Rate and Time Dependence of Defect Initiation in Crystalline Solids: The Transition State Theory Approach

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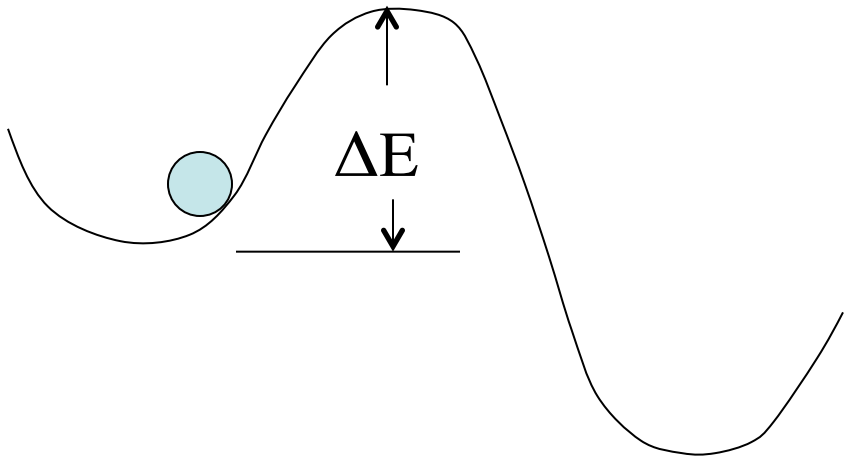
What is transition state theory?

In basic terms, transition state theory estimates the fraction of escape attempts from a potential energy minimum by a thermally-excited particle, or system of particles, that will be successful.



Harmonic transition state theory (hTST) is of particular applicability to the behavior of crystalline solids. Here it is assumed that the atoms spend most of their time in the neighborhood of the equilibrium position, where the potential energy surface is locally quadratic.

There have been a number of recent efforts to apply a 1-D hTST model to defect nucleation in crystalline solids, e.g., Mason, Lund and Schuh (2006), Zhu et al. (2008). Ryu, Kang, and Cai (2011) have recently suggested that the energy barrier is a free energy barrier, *i.e.*, $\Delta F = \Delta E - T\Delta S$.

Our approach is to use a hTST model of moderately high dimension (1000-3000) in conjunction with a recently developed model of zero-temperature defect initiation.

The hTST Model

The basic equation of TST is

$$\frac{dF}{dt} = -kF$$

where F is the fraction of *unsuccessful* attempts to escape from the potential energy well and *k* is the TST rate factor.

Suppose that the mechanical loading is characterized by a monotonically increasing loading parameter λ(t) upon which the TST rate factor *k* will depend. Then

$$\frac{dF}{dt} = \dot{\lambda}\frac{dF}{d\lambda} = -k\left(\lambda\right)F \quad ; \quad F(\lambda = 0) = 1$$

$$F(\lambda) = \exp\left(-\int_0^{\lambda} \frac{k(\Lambda)}{\dot{\Lambda}}\, d\Lambda\right)$$

and

$$k = \frac{N_s}{2\pi}\sqrt{\frac{1}{m}}\frac{\prod_{i=1}^{3N}\sqrt{\kappa_i}}{\prod_{i=1}^{3N-1}\sqrt{\nu_i}}\exp\left(-\frac{\Delta E}{kT}\right)$$

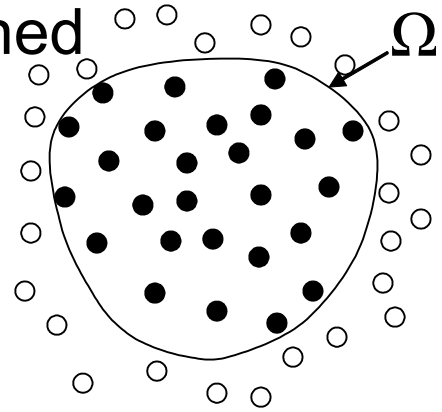
where κ_i and ν_i are, respectively, the principal curvatures of the potential energy surface at the current loading point and at the saddle point.

The problem is to determine the energy barrier ΔE and the surface curvatures κ_i and v_i. We obtain these from a recently developed criterion for zero-temperature defect nucleation (Delph, Zimmerman, Rickman, & Kunz, 2009; Delph & Zimmerman, 2010).

