Entropy Effect on Dislocation Nucleation

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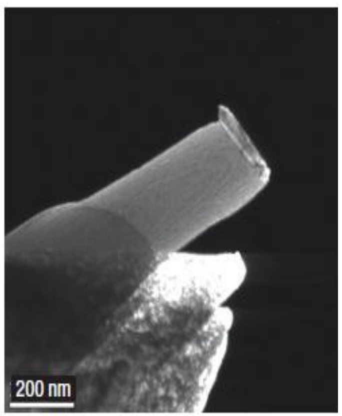
Outline

1. Why dislocation nucleation?
2. Classical Nucleation theory
3. Activation Free Energy by Umbrella Sampling
4. Activation Entropy – two different ones?

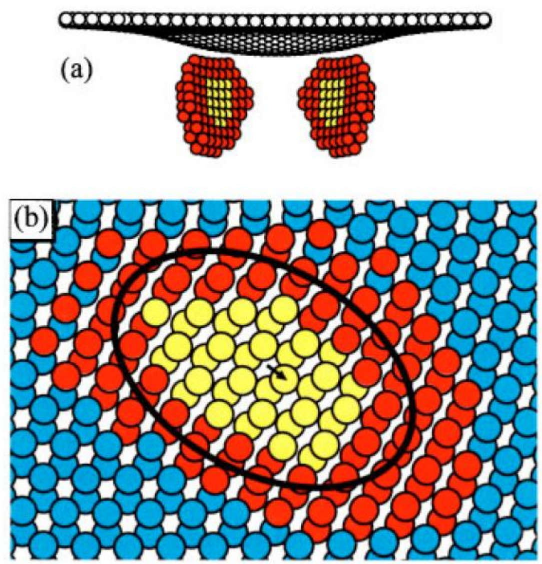
Nucleation Becomes More Important at Nano Scale

“dislocation starved” nano-pillars nano-wires require dislocation **nucleation** from **surface** for plasticity

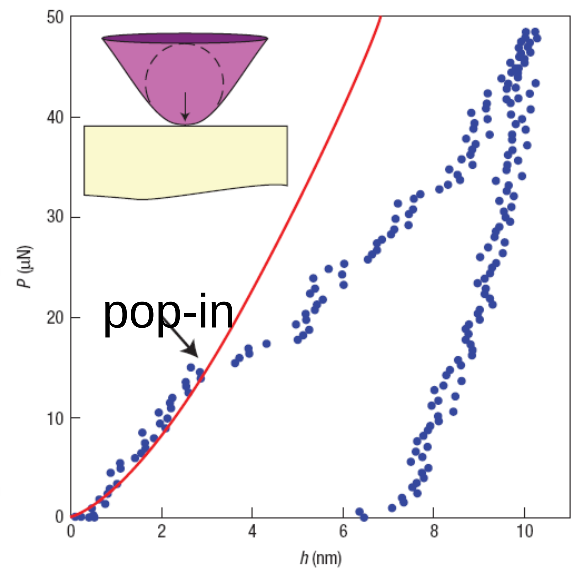
“pop-in” events in nano-indentation has often been linked to **homogeneous** dislocation **nucleation** beneath indenter



Ni FCC D = 160 nm
Shan et al. Nature Mat. (2008)



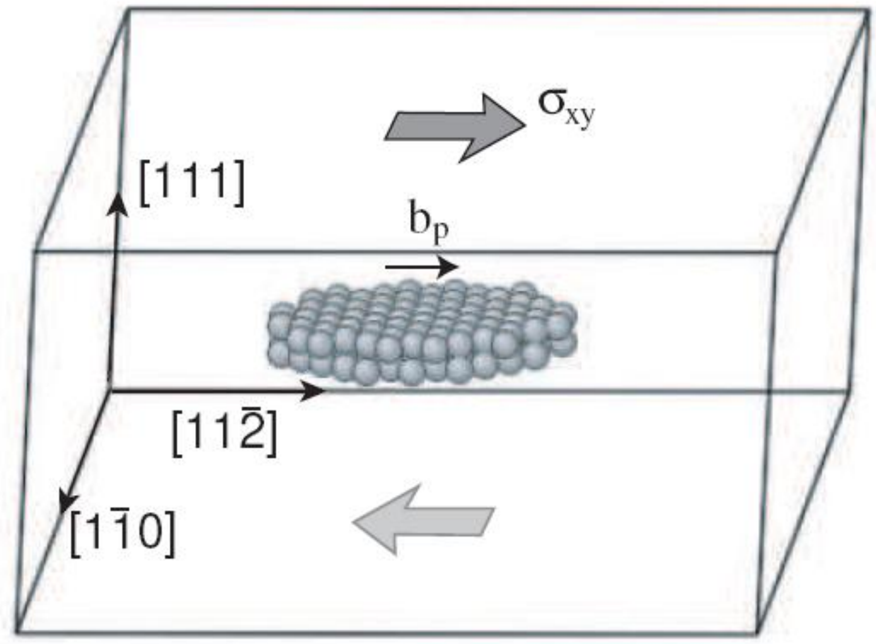
Kelchner et al. PRB 58, 11085 (1998)



Schuh et al. Nature Mater 4, 617 (2005)

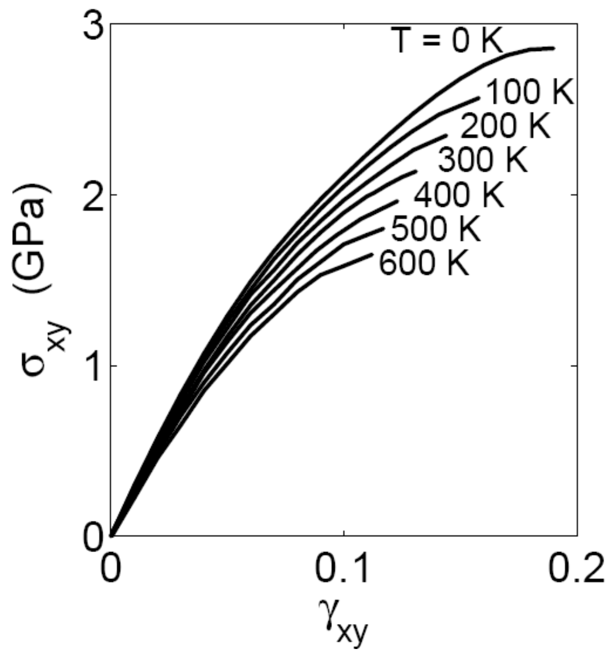
Avoid dislocations during growth of high quality semiconductor films

Homogeneous Dislocation Nucleation Rate



FCC Cu EAM Mishin Potential

Nucleation of *partial* dislocation under pure shear stress σ_{xy}



Nucleation is a **random event** characterized by:

nucleation rate $I(\sigma, T)$

T = 0 K Energy barrier computed in
T. Zhu, J. Li, et al. Phys. Rev. Lett. 100, 025502 (2008).

Nucleation Theories

(direct rate calculation from MD simulations is usually impossible)

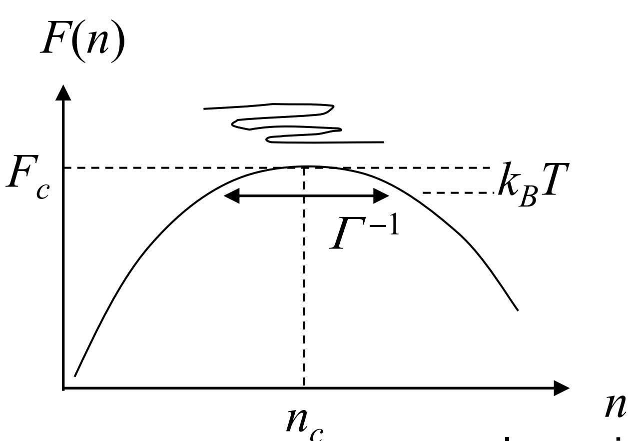
Transition State Theory (TST) -- nucleation rate at constant strain γ

$$I^{TST} = \nu_0 \exp\left(-\frac{F_c(\gamma, T)}{k_B T} \right)$$

where $\nu_0 = \frac{k_B T}{h} \approx 10^{13} \mathrm{s}^{-1}$ at T = 300K

$F_c(\gamma, T)$ **Activation (Helmholtz) free energy**

Eyring, J. Chem. Phy. 3, 107 (1935).
Hanggi et al. Rev. Mod. Phys. 62, 251 (1990).



