Study of Intermetallic Nanostructures for Light-Water Reactor Materials

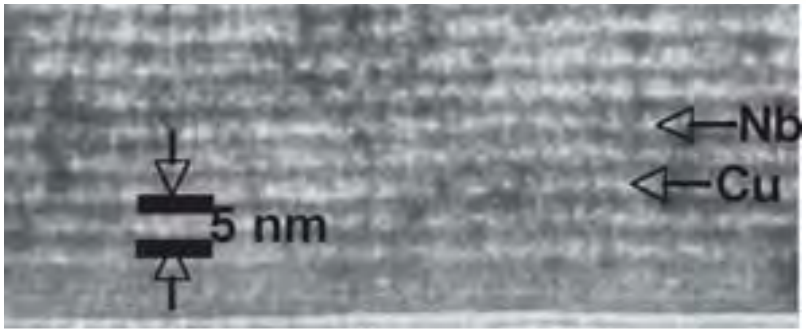
M. Asta, *B. Beeler*, P. Hosemann, N. Grønbech-Jensen, S.A. Maloy

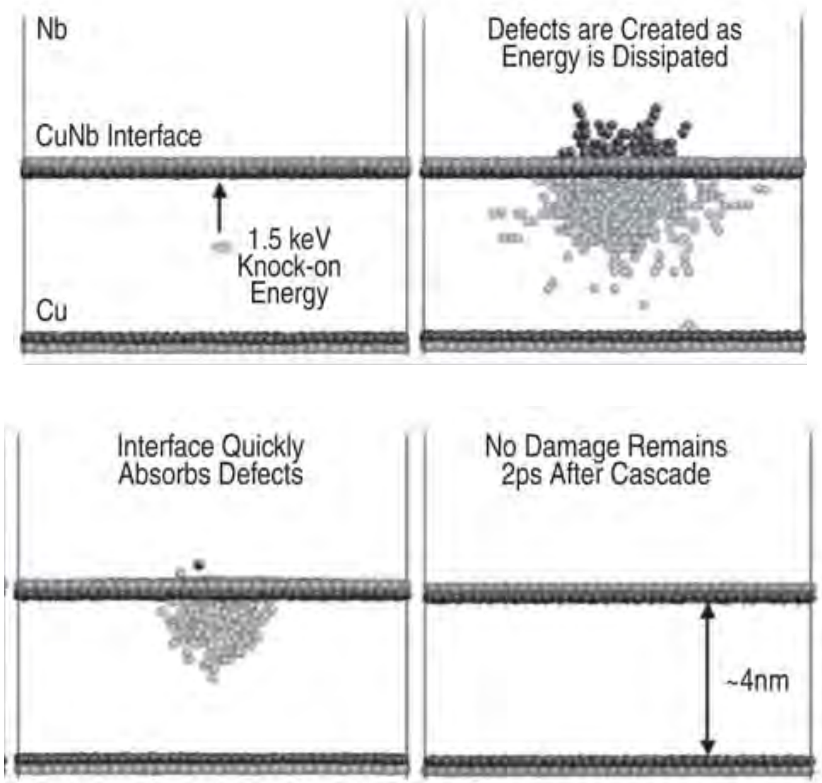
University of California - Berkeley
University of California - Davis
Los Alamos National Laboratory

OUTLINE

- The idea/concept (pursuing interfaces as sinks for defects)
- Requirements for a new intermetallic forming steel in nuclear environment (simple manufacturing, reduced cost, good properties)
- Aging and heat treatment evaluation of the intermetallic forming steels
- Radiation damage study. The beginning.
- Theoretical work (broad development of tools with specific directed applications: algorithms, potentials, simulations)
- Future plans

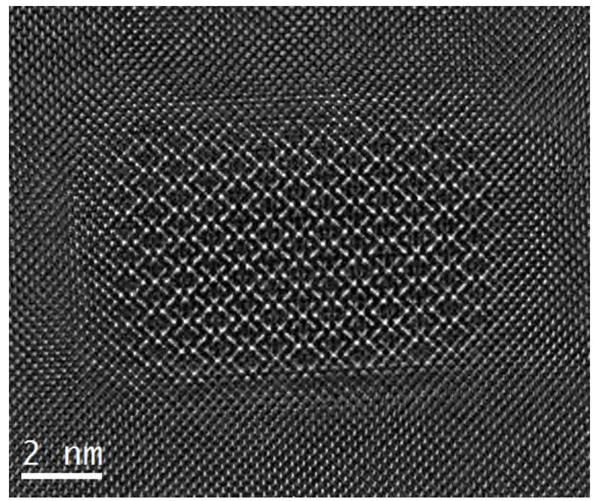
The idea





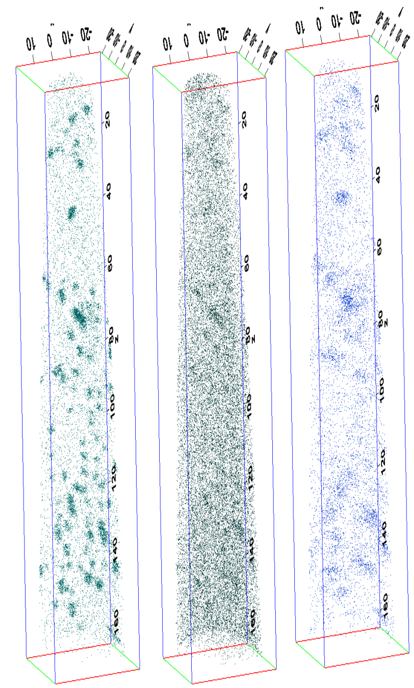
Amit Misra & Mike Demkowicz, JOM

Radiation tolerant materials are materials with high interface density.
Cu/Nb layered interfaces or ODS alloys have been studied for decades.