The Wallace Criterion

This criterion is based upon the idea that zero-temperature defect initiation can be predicted by examining the lowest eigenvalue of the Hessian matrix of the potential energy function $E(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ for a moderate-sized system of N atoms, $N << N_A$. A negative eigenvalue indicates instability. The principal potential energy curvatures are the eigenvalues of the Hessian matrix and the value of E at instability yields ΔE.

The required atomic coordinates may be obtained by various means, e.g., Cauchy-Born or MD codes at T = 0.



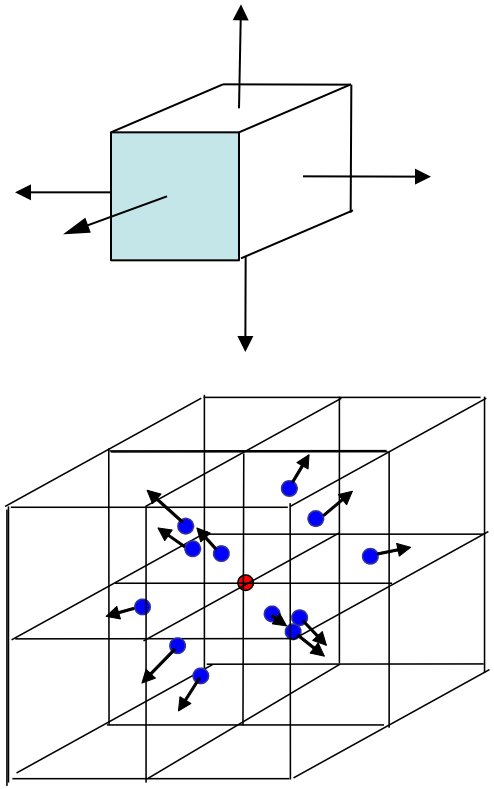
Computational Approach

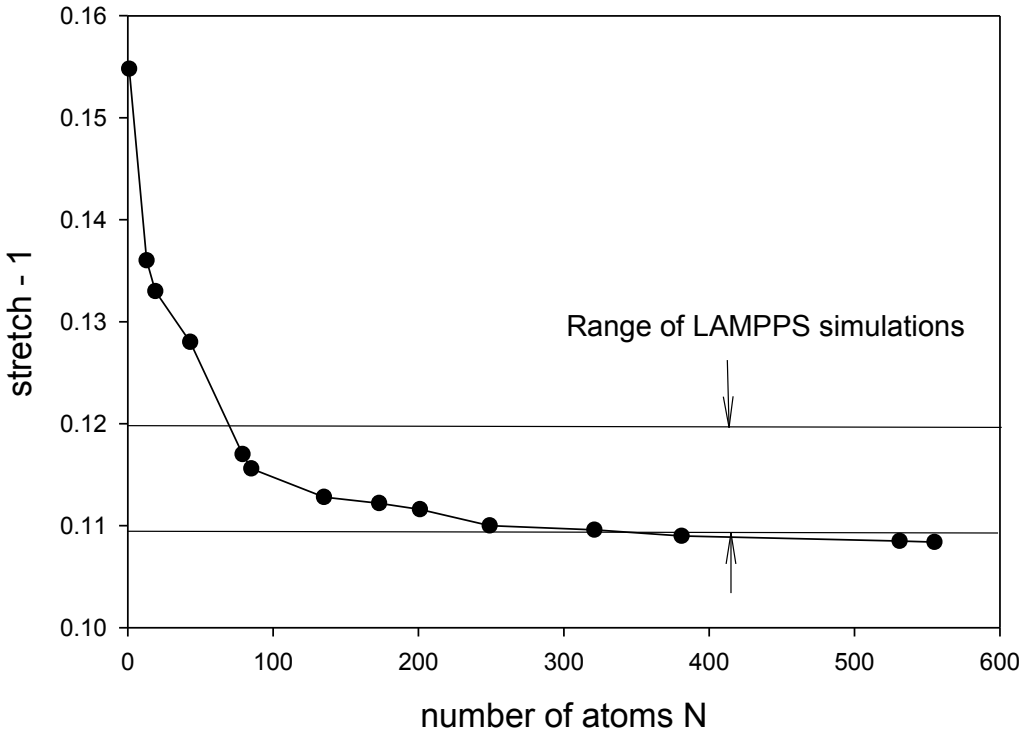
1. Use the Wallace method to calculate the principal curvatures of the potential energy surface for a reduced ensemble of atoms ($N << N_A$) for points along the loading path and at the instability point (saddle point). This also yields the energy barrier ΔE.

