15	NEB	PRB **90** (2014) 014102
0.24~0.32	Expt.	JAP **56** (1984) 983 PRL **42** (1979) 515

Non-Equilibrium Diffusion: Brownian Motion

- *The necessity to describe diffusion as a dynamical process was already apparent in the investigation of the Brownian motion by Einstein (1905), Smoluchowski (1906), Kramers (1940), Chandarsekhar (1943), ….: the Brownian particle diffuses in an external periodic potential.*
- *Impurity Dynamics:*
  - *Langevin Equation*

$$m\ddot{\boldsymbol{r}} = -\nabla U(\boldsymbol{r}) - m\gamma\dot{\boldsymbol{r}} + \sigma\boldsymbol{\xi}(t)$$

$$\langle \xi_\alpha(t)\rangle = 0 \quad \langle \xi_\alpha(t)\xi_\beta(t')\rangle = \delta_{\alpha\beta}\delta(t-t')$$

$$\sigma^2 = 2m\gamma k_B T$$

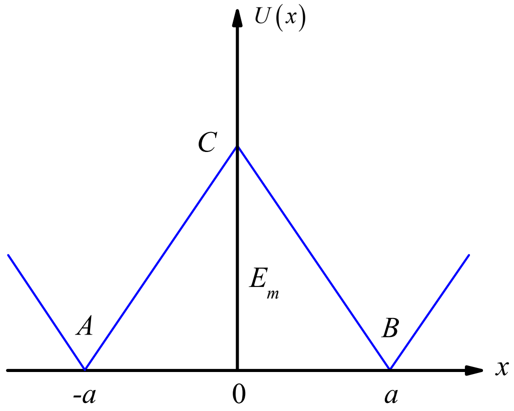
Fokker-Planck Equation and Fick’s Law

$$\frac{\partial}{\partial t}P(\boldsymbol{r},t) = \nabla\cdot\left[\frac{\nabla U}{m\gamma}P(\boldsymbol{r},t)\right] + D_E\nabla^2 P(\boldsymbol{r},t) = -\nabla\cdot\boldsymbol{j}(\boldsymbol{r},t)$$

$$\boxed{\boldsymbol{j}(\boldsymbol{r},t) = -D_E e^{-U(\boldsymbol{r})/k_B T}\nabla\left(e^{U(\boldsymbol{r})/k_B T}P(\boldsymbol{r},t)\right) \equiv -D\nabla C(\boldsymbol{r},t)}$$

$$D_E = \frac{k_B T}{m\gamma} = \frac{\sigma^2}{2m^2\gamma^2}$$

Simplified Analytic Model: U = U(r)



$E_m = U(x_C) - U(x_A)$

$$\boldsymbol{j}(\boldsymbol{r},t) = -D_E e^{-U(\boldsymbol{r})/k_B T} \nabla\left(e^{U(\boldsymbol{r})/k_B T} P(\boldsymbol{r},t)\right) \equiv -D \nabla C(\boldsymbol{r},t)$$

$$U(x) = \begin{cases} E_m(1 + x/a) & -a < x < 0 \\ E_m(1 - x/a) & 0 < x < a \end{cases}$$

$$D = \frac{a^2}{2\tau} = \frac{D_E}{2} \frac{(E_m/k_B T)^2}{\left(e^{E_m/k_B T} - E_m/k_B T - 1\right)}$$

$$= \begin{cases} D_E \exp(-E_m/k_B T) & E_m >> k_B T \\ D_E & E_m << k_B T \end{cases}$$

