

Ab-initio MD Simulation of GeTe

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Outline

- I. What is GeTe
- II. Ab-initio MD
- III. Radial Distribution Function
- IV. Results from [3] Liquid
- V. Results from [1] Amorphous
- VI. Results from [2] Amorphous and GST

Papers

[1] J. Akola, R.O. Jones Phys. Rev. Lett. 100, 205502 (2008). **(Simulation)**

[2] J. Akola, R.O. Jones Phys. Rev. B 76, 235201 (2007). **(Simulation)**

[3] J.Y. Raty, et al., Phys. Rev. B 65, 115205 (2002). **(Experiment and Small Simulation)**

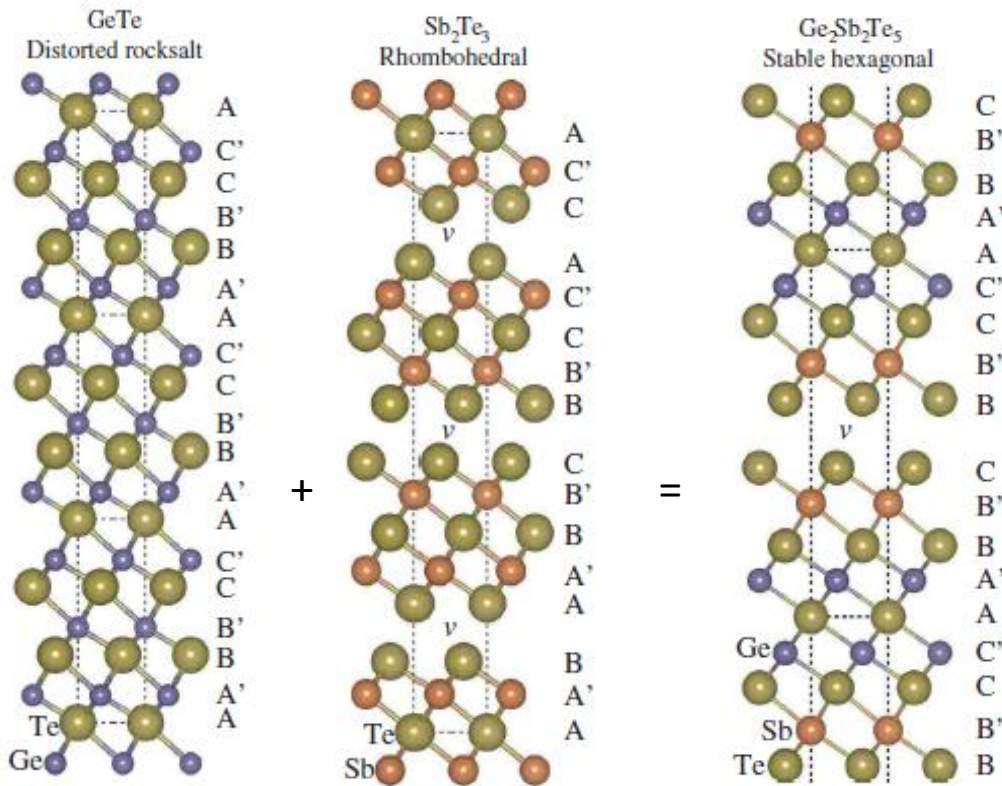
[4] K. Hirota, et al., J. Appl. Phys. 82(1), 1997. **(Experiment)**

[5] D.B. Dove, et al., Appl. Phys. Lett. 16, 3 (1970). **(Experiment)**

All focus on the structural change from crystal->liquid->amorphous

I. What is GeTe/PC Materials?

- Phase Change Materials: Alloys of Ge, Sb, and Te.
- Most Popular: $\text{Ge}_2\text{Sb}_2\text{Te}_5$
- Composed of layers of GeTe and Sb_2Te_3 with vacancies



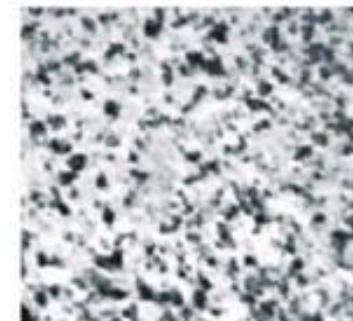
Contrast in Optical/Electrical properties between crystalline and amorphous phases.

Ex: difference in resistance 1K-1M Ohm.

a) Amorphous
High resistivity
Low reflectivity



b) Crystalline
Low resistivity
High reflectivity



Read/write: liquify, quench to amorphous, heat above re-crystallization T (~50 ns).