Becker-DÖring Theory

Ann. Phys. (N.Y.) 24, 719 (1935).

$$\nu_0 = f_c^+ \Gamma$$

f_c^+ "molecular attachment rate"

$$\Gamma \equiv \left(\frac{\eta}{2\pi k_B T} \right)^{1/2} \quad \eta = - \left. \frac{\partial^2 F(n)}{\partial n^2} \right|_{n=n_c}$$

Zeldovich factor

Activation Entropy

activation (Helmholtz) free energy — activation energy — **activation entropy**

$$F_c(\gamma, T) = E_c(\gamma) - T\,S_c(\gamma)$$

$$S_c(\gamma) \equiv -\left.\frac{\partial F_c(\gamma,T)}{\partial T}\right|_{\gamma}$$

difficult to calculate

$$I^{NUC} = \nu_0 \exp\left(-\frac{F_c(\gamma,T)}{k_B}\right)$$

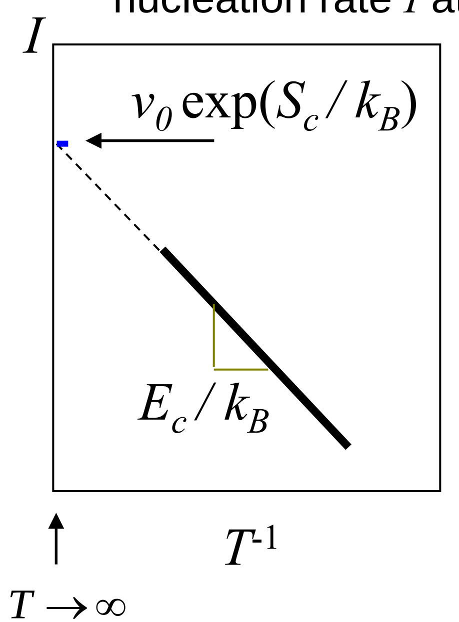
easier to calculate
Nudged elastic band (NEB) method

$$= \nu_0 \exp\left(\frac{S_c(\gamma)}{k_B}\right)\exp\left(-\frac{E_c(\gamma)}{k_B T}\right)$$

$$\approx \nu_D \exp\left(-\frac{E_c(\gamma)}{k_B T}\right) \longleftarrow \text{Harmonic Approximation}$$

Debye frequency: $\nu_D \approx 10^{13}\,\mathrm{s}^{-1}$

Arrhenius plot of nucleation rate I at given strain γ



S_c	$\exp(S_c/k_B)$
$3\,k_B$	$\sim 10^1$
$10\,k_B$	$\sim 10^4$
$20\,k_B$	$\sim 10^8$

Harmonic Transition State Theory (HTST)

$$I^{TST} = \nu_0 \exp\left(-\frac{F_c(\gamma,T)}{k_B T}\right) = \nu_0 \exp\left(\frac{S_c(\gamma)}{k_B}\right) \exp\left(-\frac{E_c(\gamma)}{k_B T}\right)$$

where $\nu_0 = \frac{k_B T}{h} \approx 10^{13}\mathrm{s}^{-1}$ at T = 300K

Harmonic approximation

metastable state

$$I^{HTST} = \frac{\prod_{i=1}^{N} \nu_i^m}{\prod_{i=1}^{N-1} \nu_i^a} \exp\left(-\frac{E_c(\gamma)}{k_B T}\right) \approx \nu_D \exp\left(-\frac{E_c(\gamma)}{k_B T}\right)$$

activated state

Assuming no big changes in vibration frequencies (not always justified)

$$S_c(\gamma) = k_B \ln\left(\frac{\prod_{i=1}^{N} \nu_i^m}{\nu_0 \cdot \prod_{i=1}^{N-1} \nu_i^a}\right)$$

where *Debye frequency*: $\nu_D \approx 10^{13}\mathrm{s}^{-1}$

This would mean $\exp(S_c / k_B)$ **is not significant.**

Constant Strain v.s. Constant Stress

nucleation rate in bulk sample independent of stress/strain control

$$I^{TST} = \nu_0 \exp\left(-\frac{F_c(\gamma, T)}{k_B T} \right) \quad = \quad I^{TST} = \nu_0 \exp\left(-\frac{G_c(\sigma, T)}{k_B T} \right)$$

$F_c(\gamma, T) = E_c(\gamma) - T\, S_c(\gamma)$

Activation **Helmholtz** Free Energy; Activation Energy; Activation Entropy

$G_c(\sigma, T) = H_c(\sigma) - T\, S_c(\sigma)$

Activation **Gibbs** Free Energy; Activation Enthalpy; Activation Entropy

$$S_c(\gamma) \equiv -\frac{\partial F_c(\gamma, T)}{\partial T}\bigg|_{\gamma} \quad \neq \quad S_c(\sigma) \equiv -\frac{\partial G_c(\sigma, T)}{\partial T}\bigg|_{\gamma}$$

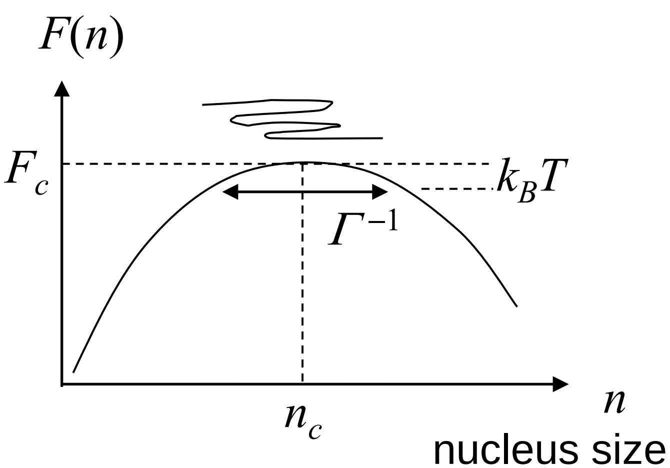
More convenient in atomistic simulation

More convenient in experiment literature

$$F_c(\gamma, T) = G_c(\sigma, T) + O(V^{-1})$$

when $\sigma = \sigma(\gamma, T)$ J. Mater. Res. 26, 2335 (2011).

Order Parameter n for Free Energy Curve



Order parameter: $n(\{r_i\})$ is the number of atoms enclosed by the dislocation loop

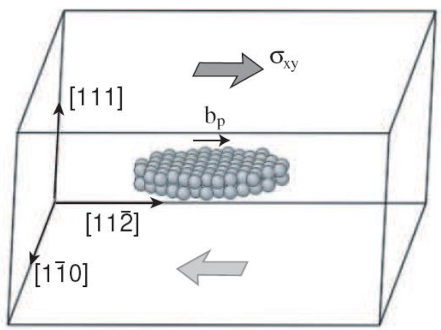
Ryu, Kang, Cai, Proc. Natl. Acad. Sci. USA 108, 5174 (2011).

1. For each atom i, if $\max_j (|r_{ij} - r_{ij}^0|) > d_c$ atom i is labeled as "slipped"

2. "Slipped" atoms closer to each other than r_c are grouped into one cluster.

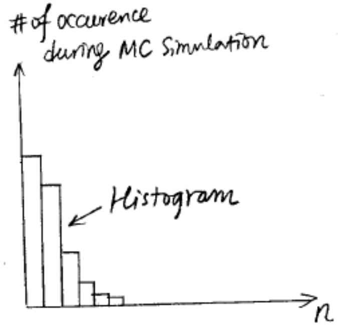
3. $n(\{r_i\})$ is the number of atoms in the largest cluster

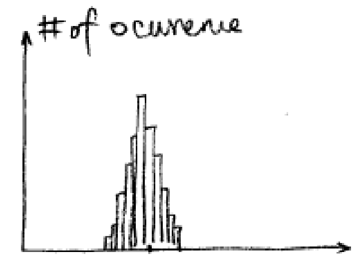
same as in Zuo, Ngan, Zheng, PRL, 94, 095501 (2005)



A slightly modified parameter does not change major results
Ryu, Kang, Cai, J. Mater. Res. 26, 2335 (2011).

Umbrella Sampling for Activation Free Energy

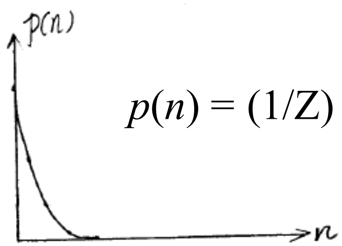




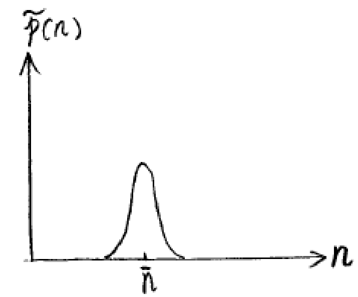
Available from
unbiased simulation

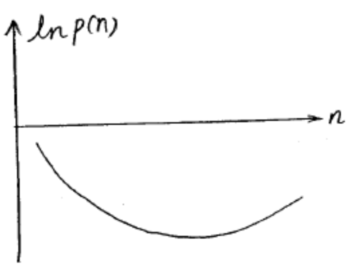
$F(n)$ = -$k_B T$ ln $p(n)$ + const

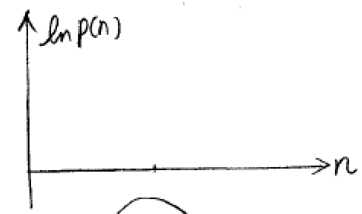
$p(n)$: probability of finding
nucleus of size n



$p(n)$ = (1/Z) exp[-$F(n)/(k_B T)$]