HR TEM image of MA957

TiO Ti O

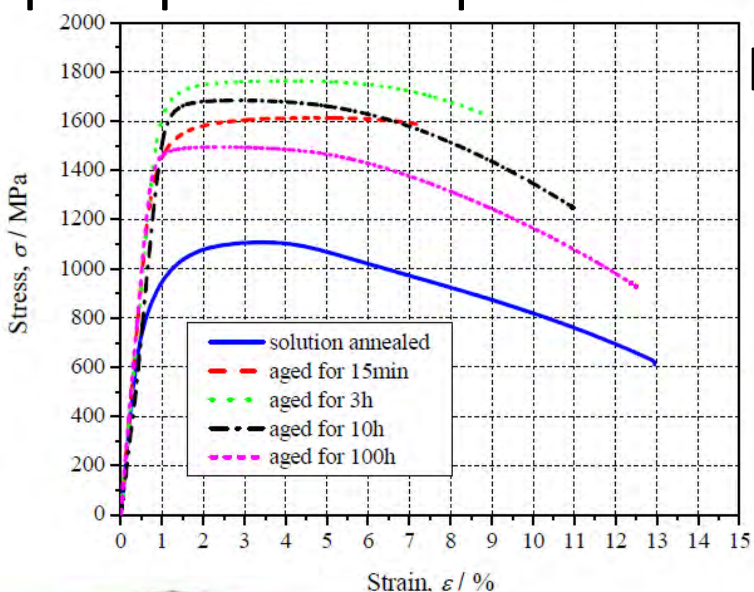


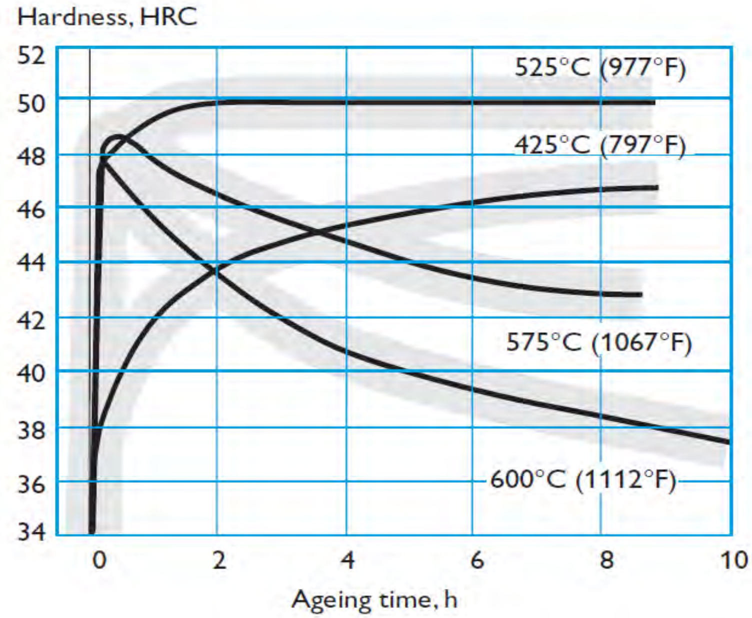
AtomProbeTomography data on MA957

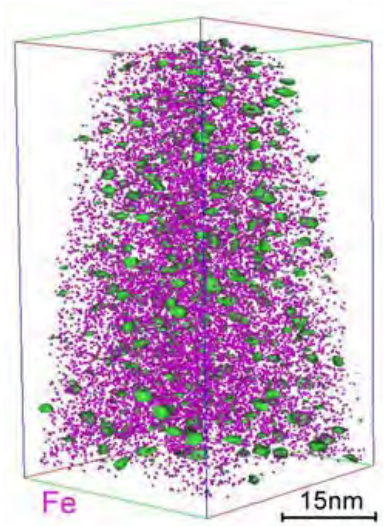
What about intermetallic's??

Intermetallic forming steels

Mar(tensite)aging steels are known to form NiAl and Ni_3Al precipitates at specific heat treatments leading to extraordinary properties







Green: NiAl
Red: Fe
Also Cr

APT measurement by M. Schober et al. Univ. of Leoben, Austria NiAl precipitates shown green

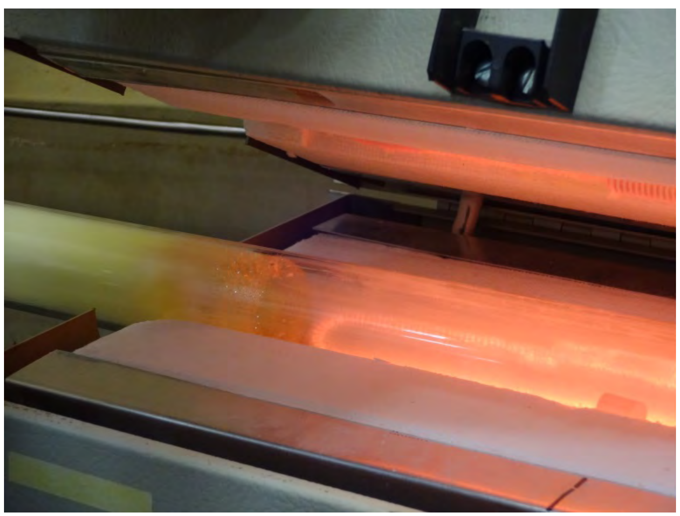
Corrax

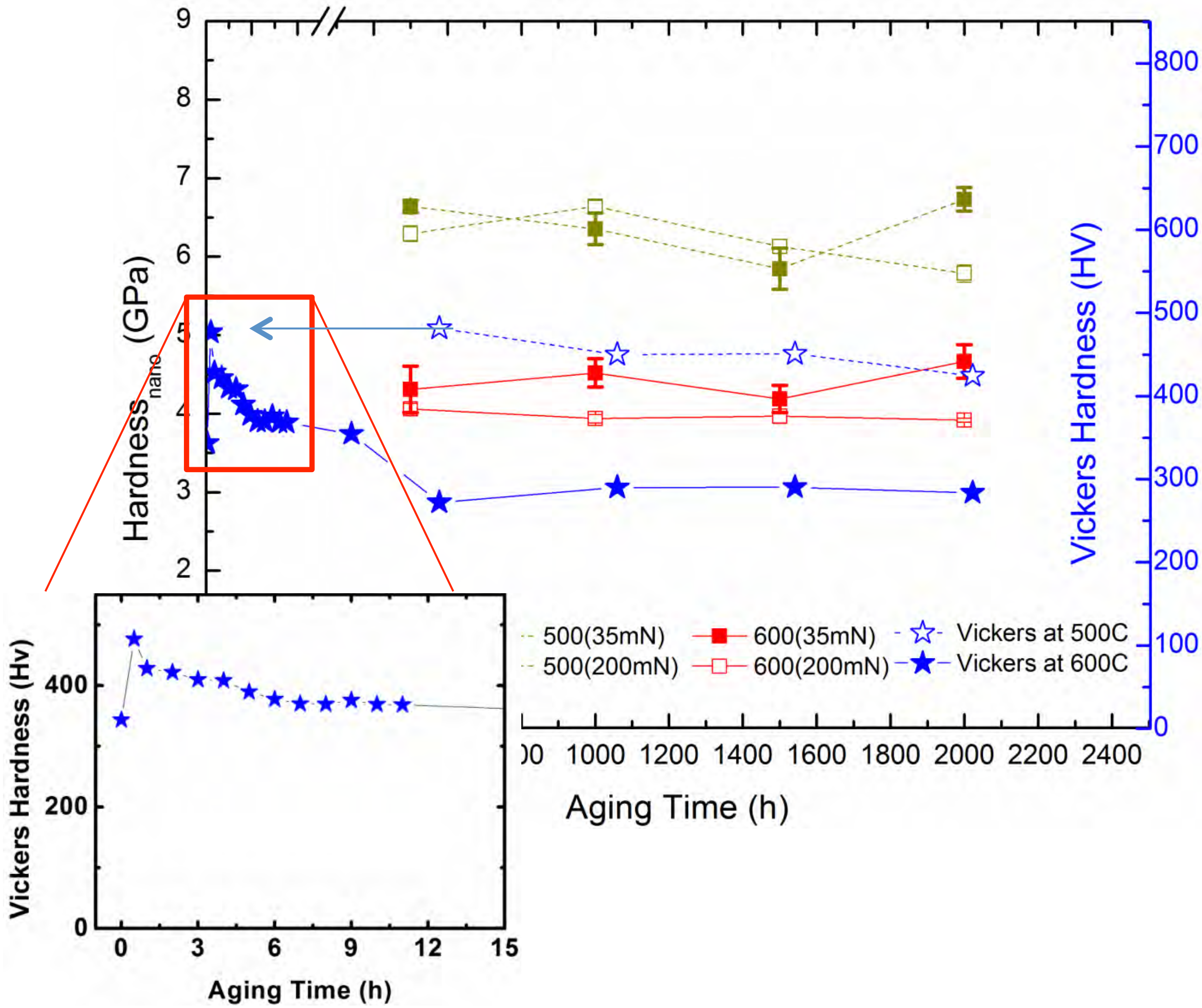
Typical analysis %	C 0,03	Si 0,3	Mn 0,3	Cr 12,0	Ni 9,2	Mo 1,4	Al 1,6
Delivery condition	Solution treated to ~34 HRC						
Colour code	Black/grey						

Requirements for new materials

Stability under radiation	→ radiation damage studies
Stability at high elevated temperatures for an extended period of time.	→ Aging studies
Understanding the precipitation in relevant environments	→ Aging studies
Reasonable strength,	→ Mechanical properties
Reasonable elongation/ ductility	→ Mechanical properties
Reasonably low activation in a neutron environment	→ Co free materials