II. Ab-initio MD

- Feynman-Hellman Theorem:

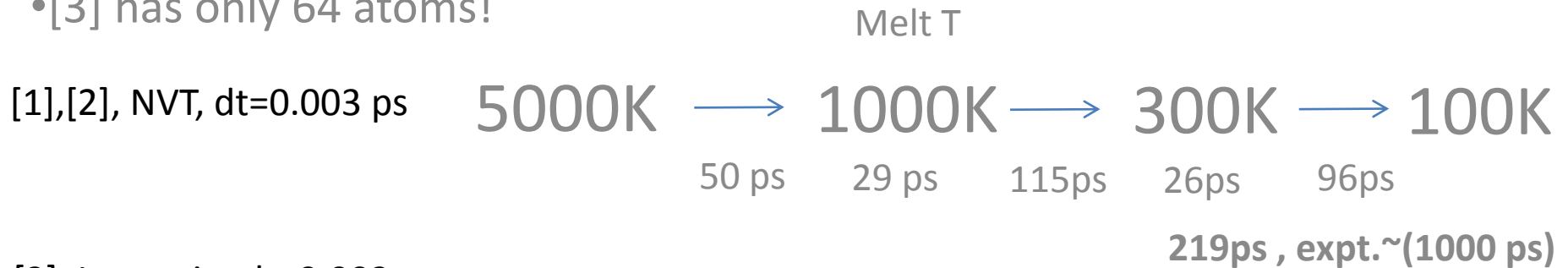
$$-\frac{\partial E[\{c_k^i\}, \{\mathbf{R}_\alpha\}]}{\partial \mathbf{R}_\alpha} = \langle \Psi | \frac{\partial \mathcal{H}}{\partial \mathbf{R}_\alpha} | \Psi \rangle \quad \vec{F} = -\nabla U = m\vec{a}$$

- Assumption: electrons stay in their ground state as nuclei move.

- Recipe
 - 1) Given location of nuclei, species, calculate electronic structure.
 - 2) Take the (analytic) derivative above.
 - 3) Move nuclei (with say Verlet integration).
 - 4) Repeat.
- Most of time (again) in calculating forces, so solving $\mathcal{H}\Psi = E\Psi$ better be fast!
- CPMD code: <http://www.cpmd.org/>
- Flexible: if I want to go from GeTe->GST, simple!

Computational Details

- Calculation [1], [2] run on IBM Blue Gene/L, 512 CPUs for 1 month.
- [1] includes 216 atoms in a 18.6 Ang. cube.
- [2] includes same, 460 atoms GST.
- [3] has only 64 atoms!



[3], Langevin, dt=0.003 ps

-A similar melting cycle, but everything done in 11 ps!!!

- Do results depend on this difference in quench times? NVE vs. NVT?
- The entire read/write cycle takes ~50 ns, good luck...
- No force-field potentials exists for these materials, so this is as good as it gets.



III. Radial Distribution Function

- Radial Distribution Function (RDF) gives idea of short-range order for liquid/amorphous:

$$g(r) = n(r) / (\rho 4\pi r^2 dr)$$

- For LJ system, first peak in RDF very nearly same as FCC. True in general??
- For multi-species systems, I can have multiple RDFs (looking at say Ge-Ge, Te-Te only).