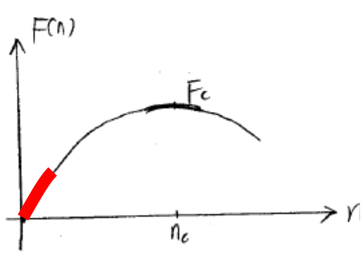


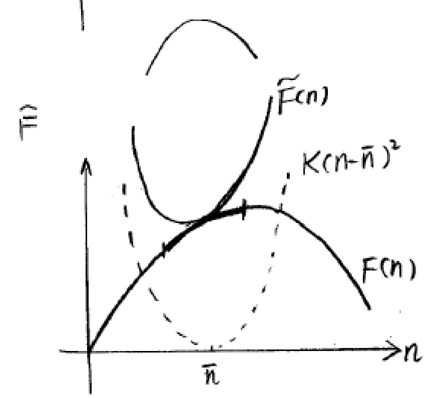


original
potential

$$U^{new}(\{r_i\}) = U^{EAM}(\{r_i\}) + K\cdot(n(\{r_i\}) - \bar{n})^2$$

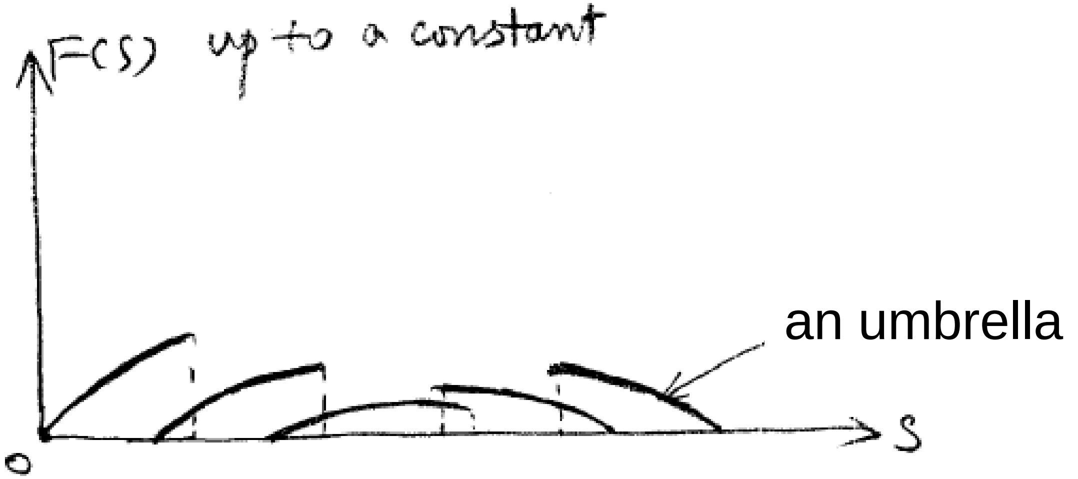
bias
potential

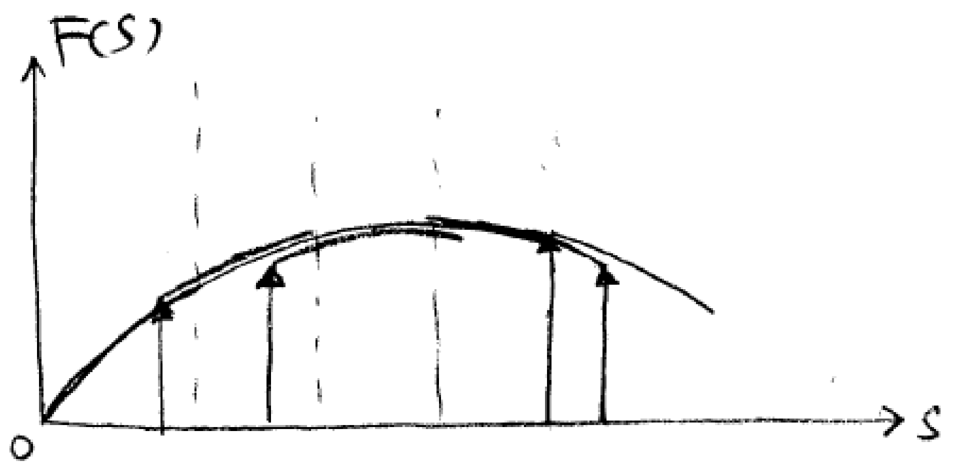




$$F(n) = \widetilde{F}(n) - K\cdot(n - \bar{n})^2$$

Overlapping Umbrellas

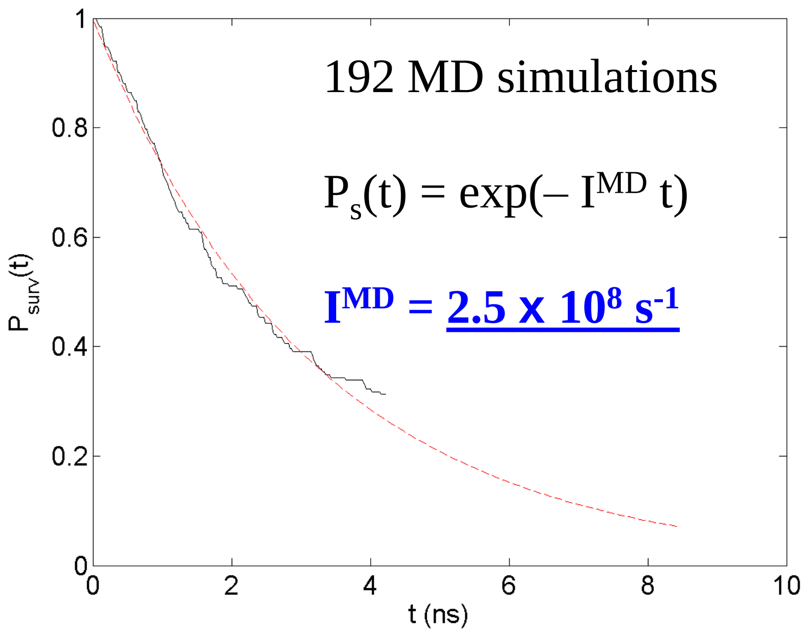




Testing Becker-Döring Theory for Dislocation Nucleation

Benchmark from brute-force MD

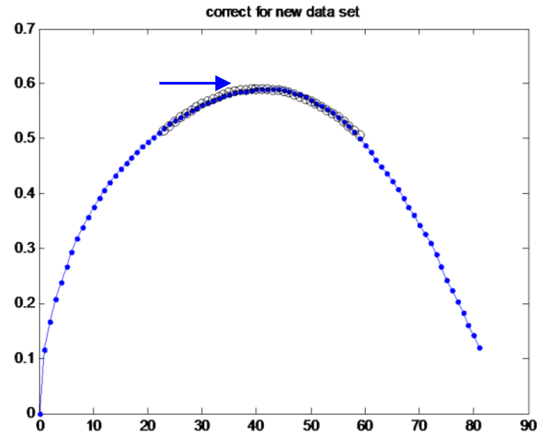
$\gamma_{xy} = 0.135 \quad \sigma_{xy} = 2.16$ GPa $\quad T = 300$ K

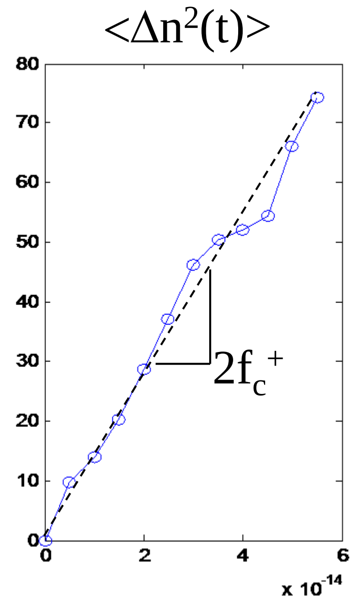


Prediction from Becker-Döring Theory

$$I^{BD} = f_c^+ \Gamma \exp\left(- \frac{F_c(\gamma, T)}{k_B T} \right)$$

rate per nucleation site





$F_c = 0.53$ eV $\quad \Gamma = 0.055$

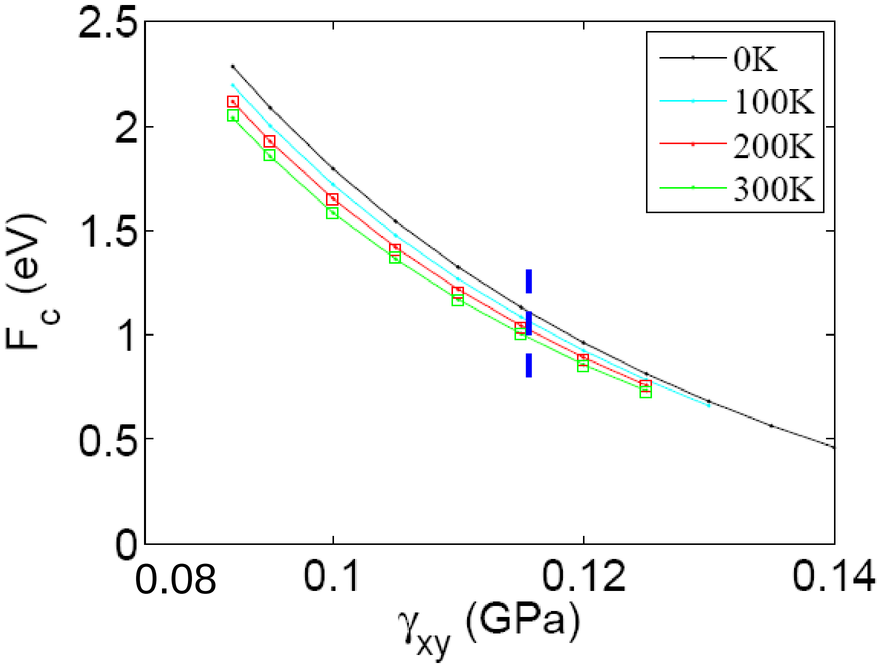
$N_{tot} = 14976$ (atoms)