Experimental work performed on long term aging



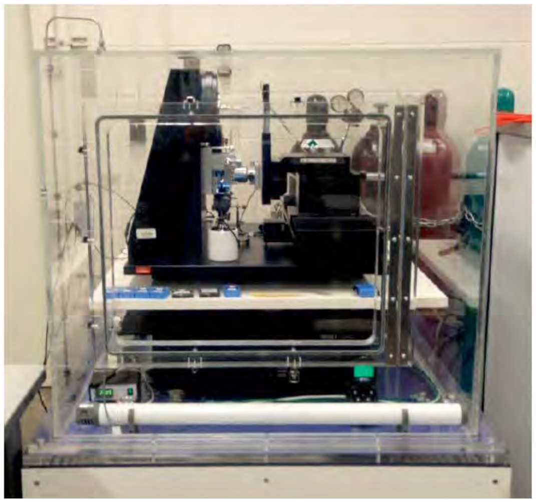


35mN and 200mN nanoindentation results

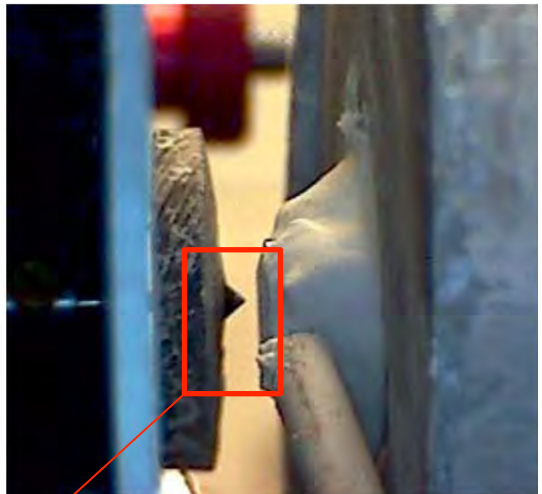
Vickers measured with 200g load (HV0.2)

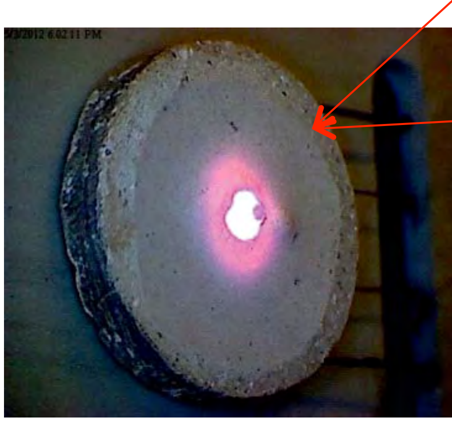
Experimental work performed on heat treatments

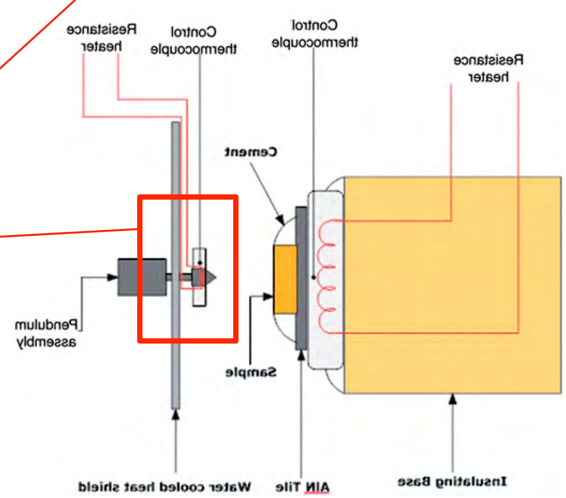
Hardness testing at temperature allows to evaluate the property of the material at operation condition



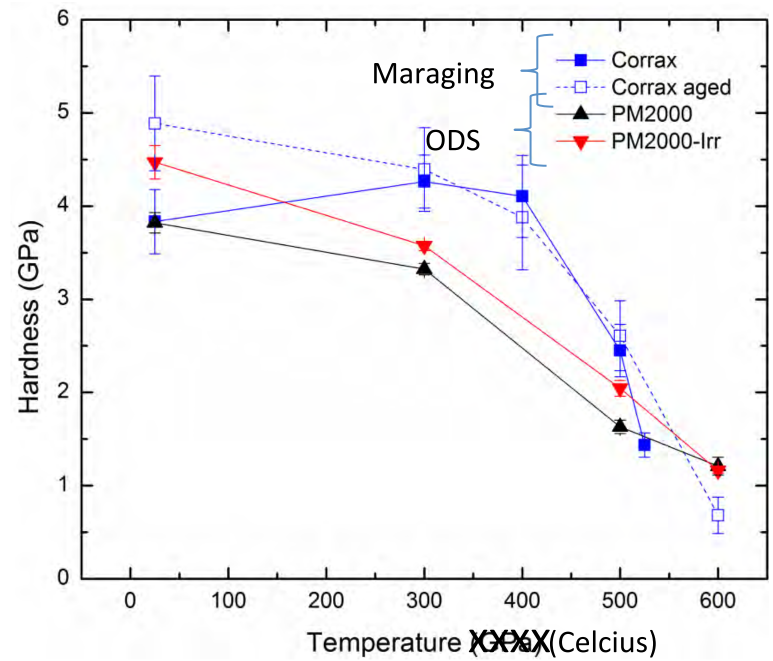
Nanoindeter at UCB



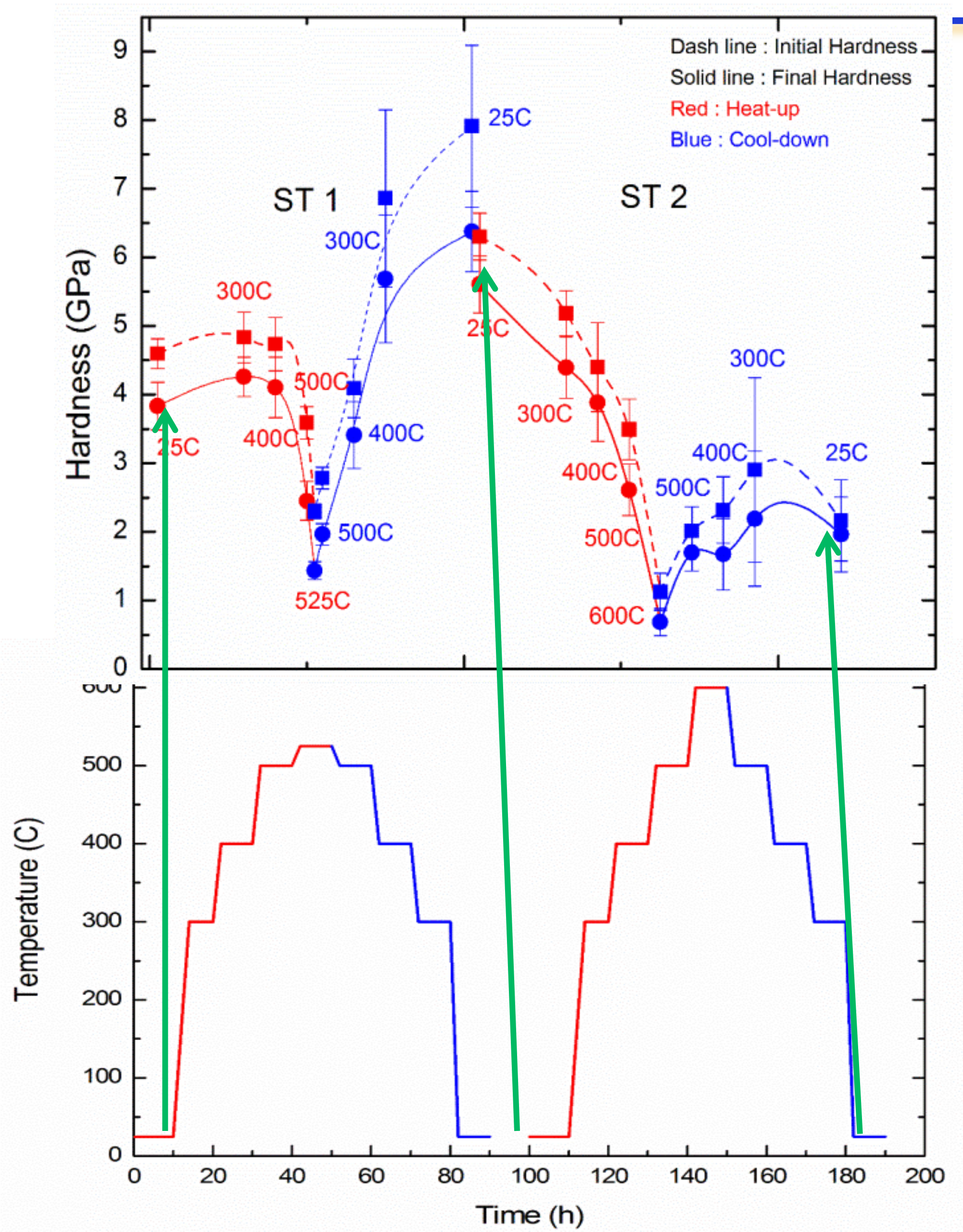




Hardness measurement at temperature



Experimental work performed on heat treatments



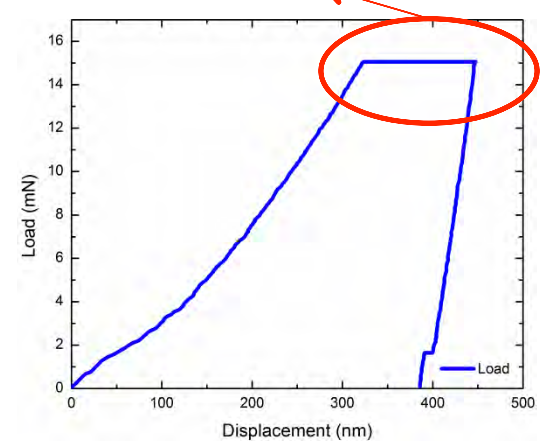
Material softens at temperatures above 400C rapidly.