2. From the principal curvatures and ΔE, calculate the hTST rate factor $k(\lambda)$. Then the fraction of unsuccessful attempts may be calculated for any loading point λ by standard numerical quadrature.

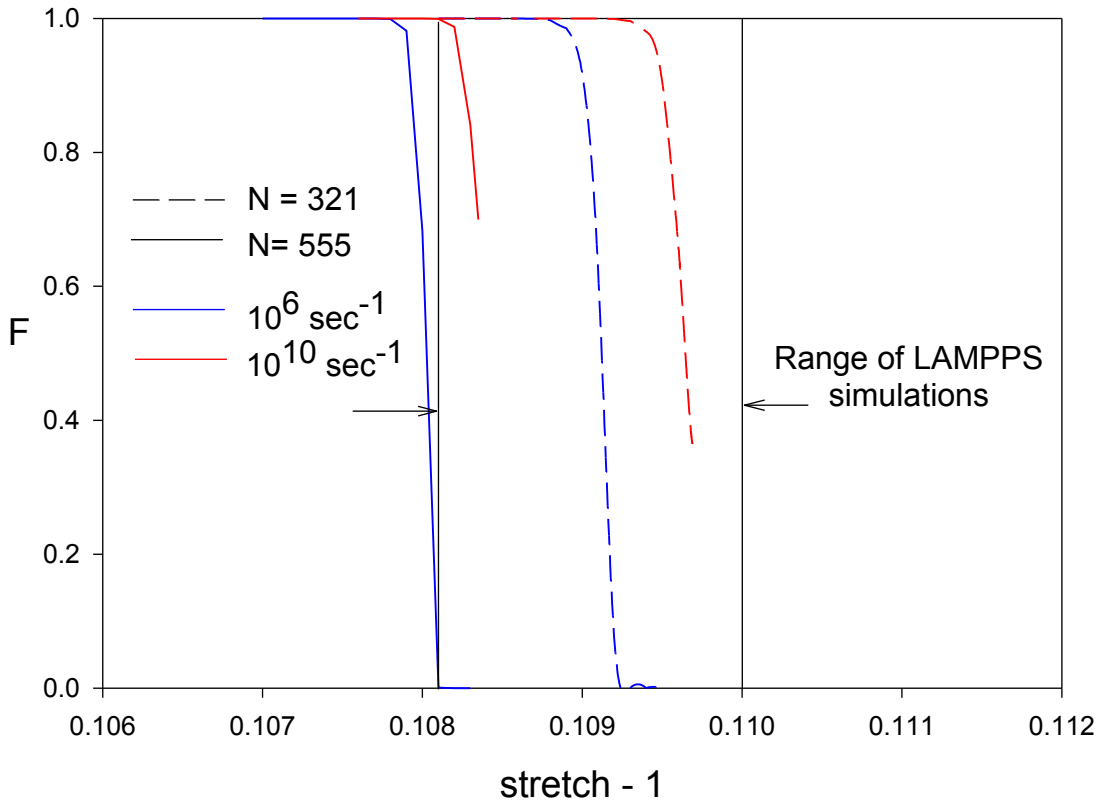
Triaxial stretching of an FCC crystal (Lennard-Jones)

The failure mode at T = 0º is spherical cavitation (Delph et al., 2009).