$f_c^+ = 5.3 \times 10^{14}\ s^{-1}$

$N_{tot}\, I^{BD}$ = 5.5 x 10^8 s^{-1}

$f_c^+ \Gamma = 3 \times 10^{13}\ s^{-1} \sim \nu_D$

Activation Helmholtz Free Energy $F_c(\gamma, T)$



Activation entropy at const γ

$$S_c(\gamma) \equiv -\left.\frac{\partial F_c(\gamma, T)}{\partial T}\right|_{\gamma}$$

describes how fast F_c decreases with T

at constant γ

Activation Entropy at Strain $\gamma = 0.092$

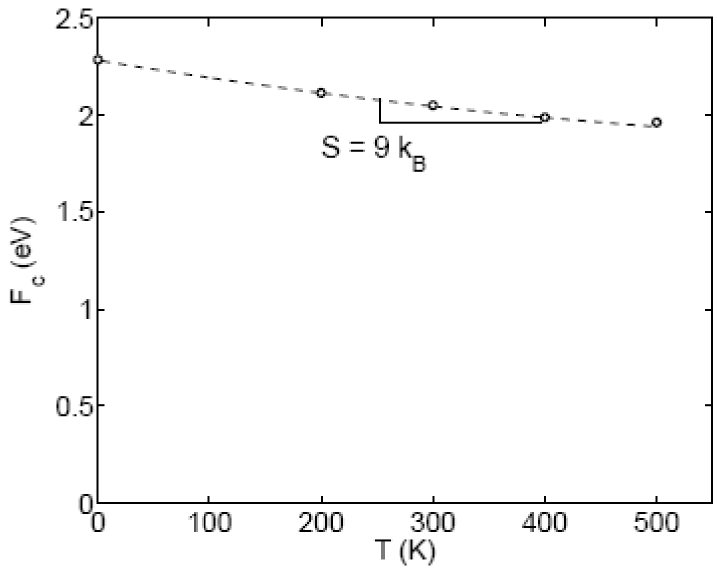
$F_c = E_c - T S_c$

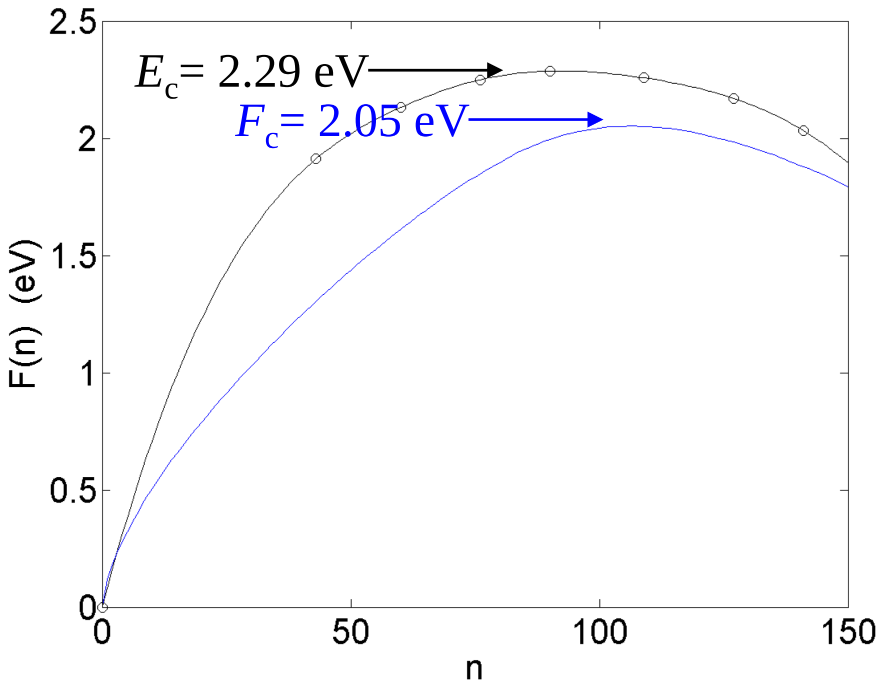
$E_c - F_c = T S_c = 0.24\ \text{eV} \qquad T = 300\ \text{K}$

$\boldsymbol{S_c(\gamma) = 9\, k_B \qquad \exp(S_c(\gamma)/k_B) \sim 10^4}$

$\gamma_{xy} = 0.092 \quad \sigma_{xy} = 2.0\ \text{GPa} \quad T = 0\ \text{K}$

$\gamma_{xy} = 0.092 \quad \sigma_{xy} = 1.8\ \text{GPa} \quad T = 300\ \text{K}$





What is the origin of this activation entropy?

$S_c(\gamma) = 9.0\ k_B$

$\exp(\ S_c(\gamma) / k_B\ ) \sim 10^4$

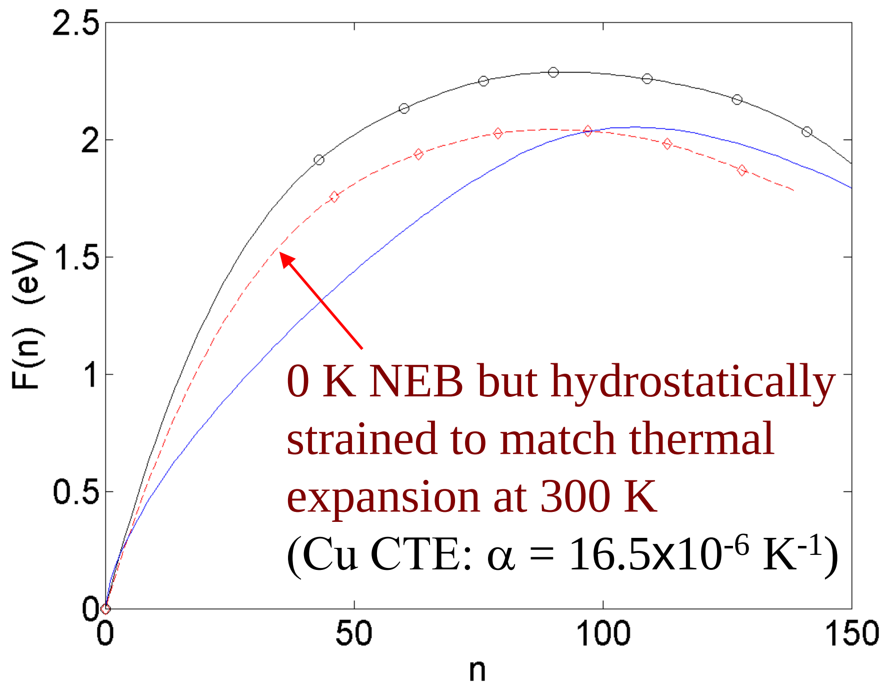
~~Vibrational entropy or~~ (harmonic)

Thermal expansion ? (anharmonic)

- atoms separated further
- interaction becomes weaker
- crystal is easier to shear

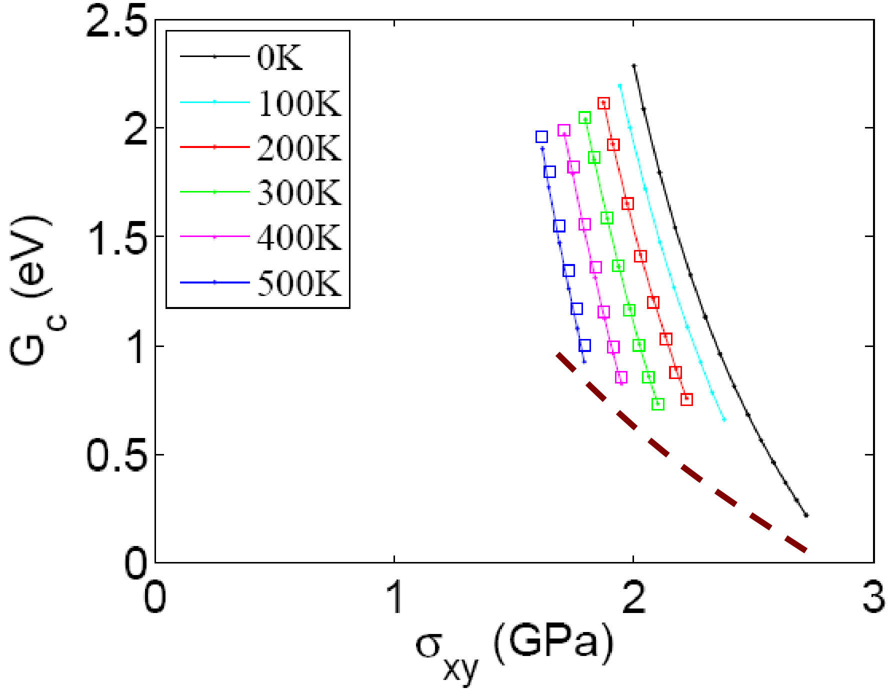
$\gamma_{xy} = 0.092$ $\sigma_{xy} = 2.0$ GPa $T = 0$ K