The hardness at the end of the heat treatment is significantly higher than at the beginning.

The hardness after 600C heat is reduced due to over aging of the material.

Therefore service temperature above 400C is not desirable. Ongoing long term aging study at 400-450C

The indentation hardness might also allow the analysis of creep



Experimental work performed on ion beam irradiation

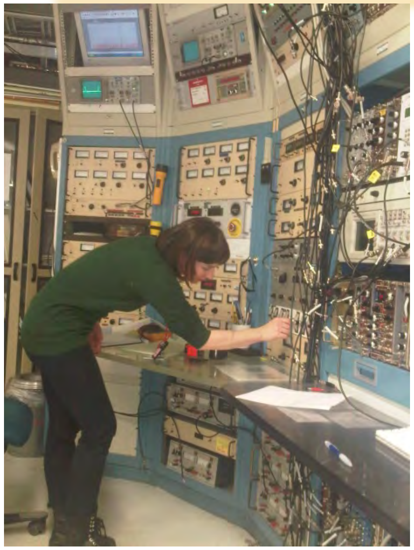
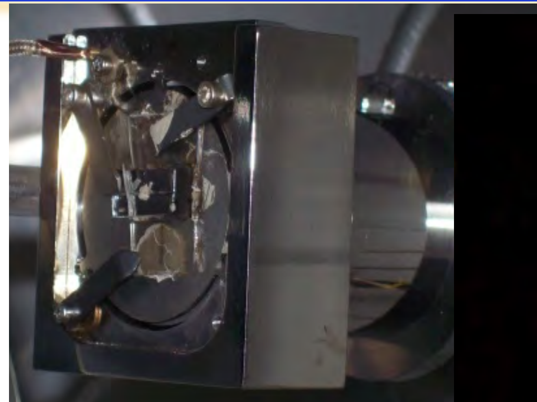
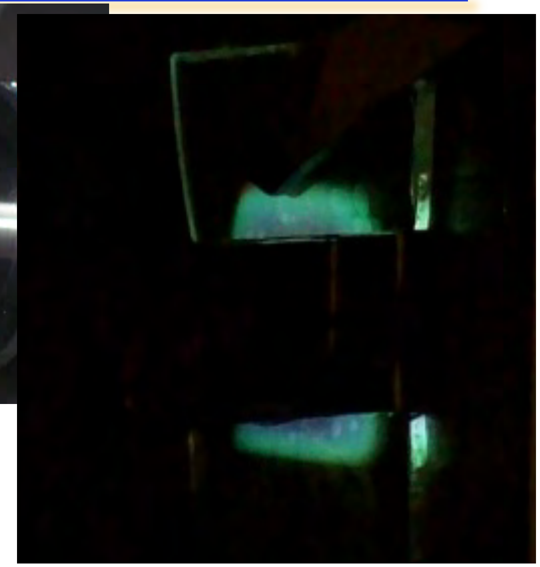


Figure 4: A UCB student refocusing the beam at the IBML facility at LANL

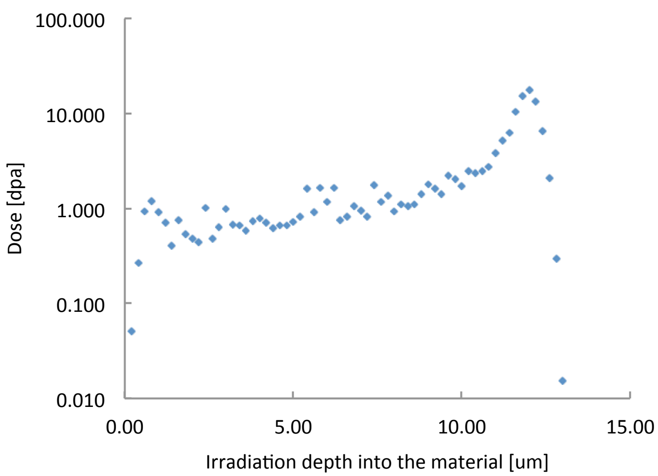
Sample holder paper burn





Sample in beam

Dose calculations on SRIM

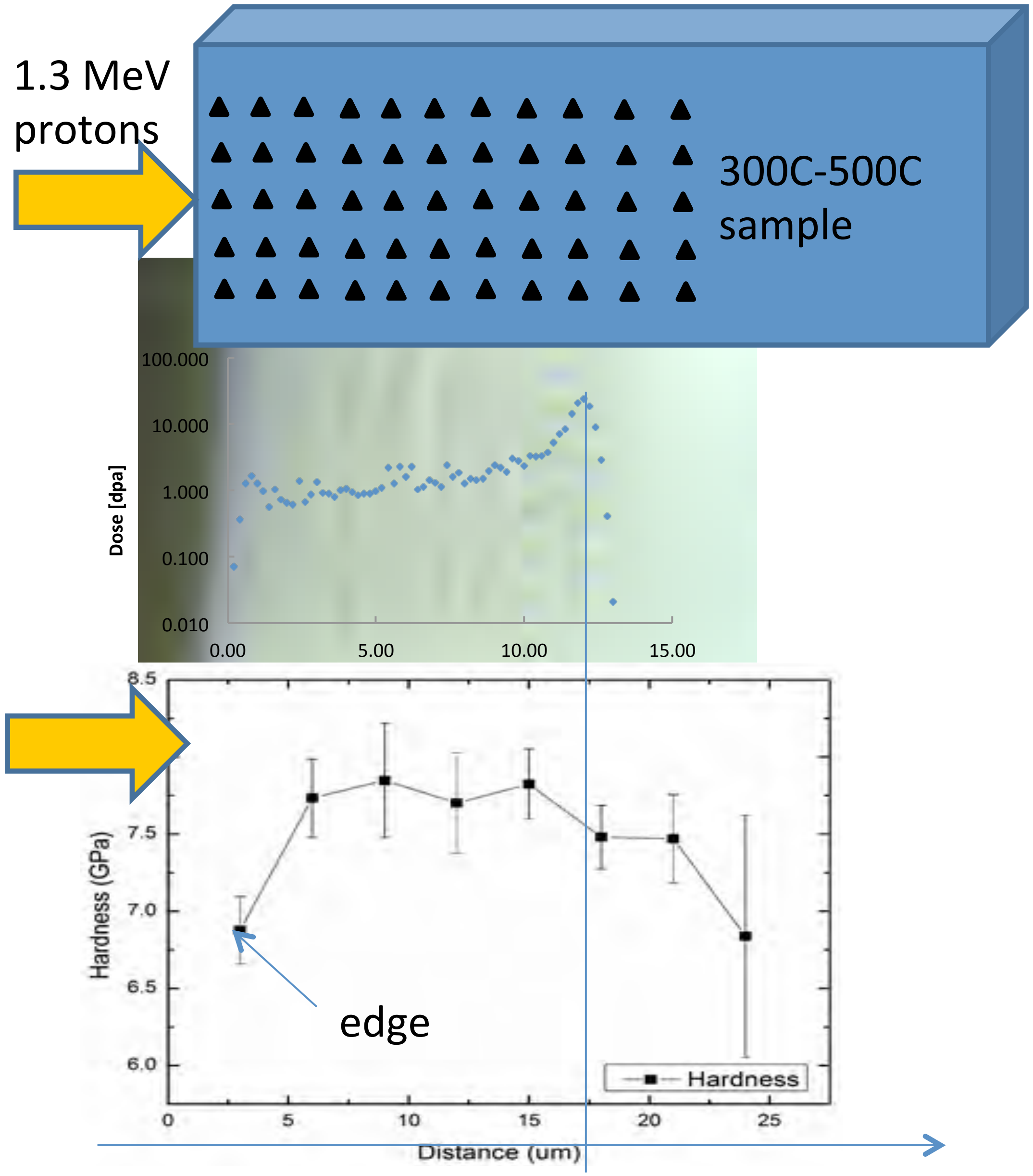


2 irradiations on a total of 4 samples were carried out at this point.