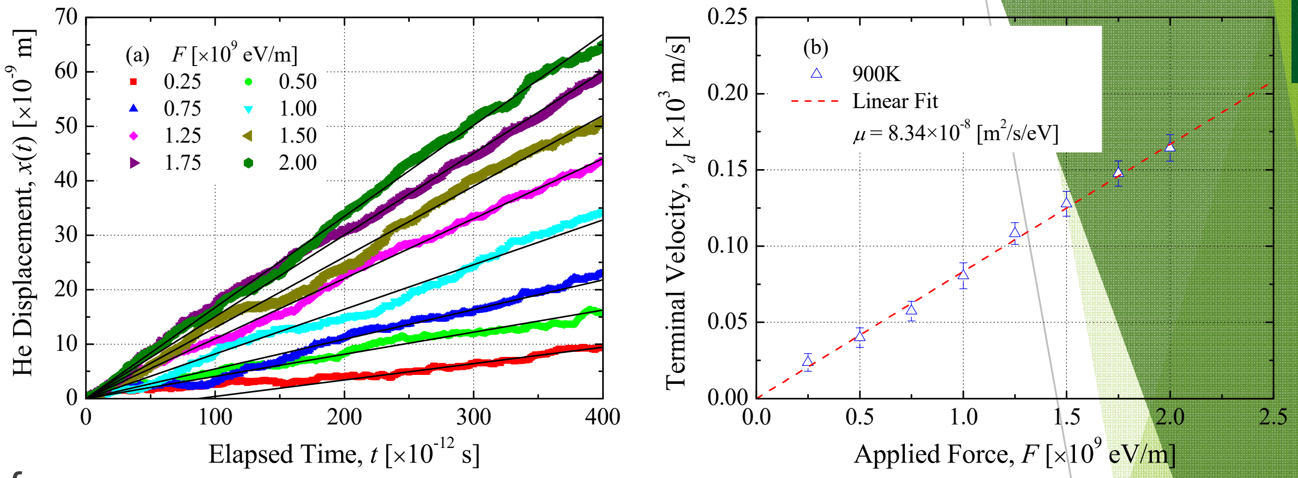
- *The diffusivity of impurity in metals is determined by the migration energy and mobility,* E_m and $\mu = 1/m\gamma$
- *The competition between the stochastic force (thermal energy) and the restoring force (periodic potential) determines the impurity diffusion behavior*

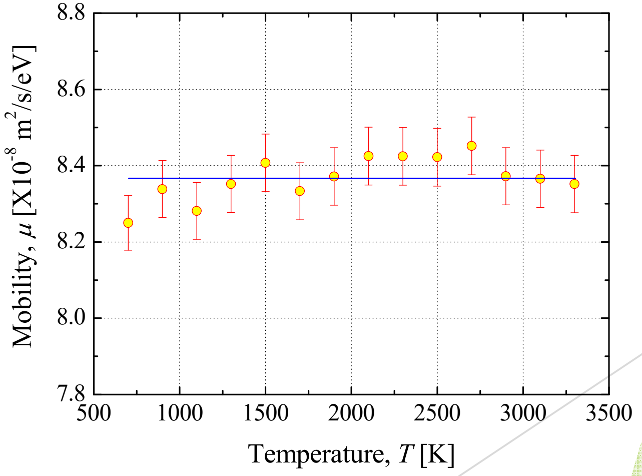
Mobility

- *Characterize the Brownian motion*
- *The response of a Brownian particle to a small force in a diffusive medium*
- *Describe the “phonon wind” of a diffusive medium exerted by the impurity*