$\gamma_{xy} = 0.092$ $\sigma_{xy} = 1.8$ GPa $T = 300$ K



$S_c(\gamma)$ may be captured by quasi-harmonic approximation (QHA) for homogeneous nucleation. But this is not easy to do for heterogeneous nucleation

Activation Gibbs Free Energy $G_c(\sigma, T)$



$$G_c(\sigma,T) = F_c(\gamma(\sigma,T),T)$$

J. Mater. Res. 26, 2335 (2011).

Activation entropy at const σ

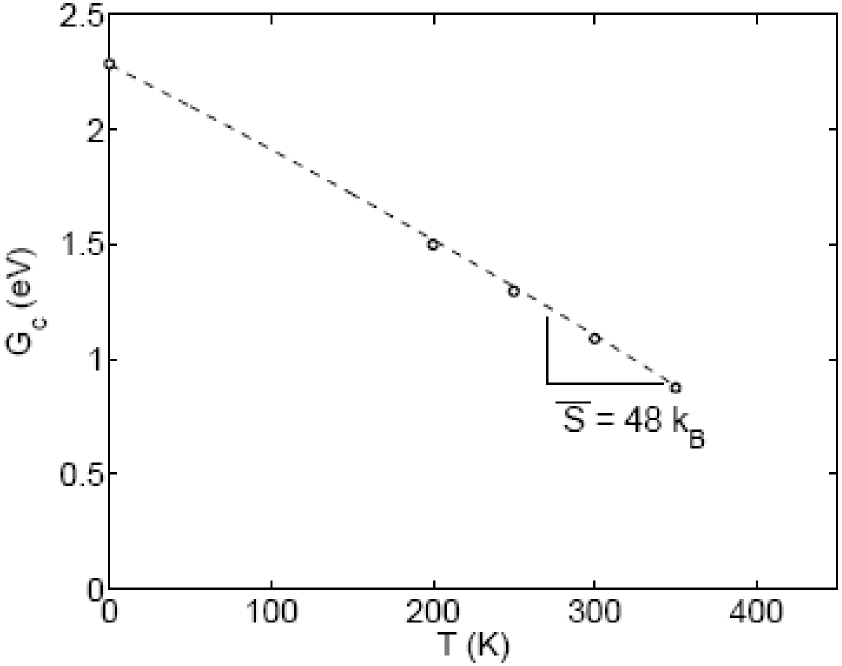
$$S_c(\sigma) \equiv -\frac{\partial G_c(\sigma,T)}{\partial T}\bigg|_\sigma$$

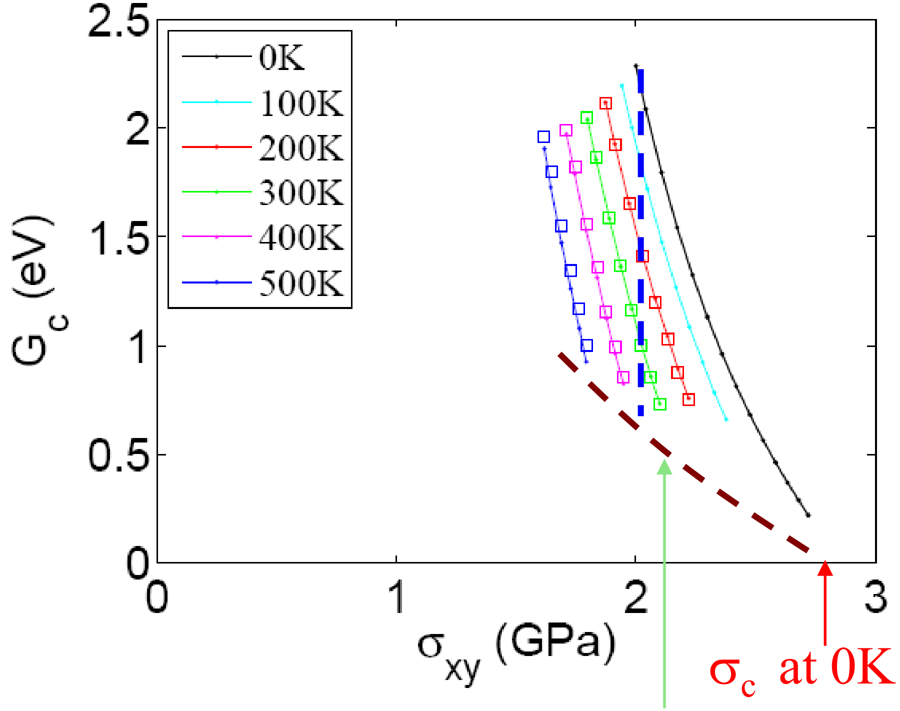
describes how fast G_c decreases with T

at constant σ

Activation Entropy at Stress σ = 2.0 GPa

at σ = 2.0 GPa





$\exp(\, S_c(\sigma) / k_B \,) \sim 10^{20}$ This is enormous!

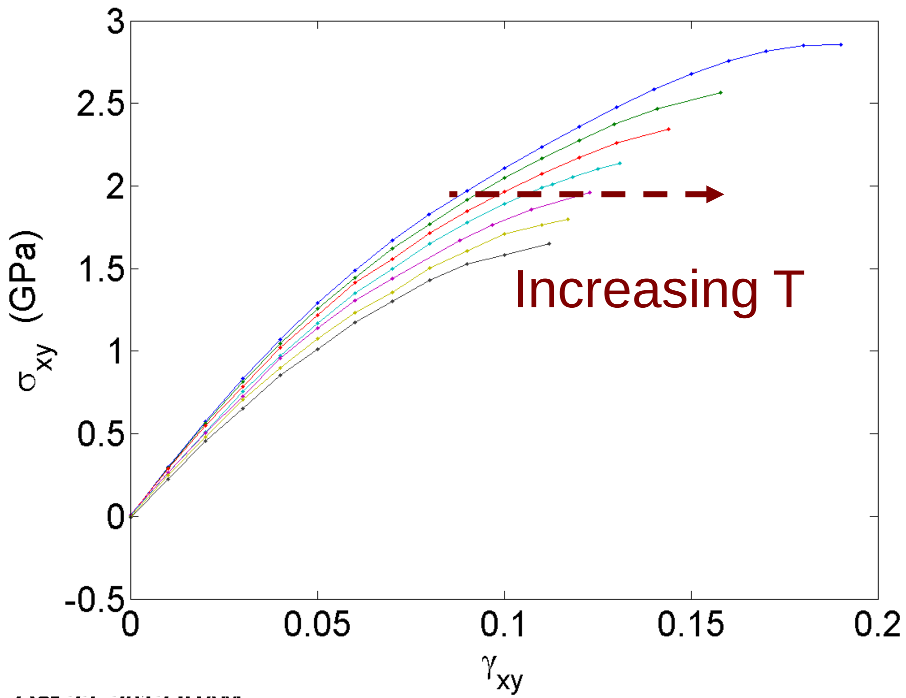
Why is $S_c(\sigma)$ so much larger than $S_c(\gamma)$?

Because $$G_c(\sigma,T) = F_c(\gamma(\sigma,T),T)$$

$$S_c(\sigma) \equiv -\left.\frac{\partial F_c(\gamma(\sigma,T),T)}{\partial T}\right|_\sigma = -\left.\frac{\partial F_c(\gamma,T)}{\partial T}\right|_\gamma - \left.\frac{\partial F_c(\gamma,T)}{\partial \gamma}\right|_T \cdot \left.\frac{\partial \gamma}{\partial T}\right|_\sigma$$

Activation Volume **very large** for disl nuc

$$S_c(\sigma) = S_c(\gamma) - \Omega_c(\sigma) \cdot \left.\frac{\partial \sigma}{\partial T}\right|_\gamma$$



Thermal softening (negative):

at constant σ –

- Increasing T → increases γ
- G_c decreases even faster than when γ is constant

* Another way to see the difference $S_c(\sigma) - S_c(\gamma)$

Legendre transform of each other

$$F_c(\gamma,T) \equiv F(n_c,\gamma,T) - F(n=0,\gamma,T) \qquad G_c(\sigma,T) \equiv G(n_c,\sigma,T) - G(n=0,\sigma,T)$$

$\partial / \partial T$

$$S_c(\gamma,T) = S(n_c,\gamma,T) - S(n=0,\gamma,T) \qquad S_c(\sigma,T) = S(n_c,\sigma,T) - S(n=0,\sigma,T)$$

Entropy is a **state function**, i.e. **independent** of choice of **ensemble**

$$S(n,\gamma,T) = S(n,\sigma,T)$$ for any *n*, as long as $\sigma = \sigma(n,\gamma,T)$