300C 1dpa. However, it was found that the new sample holder designed for high temperature overheated the sample and the irradiation temperature actual was more like 500C.

A second irradiation with 3 different aged materials was conducted to the same dose but with more precise temperature control at 300C.

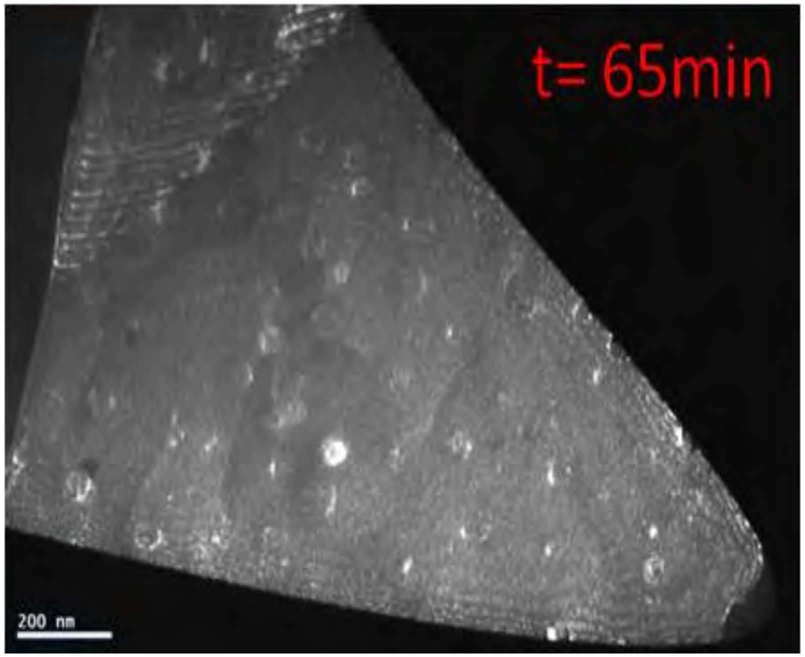
Experimental work performed on ion beam irradiation

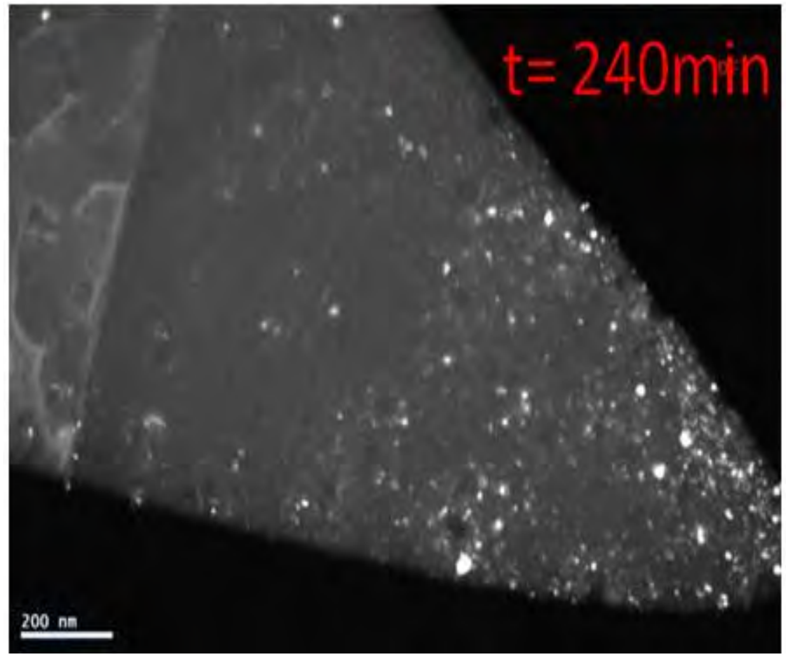


It was found that due to the faulty holder the irradiation temperature was not 300C but more likely 500C. The bulk hardness of 7GPa and a subsequent separate temperature calibration experiment confirm this.

It was found that the 1dpa irradiated zone at ~500C caused a hardening from 3.5GPa to 7.8 GPa. This is close to the peak hardening observed at 525C aging. The bulk hardness stayed at 7GPa. The ion beam effect caused a 0.8 GPa hardness increase.

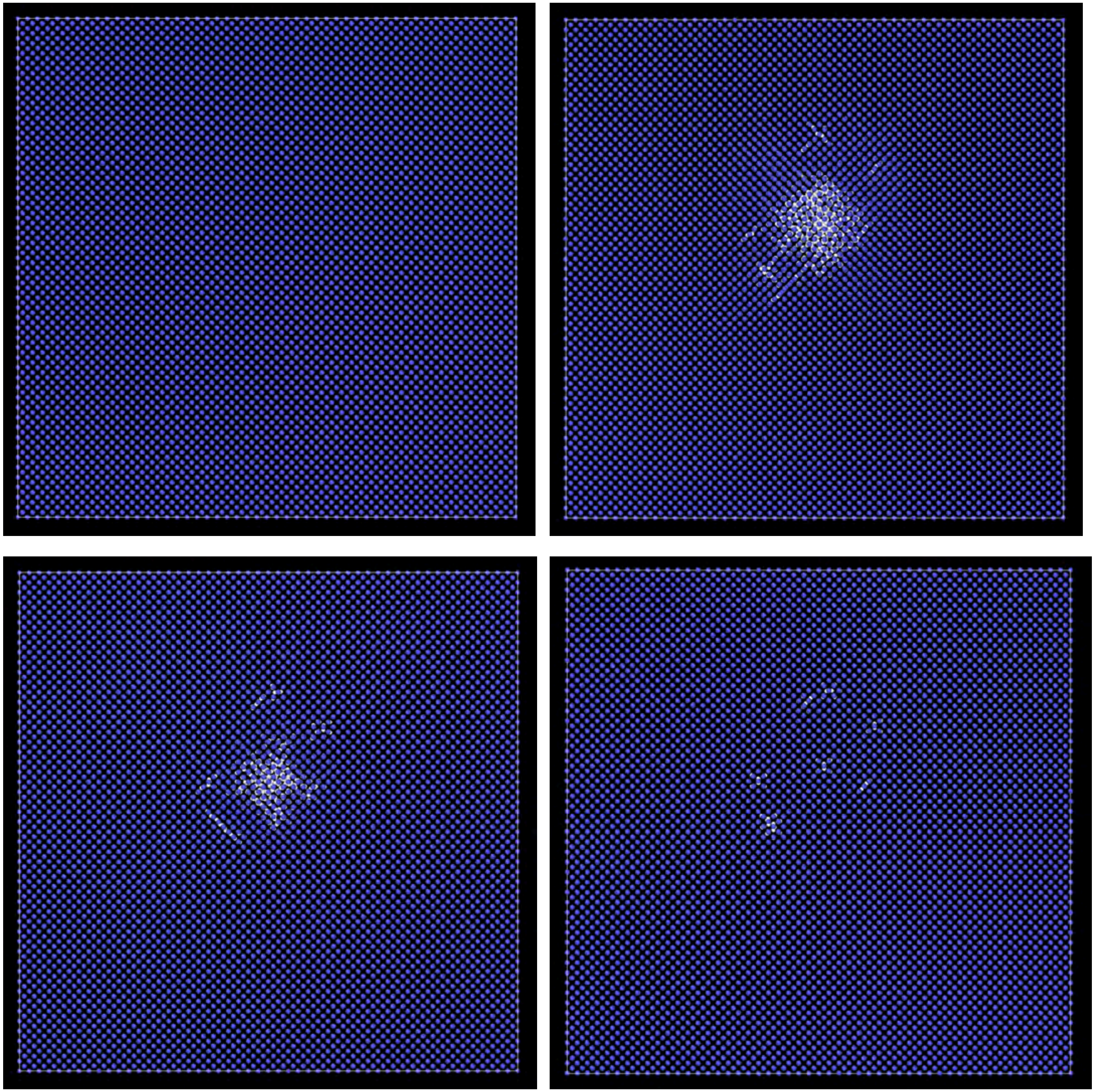
Experimental work performed on in situ ion beam irradiation at HVEM