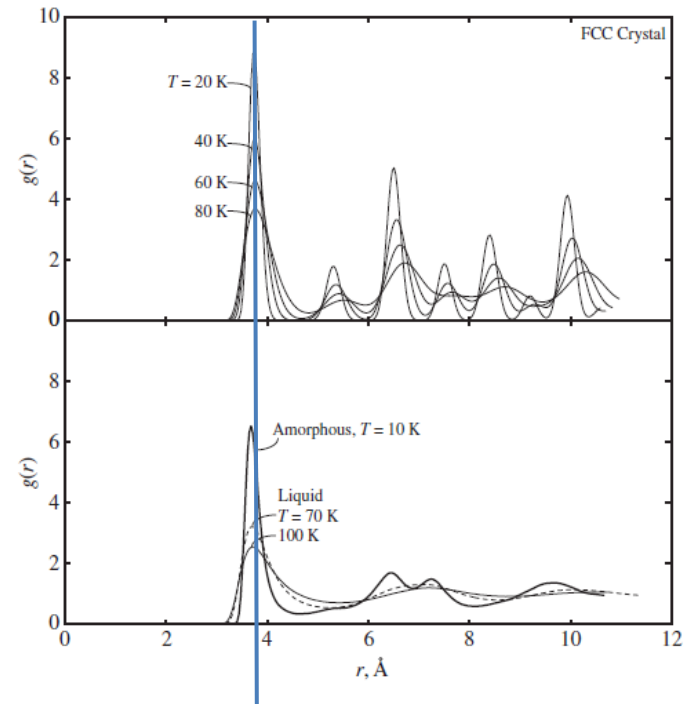


Figure 2.5: LJ RDFs for the fcc crystal at $T = 20 \text{ K}$, 40 K , 60 K , and 80 K , the amorphous phase at $T = 10 \text{ K}$, and the liquid phase at $T = 70 \text{ K}$ and $T = 100 \text{ K}$.

-McGaughey PhD. Thesis

IV. Results from [3]

Peak at ~ 2.7 Ang.

Crystal bond
Ge-Ge and Te-Te

- Liquid phase total RDF shows (much) shorter overall and Ge-Ge bonding than crystal.
- Neutron diffraction (expt.) shows similar total RDF (short bonds).
- With MD data, we can look at species-species RDFs.

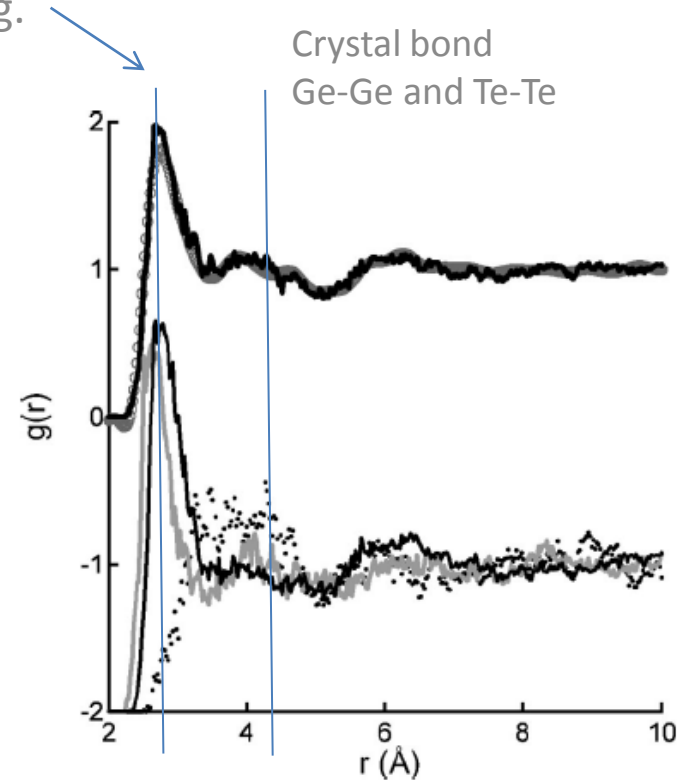


FIG. 6. Calculated total pair correlation function $g(r)$ at 1000 K (plain line) compared with neutron diffraction $g(r)$ at 1173 K (symbols). Bottom: the partial $g(r)$ (g_{GeTe} , thick line; g_{GeGe} , gray line; g_{TeTe} , dots). The partials are shifted for clarity.

V. Results from [1]

- With atom by atom data, we can decompose RDFs (structure factors) into individual components.
- We see that overall and Ge-Ge bonds are much shorter in amorphous. Te-Te is close to crystal bond length.

Crystal bond Ge-Ge and Te-Te

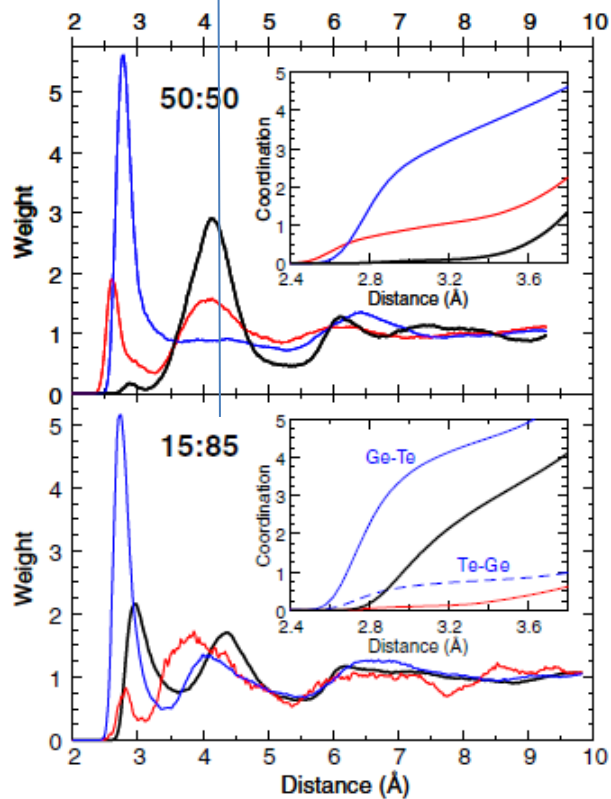
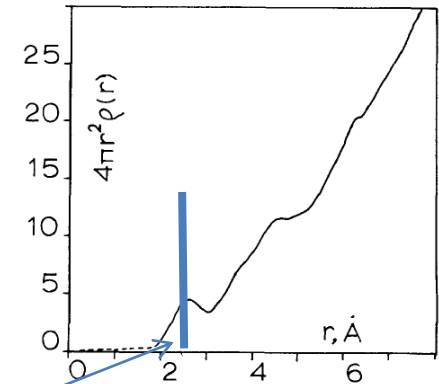