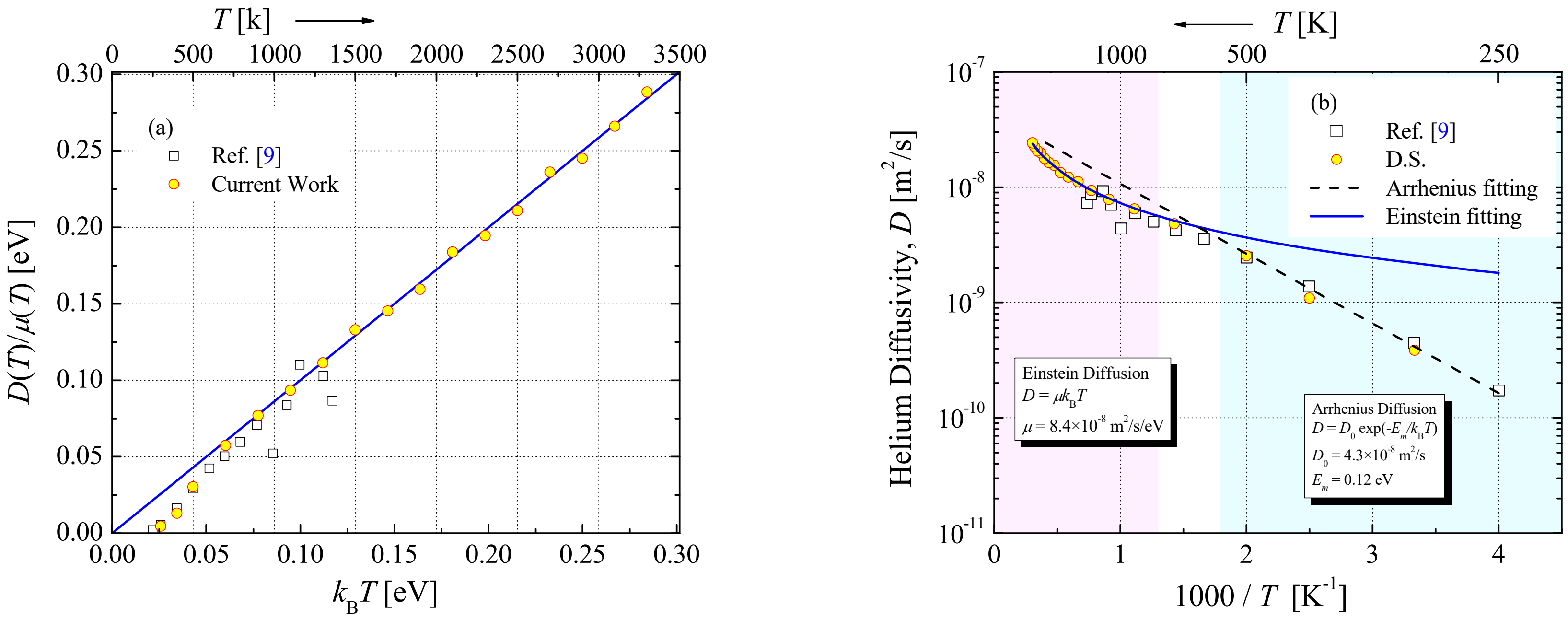
$$m\ddot{\boldsymbol{r}} = -\nabla U\left(\boldsymbol{r}\right) - m\gamma\dot{\boldsymbol{r}} + \sigma\xi\left(t\right) + \boldsymbol{F}_d$$

$$\mu = \frac{1}{m\gamma} = \lim_{F_d\to 0}\frac{v_d}{F_d} \approx 8.4\times10^{-8}\,\mathrm{m}^2/\mathrm{s}/\mathrm{eV}$$





Non-Arrhenius Diffusion of He in W



- *Non-Arrhenius diffusion of He in W: Smoluchowski Diffusion*

$$D = \begin{cases} 4.3\times10^{-8}\times\exp\left(-0.12\,\mathrm{eV}/k_{\mathrm{B}}T\right)\left[\mathrm{m}^2/\mathrm{s}\right] & T < 500\mathrm{K} \\ 8.4\times10^{-8}\,k_{\mathrm{B}}T\left[\mathrm{m}^2/\mathrm{s}\right] & T > 700\mathrm{K} \end{cases}$$

Summary and Conclusion

- The Non-Arrhenius diffusion behavior of Helium in BCC W could not be explained in the framework of Arrhenius law.
- It is originated from the irreversible nature: Brownian motion in an external periodic force field, Smoluchowski diffusion.
- The diffusivity is determined by the mobility and the migration energy.
- The competition between the stochastic force (thermal energy) and the restoring force (periodic potential) determines the diffusion behavior
  - > : High temperatures, Einstein diffusion, D~T
  - < : Low temperatures, Arrhenius diffusion, D~exp(Em/kT)
  - ~ : Mid-temperatures, mixed diffusion

Thanks for Your Attention!

Q & A