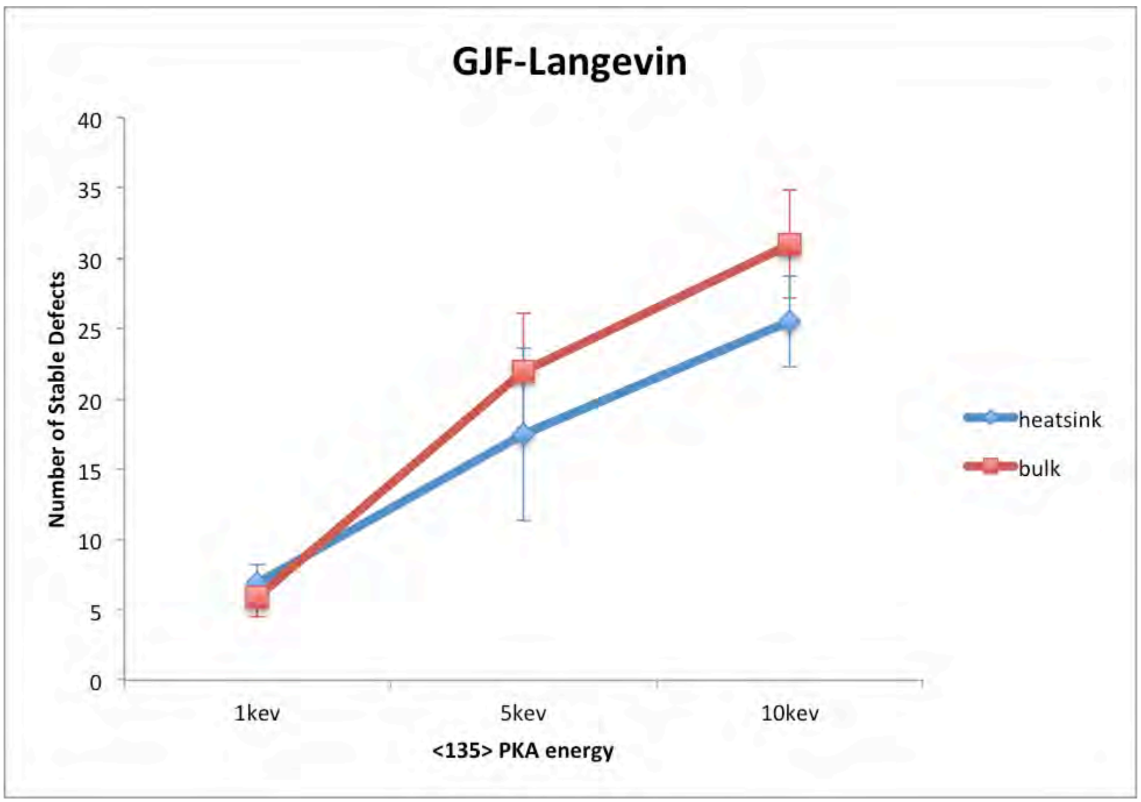
DF-TEM image of the material CORRAX after 65min of irradiation and 240 minutes of irradiation with Kr ions at 500C (exact dose still evaluated). Small white dots (radiation induced precipitates) while other precipitates already pre-exist.

Experiment performed at ANL



Objective of Theory and Simulations

- Electronic structure calculations for the development of Fe-Ni-Al-Fe potentials
- Understand the stability of interfaces and precipitates
  Thermal and Radiation studies
- Inclusion of Electronic Stopping and Inelastic Collisions
- ``Byproduct'': New algorithms for general use in Materials Modeling
  New, improved Thermostat and Barostat for extended simulations



PKA simulation of long-lived resulting lattice defects with LAMMPS, Including the NEET-developed G-JF Thermostat

Relevant physical systems – Newtonian dynamics

Self-contained systems:

$$m_i \frac{d^2 r_i}{dt^2} \;=\; -\nabla_i U(\{r_j\}) \;=\; f_i$$

Ensembles of second order deterministic differential equations:

- Planetary motion, cosmology, Atomic and Molecular Dynamics
- Ballistic motion
- (coupled) oscillator systems, including hyperbolic PDEs

Properties include Energy, (Angular) Momentum conservation.

Noisy systems with hidden degrees of freedom:

$$m_i \frac{d^2 r_i}{dt^2} + \alpha_i \frac{dr_i}{dt} \;=\; -\nabla_i U(\{r_j\}) + \eta_i(t) \;=\; f_i + \eta_i(t)$$

Ensembles of second order stochastic differential equations:

- Atomic and Molecular systems coupled to, e.g., heat bath
- Diffusive motion
- (coupled) oscillator systems, including hyperbolic PDEs

Properties include equilibrium / Boltzmann distribution.

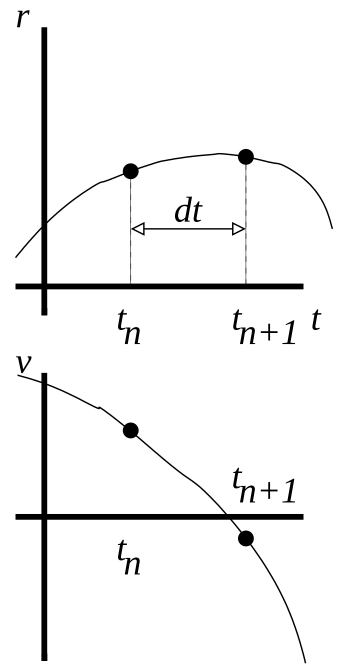
Discretizing time – Approximating the derivatives

$$\begin{aligned} v^{n+1} &= v^{n+\frac{1}{2}} + \frac{dt}{2} a^{n+\frac{1}{2}} + \frac{dt^2}{8} \dot{a}^{n+\frac{1}{2}} + \mathcal{O}(dt^3) \\ v^{n} &= v^{n+\frac{1}{2}} - \frac{dt}{2} a^{n+\frac{1}{2}} + \frac{dt^2}{8} \dot{a}^{n+\frac{1}{2}} + \mathcal{O}(dt^3) \end{aligned}$$

$$\Rightarrow \quad v^{n+1} = v^n + dt\, a^{n+\frac{1}{2}} + \mathcal{O}(dt^3)$$

$$\begin{aligned} a^{n+1} &= a^{n+\frac{1}{2}} + \frac{dt}{2} \dot{a}^{n+\frac{1}{2}} + \mathcal{O}(dt^2) \\ a^{n} &= a^{n+\frac{1}{2}} - \frac{dt}{2} \dot{a}^{n+\frac{1}{2}} + \mathcal{O}(dt^2) \end{aligned}$$

$$\Rightarrow \quad a^{n+\frac{1}{2}} = \frac{1}{2}(a^n + a^{n+1}) + \mathcal{O}(dt^2)$$



$$\Rightarrow \underbrace{\left\{ \begin{aligned} r^{n+1} &= r^n + dt\, v^n + \frac{dt^2}{2m} f^n \\ v^{n+1} &= v^n + \frac{dt}{2m}(f^n + f^{n+1}) \end{aligned} \right.}_{\text{velocity explicit Verlet}} + \mathcal{O}(dt^3)$$

Noisy systems:

$$
\begin{aligned}
m\frac{d^2r}{dt^2}+\alpha\frac{dr}{dt} &= f(t,r)+\eta(t) \quad , \qquad \alpha > 0 \\
\langle \eta(t) \rangle &= 0 \\
\langle \eta(t)\eta(t') \rangle &= 2\alpha k_B T \delta(t-t')
\end{aligned}
$$

Can we fit this into the Verlet method?
What is now important to retain?