So how can $S_c(\gamma,T) \neq S_c(\sigma,T)$ **?**

* Another way to see the difference $S_c(\sigma) - S_c(\gamma)$

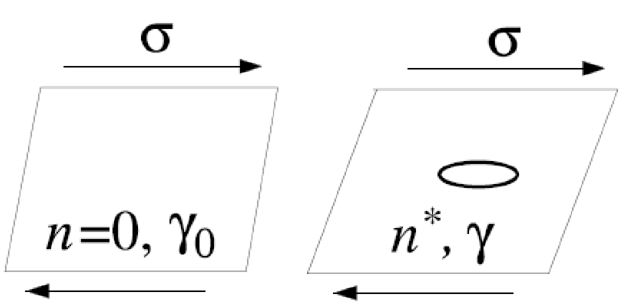
$$F_c(\gamma,T) \equiv F(n_c,\gamma,T) - F(n=0,\gamma,T) \qquad G_c(\sigma,T) \equiv G(n_c,\sigma,T) - G(n=0,\sigma,T)$$

$$S_c(\gamma,T) = S(n_c,\gamma,T) - S(n=0,\gamma,T) \qquad S_c(\sigma,T) = S(n_c,\sigma,T) - S(n=0,\sigma,T)$$

If we choose σ to make these equal

then these two terms won't be equal

Dislocation nucleation changes strain (**plastic strain**) if stress is held constant



$$\sigma(n_c,\gamma,T) = \sigma(n=0,\gamma_0,T)$$

$$S(n=0,\sigma,T) = S(n=0,\gamma_0,T)$$

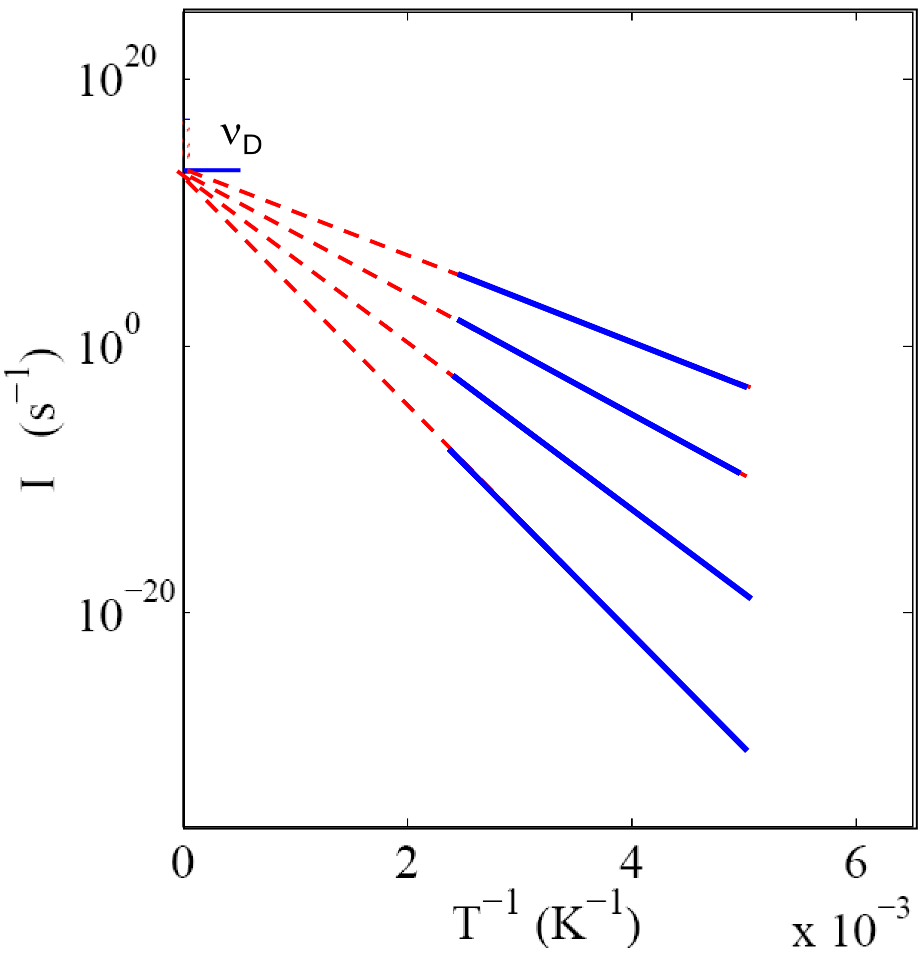
$$S_c(\sigma) - S_c(\gamma) = S(n=0,\gamma,T) - S(n=0,\gamma_0,T)$$

Difference of activation entropies

Entropy difference of perfect crystal at two different strains.

$\gamma - \gamma_0 \sim O(V^{-1})$, $G_c(\sigma) - F_c(\gamma) \sim O(V^{-1})$, yet $S_c(\sigma) - S_c(\gamma) = -\Omega_c(\sigma) \cdot \left.\frac{\partial \sigma}{\partial T}\right|_\gamma$

What is the meaning of the activation entropy?



Arrehnius plot of nucleation rate if activation entropies were zero

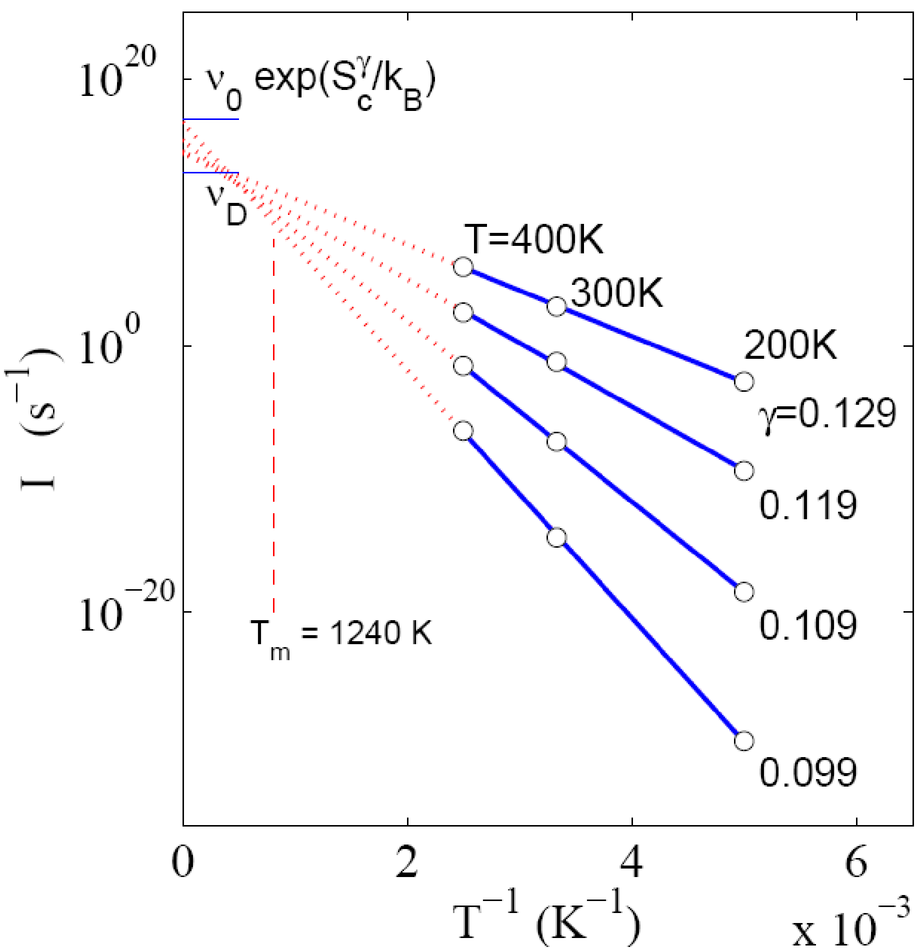
$$\ln I^{NUC} = \ln v_D - \frac{E_c(\gamma)}{k_B} \cdot \frac{1}{T}$$

$$I^{NUC} = v_D \exp\left(-\frac{E_c(\gamma)}{k_B T}\right)$$

$$I^{NUC} = v_D \exp\left(-\frac{H_c(\sigma)}{k_B T}\right)$$

Arrhenius plots of homogeneous nucleation rate

constant strain γ



$$\ln I^{NUC} = \ln \nu_D - \frac{E_c(\gamma)}{k_B}\cdot\left(\frac{1}{T} - \frac{1}{2T_m}\right)$$

$$I^{NUC} = \nu_D \exp\left(\frac{E_c(\gamma)}{2k_B T_m}\right)\exp\left(-\frac{E_c(\gamma)}{k_B T}\right)$$