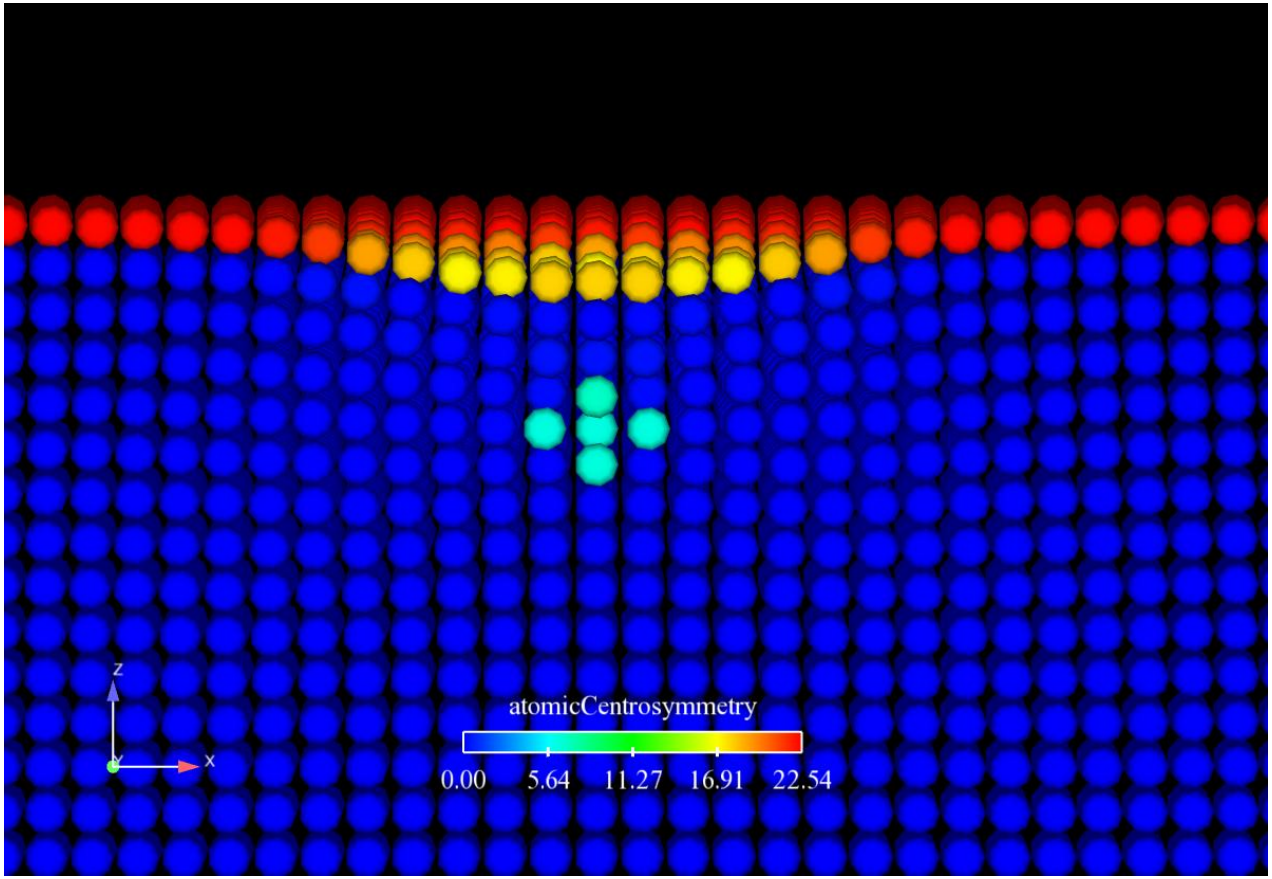




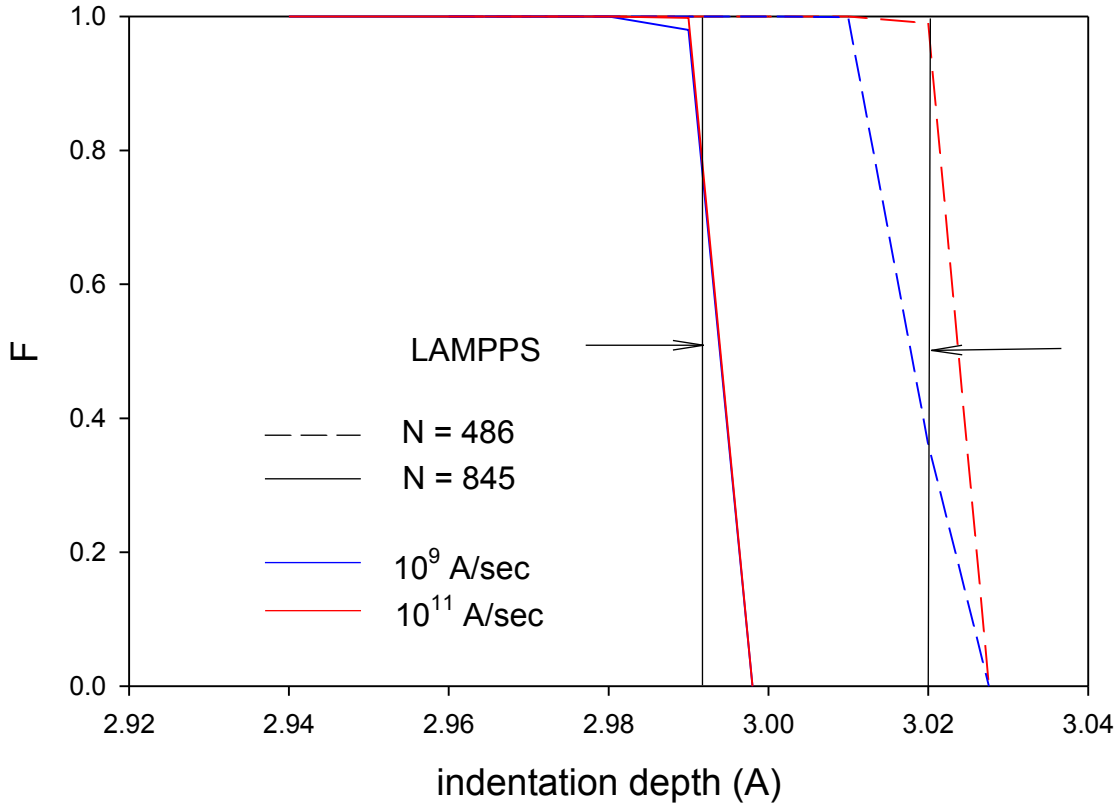
hTST predictions at T = 20^{o} K (T_m = 72^{o} K)