$f \equiv 0$:

$$D = \lim_{t\to\infty}\frac{(r(t)-r(0))^2}{2t} = \frac{k_B T}{\alpha} \quad , \quad \langle T \rangle = \frac{1}{2}m\langle v^2 \rangle = \frac{1}{2}k_B T$$

$$\rho(r) \propto \exp\left(-\frac{U(r)}{k_B T}\right) \quad \Leftrightarrow \quad U_{\text{pmf}}(r) = -k_B T \ln \rho(r)$$

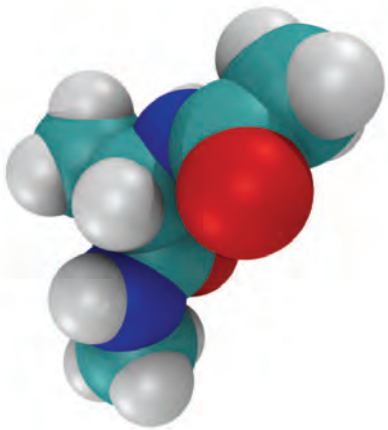
$f = f(r) = -\nabla U(r) \not\equiv 0$:

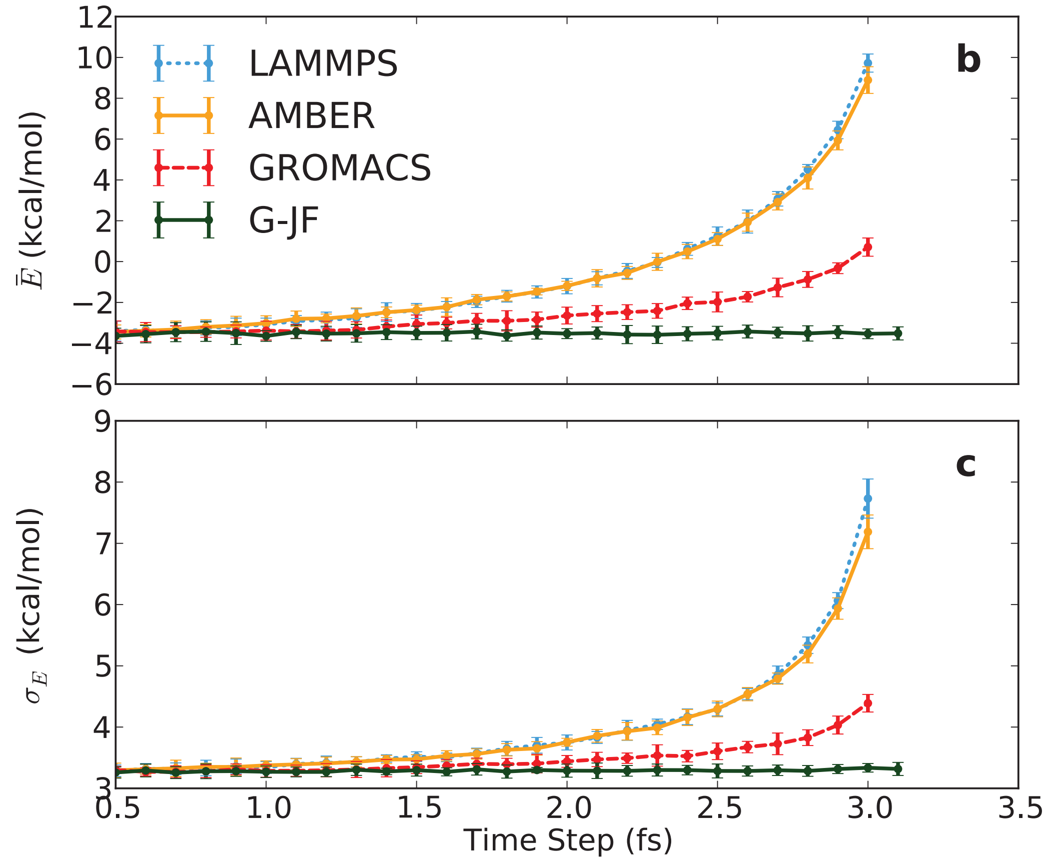
$$\langle U \rangle = \frac{1}{2}k_B T \quad , \quad \langle T \rangle = \frac{1}{2}m\langle v^2 \rangle = \frac{1}{2}k_B T$$

$$\rho(r) \propto \exp\left(-\frac{U(r)}{k_B T}\right) \quad \Leftrightarrow \quad U_{\text{pmf}}(r) = -k_B T \ln \rho(r)$$

Skeel, Izauirre, Mol Phys 100, 3885 (2002);
Mishra Schlick, J.Chem.Phys 105 299 (1996)
Melchionna, J.Chem.Phys 127 044108 (2007)

Applying and Testing the algorithm in existing codes





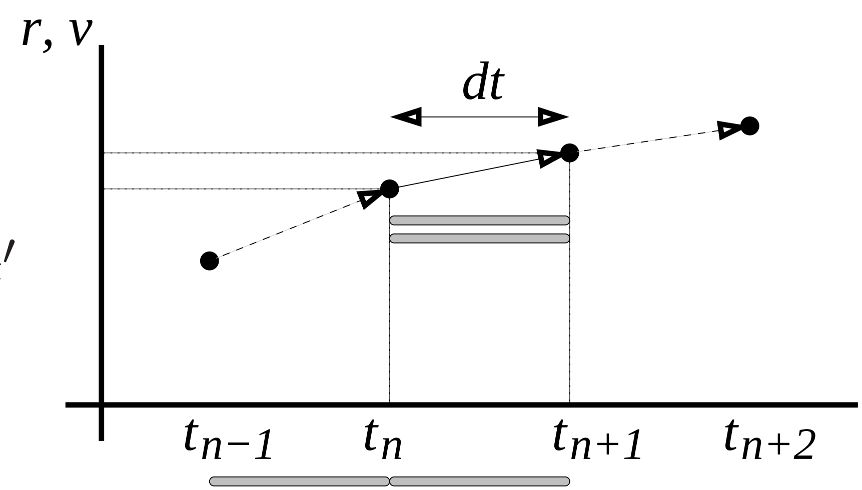
[Grønbech-Jensen, Hayre, & Farago, (2013) – arXiv:1303.7011]

Now Included into LAMMPS (June 7th, 2013);
Comparable Barostat in the works;
Projected inclusion of Electronic Stopping and Inelastic Collisions;
FeNiAl.....

Starting Over (Direct Integration):

$$
\begin{aligned}
m \int_{t_n}^{t_{n+1}} \dot{v}\, dt' &= -\alpha \int_{t_n}^{t_{n+1}} \dot{r}\, dt' + \int_{t_n}^{t_{n+1}} f\, dt' + \int_{t_n}^{t_{n+1}} \eta(t')\, dt' \\
v^{n+1} - v^{n} &= \underline{-\frac{\alpha}{m}(r^{n+1} - r^{n})} + \frac{1}{m} \int_{t_n}^{t_{n+1}} f\, dt' + \underline{\frac{dt}{m}\, \eta^{n+1}}
\end{aligned}
$$

$$
\begin{aligned}
\langle \eta^{n} \rangle &= 0 \\
\langle \eta^{n} \eta^{n'} \rangle &= 2\alpha k_B T \frac{1}{dt} \delta_{n,n'} \\
\eta^{n+1} &= \frac{1}{dt} \int_{t_n}^{t_{n+1}} \eta(t')\, dt'
\end{aligned}
$$



$$
\begin{aligned}
\int_{t_n}^{t_{n+1}} \dot{r}\, dt' &= \int_{t_n}^{t_{n+1}} v\, dt' \\
r^{n+1} - r^{n} &= \frac{dt}{2}(v^{n+1} + v^{n}) + \mathcal{O}(dt^3) \\
&= b\, dt\, v^{n} + \frac{b\, dt}{2m} \int_{t_n}^{t_{n+1}} f\, dt' + \frac{b\, dt^2}{2m} \eta^{n+1}
\end{aligned}
$$