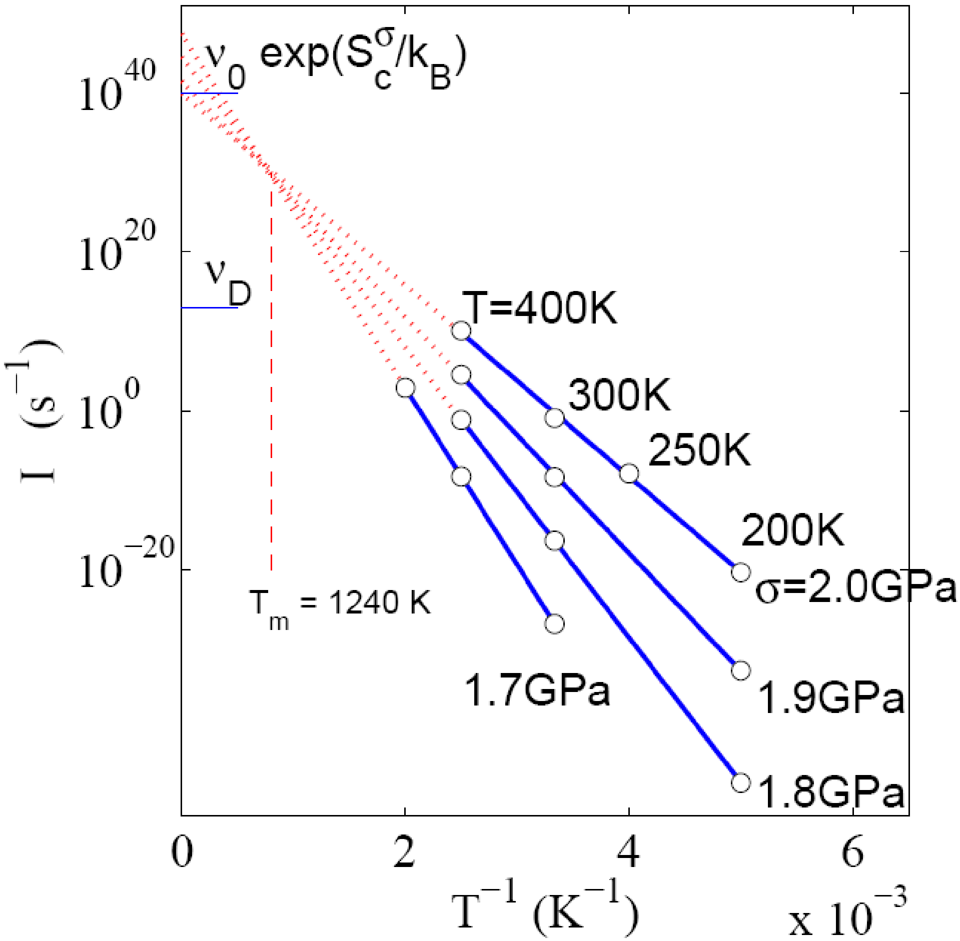
$$S_c(\gamma) = \frac{E_c(\gamma)}{2T_m}$$

Thermodynamic compensation law
Nature 243, 400 (1973).
or
Meyer-Nedel rule

"activation entropy is proportional to activation energy"

Arrhenius plots of homogeneous nucleation rate

constant strain σ



$$\ln I^{NUC} = \ln \nu_D + \hat{C} - \frac{H_c(\sigma)}{k_B} \cdot \left(\frac{1}{T} - \frac{1}{T_m} \right)$$

$$I^{NUC} = \nu_D \exp\left(\hat{C} + \frac{H_c(\sigma)}{2k_B T_m} \right) \exp\left(-\frac{H_c(\sigma)}{k_B T} \right)$$

$$S_c(\sigma) = \hat{C} + \frac{H_c(\sigma)}{k_B T_m}$$

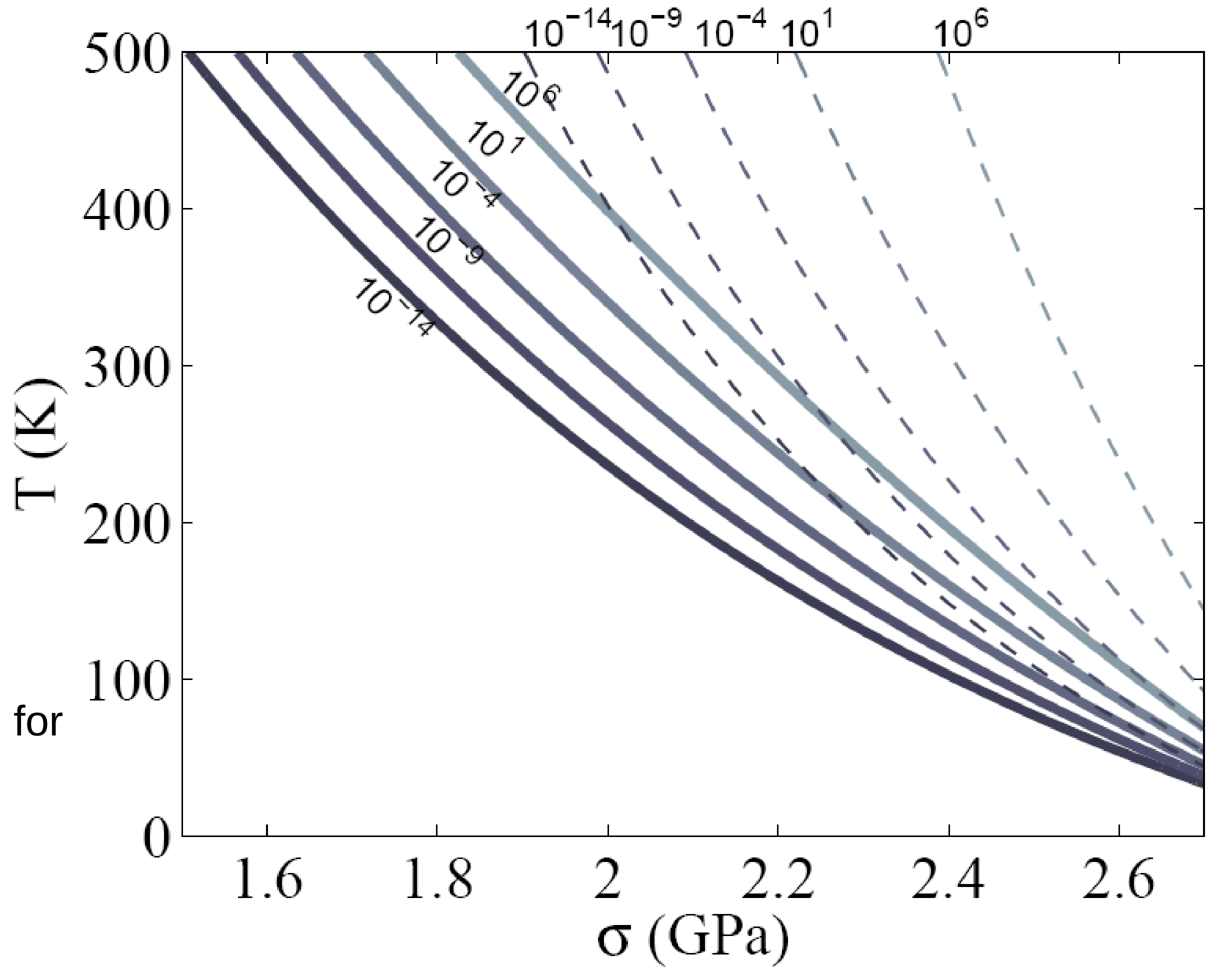
Thermodynamic compensation law

violated due to a large constant C

What is the physical consequence of activation entropy?

Contour plots of

Homogeneous nucleation rate



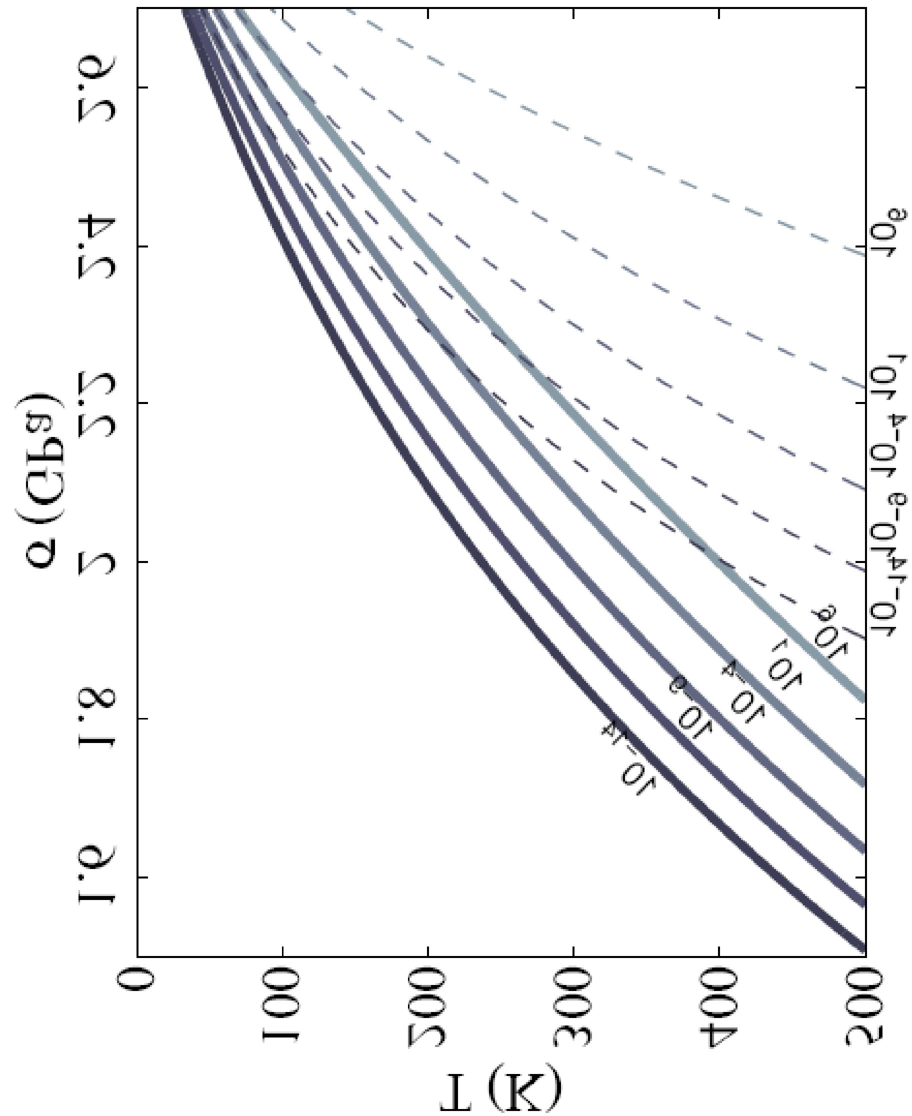
entropy accounted for

entropy ignored

What is the physical consequence of activation entropy?