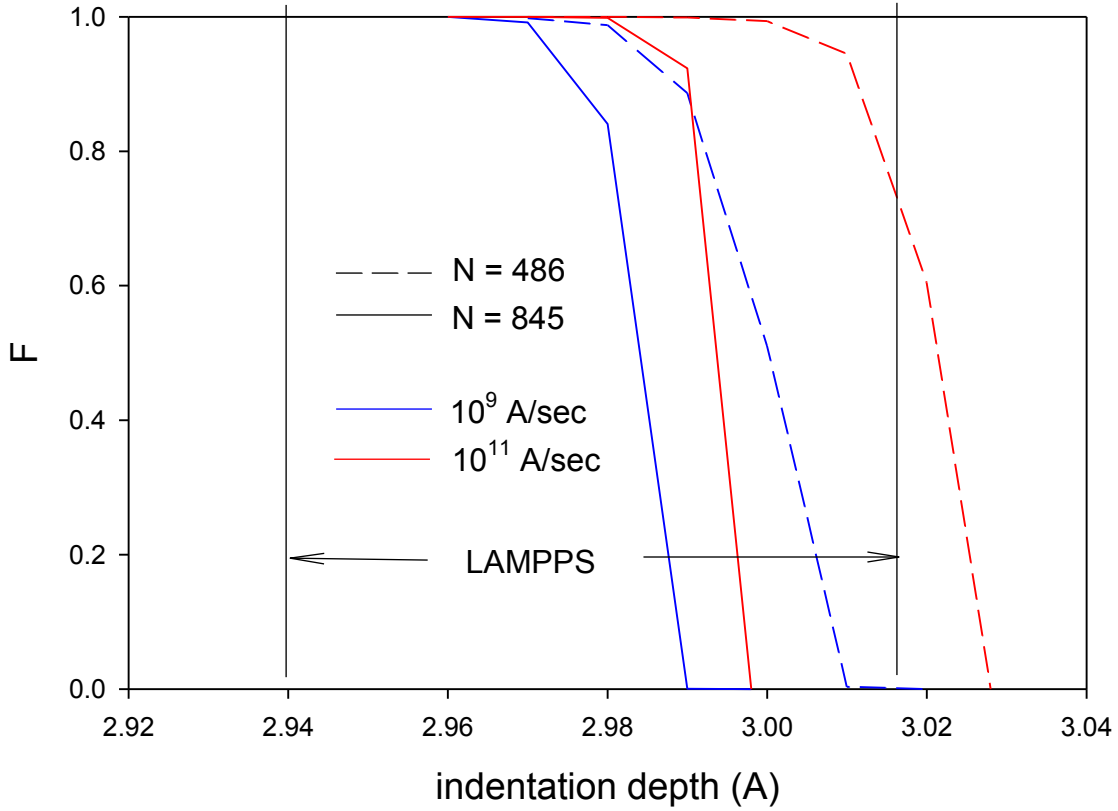
Nanoindentation of the (001) face of an Au crystal



TST predictions for T = 100^{o} K



TST predictions for T = 300^{o} K



Conclusions

- Harmonic transition state theory provides an accurate means of estimating the rate and time dependence of defect nucleation in crystalline solids.
- Even though MD codes may be used to generate the T = 0 atomic positions, hTST *is not* limited to high loading rates as are MD codes.
- The rate dependence predicted by hTST appears to be somewhat weaker than that observed from MD simulations.
- No strong entropic effects are observed.