Thus, $\cdots$ only the non-dissipative, deterministic force f needs work

$$\begin{aligned}
r^{n+1} &= r^n + b\,dt\,v^n + \frac{b\,dt}{2m}\overbrace{\int_{t_n}^{t_{n+1}} f\,dt'}^{dt\,f^n} + \frac{b\,dt^2}{2m}\eta^{n+1} \\
v^{n+1} &= v^n - \frac{\alpha}{m}(r^{n+1} - r^n) + \frac{1}{m}\underbrace{\int_{t_n}^{t_{n+1}} f\,dt'}_{\frac{dt}{2}(f^n+f^{n+1})} + \frac{dt}{m}\eta^{n+1}
\end{aligned}$$

Which can also be expressed

$$\boxed{\begin{aligned}
r^{n+1} &= r^n + b\,dt\,v^n + \frac{b\,dt^2}{2m}f^n + \frac{b\,dt^2}{2m}\eta^{n+1} \\
v^{n+1} &= av^n + \frac{dt}{2m}(af^n + f^{n+1}) + \frac{b\,dt}{m}\eta^{n+1}
\end{aligned}}$$

with

$$a = \frac{1 - \frac{\alpha dt}{2m}}{1 + \frac{\alpha dt}{2m}} \quad , \qquad b = \frac{1}{1 + \frac{\alpha dt}{2m}}$$

$$\langle \eta^n \rangle = 0 \quad , \qquad \langle \eta^n \eta^{n'} \rangle = 2\alpha\frac{k_B T}{dt}\delta_{n,n'}$$

Notice: $\alpha = 0 \Rightarrow$ Störmer-Verlet.

Result of Analysis†

For all regions within the stability limit, $\Omega_0 dt < 2$:

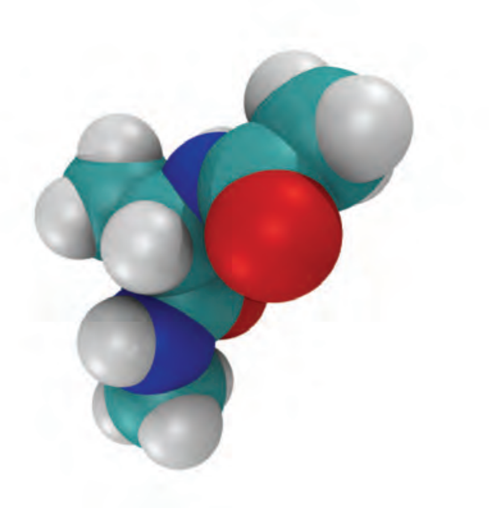
$$\begin{aligned}
\langle U \rangle &= \frac{1}{2}\kappa\langle (r^n)^2\rangle = \frac{1}{2}k_B T \\
\langle T \rangle &= \frac{1}{2}m\langle (v^n)^2\rangle = \frac{1}{2}k_B T\,(1-\frac{\Omega_0^2 dt^2}{4})
\end{aligned}$$

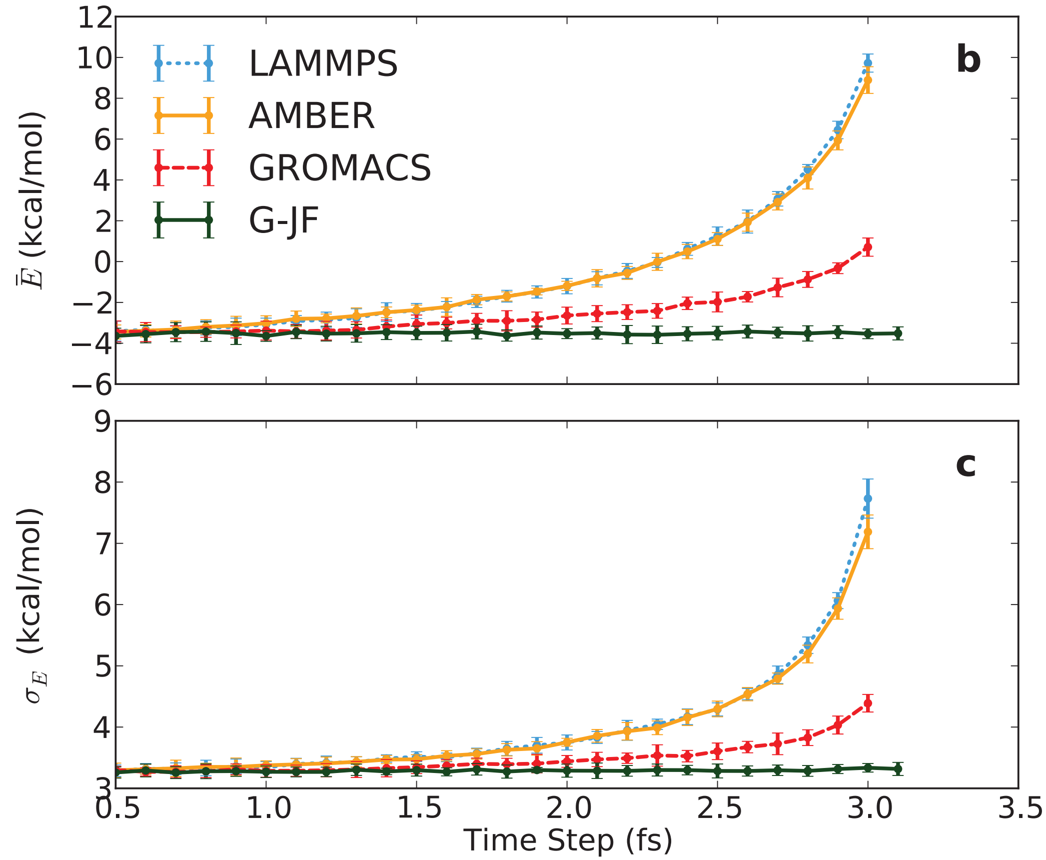
i.e., correct spatial Boltzmann distribution regardless of time step, potential curvature, temperature, and friction. Thus, regardless of numerical errors in, e.g., frequency and damping, the system samples the true, continuous time distribution!

Kinetic energy shows the well-known signs of discrete time problems with velocity, re-emphasizing that kinetic energy is a poor measure of temperature in numerical trajectories.

[arXiv:1212.1244/Grønbech-Jensen & Farago, *Molecular Physics* **111**, 983 (2013)]

Applying and Testing the algorithm in existing codes





[Grønbech-Jensen, Hayre, & Farago, (2013) – arXiv:1303.7011]

Now Included into LAMMPS (June 7th, 2013);
Comparable Barostat in the works;
Projected inclusion of Electronic Stopping and Inelastic Collisions;
FeNiAl.....

Applying and Testing the algorithm.....

• New algorithm implemented at no cost – combining the benefits of Verlet with correct dissipation-fluctuation balance

• Equivalently true for multi-dimensional linear systems; e.g., lattices, PDEs, nonlocal noise. Diagonalization shows that each mode is covered
Now all simulated frequencies respond statistically correct.

• Nonlinear systems.....e.g., comparing PMFs
Time step errors due to deterministic forces remain
Discrete time dissipation-fluctuation balance correct
Tuning α from zero (deterministic) to large is "MD" to "MC"
Large α increasingly accurate even for $\Omega_0 dt \to 2_-$.

• Do not use kinetic energy measures for temperature; use stochastic method and trust thermodynamics.

[arXiv:1212.1244/Grønbech-Jensen & Farago, *Molecular Physics* **111**, 983 (2013)]

Direction

- Complete ion beam radiation study
  different temperatures and radiation doses
  radiation induced coarsening of precipitates
- Complete heat treatment study
  stability of precipitates
- Helium implantation to trace efficiency of interfaces
- Connect with Modeling (as outlined above)
  simulations of precipitates (Temp, dose, defects, composition
  investigation of new barostat
  inclusion of bulk friction (ES & Firsov)
- ``Byproduct'': New algorithms for general use in Materials Modeling
  New, improved Thermostat and Barostat for extended simulations

- Understand operational stability and ``sink-efficiency'' of precipitates