Contour plots of

Homogeneous nucleation rate

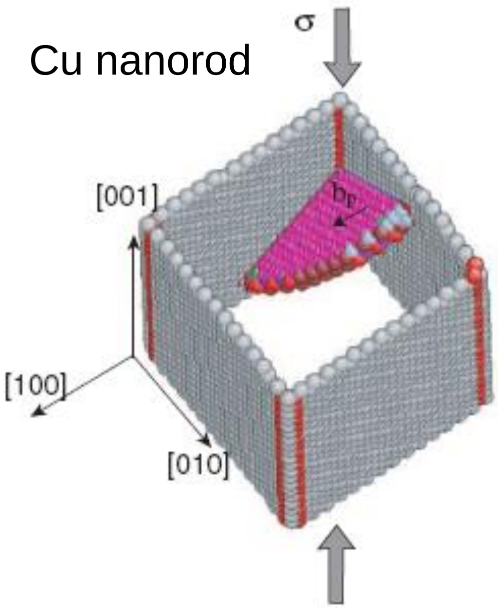


—— entropy accounted for

- - - - entropy ignored

Heterogeneous Nucleation

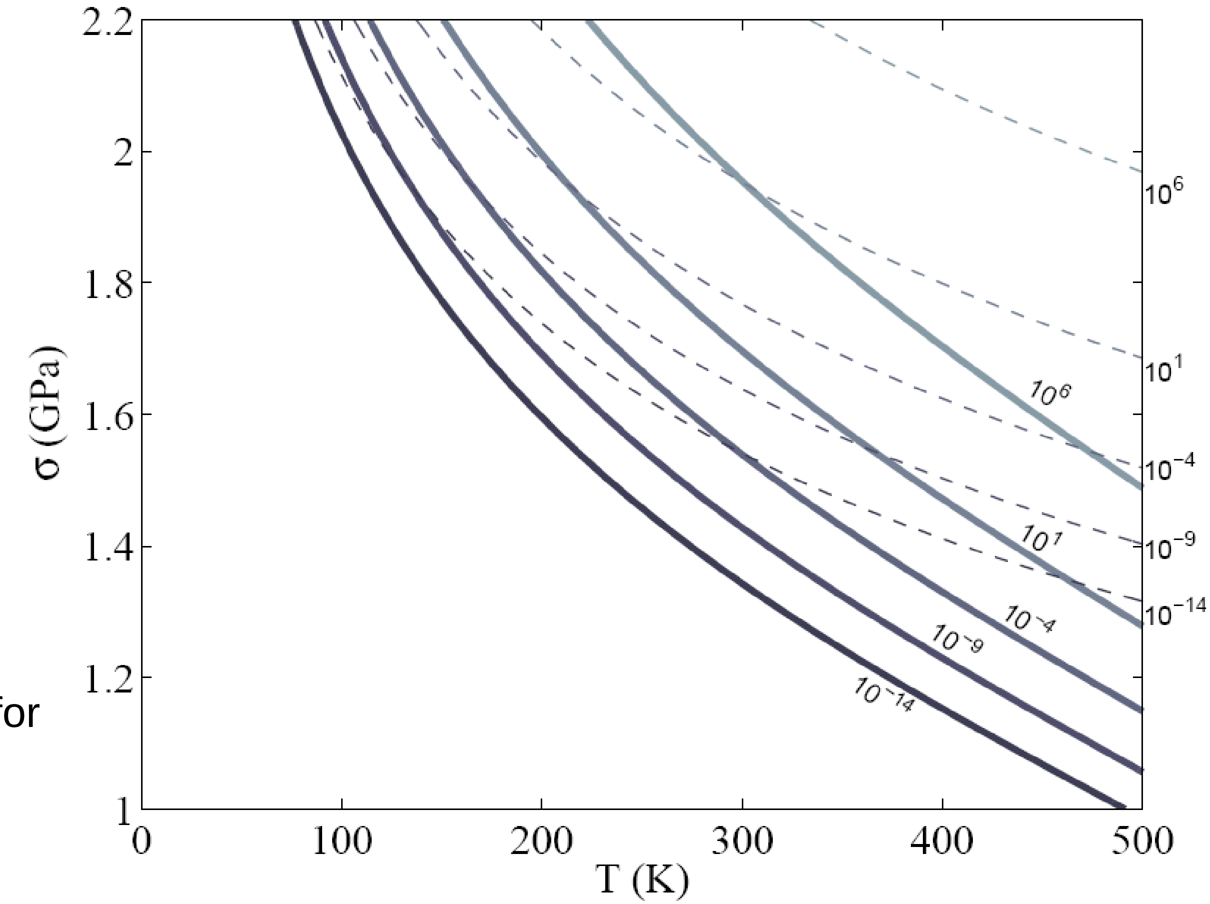
Cu nanorod



entropy accounted for

entropy ignored

Contour lines of nucleation rate (s^{-1})



Summary – two huge activation entropies!

- Rate predicted by Becker-Döring theory matches well with MD
- Very large entropy contribution $S_c(\sigma) \sim 48\ k_B$

  - Thermal expansion (weakens bond) $S_c(\varepsilon) \sim 9\ k_B$
  - Thermal softening (same σ produce larger γ at higher T)

  } **Anharmonic effects**

- Entropic contribution to nucleation rate cannot be ignored

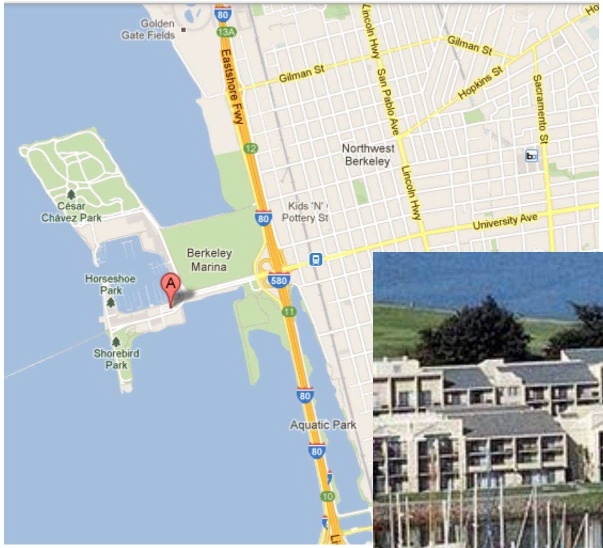
Ryu, Kang, Cai, Proc. Natl. Acad. Sci. USA 108, 5174 (2011).

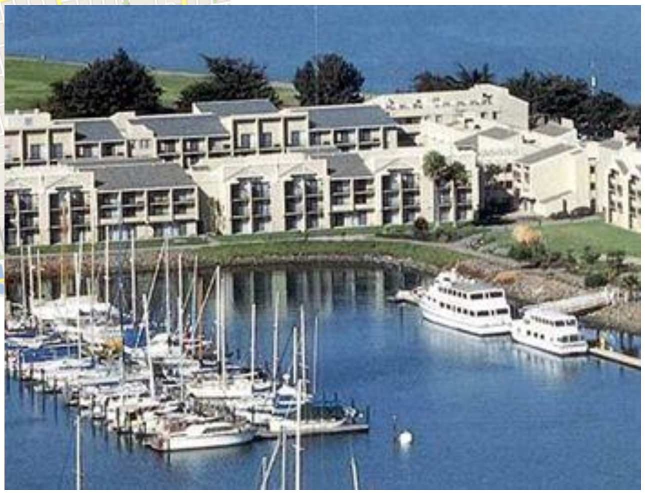
J. Mater. Res. 26, 2335 (2011).

MMM2014 San Francisco Bay Area

Tentative date: October 6-10, 2014

Tentative location: Berkeley Marina
Hilton Double Tree





Wei Cai
(chair)

co-organizers

Vasily Bulatov   Tom Arsenlis

Giulia Galli   Andy Minor

Coming soon:
Call for symposium organizers