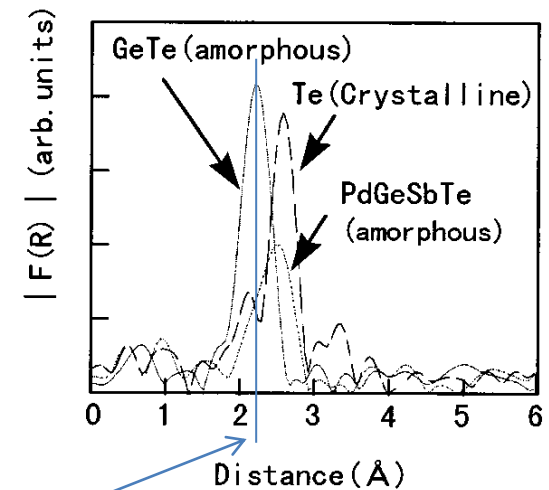
FIG. 1 (color online). Partial RDF of a -GeTe and a -Ge_{0.15}Te_{0.85} at 300 K. Black (thick) line, Te-Te; blue (peaked) line, Ge-Te (Te-Ge); red (middle) line, Ge-Ge. Insets: Coordination numbers as a function of cutoff distance (here 3.2 Å).

[5]



Peak at ~2.6 Ang.

[4]



Peak at ~2.6 Ang.
(small diff. between graph and actual).

VI. Results from [2]

- Again, shortened Ge-Ge and overall bonds, Te-Te nearly same as crystal.
- Results for GST materials show similar trends, shortened overall bonds except Te-Te.

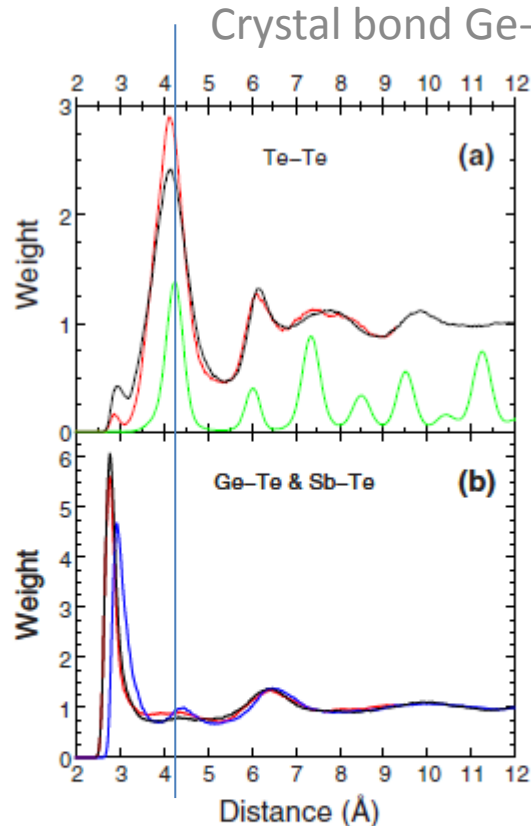


FIG. 2. (Color online) Radial distribution functions of a -GST and a -GeTe at 300 K. (a) Te-Te [black, a -GST; red, a -GeTe; and green (scaled by 0.25), metastable GST crystal at 300 K]. (b) Partial RDF (black, Ge-Te bonds in a -GST; red, Ge-Te bonds in a -GeTe; and blue, Sb-Te bonds in a -GST).

TABLE I. Calculated structural properties of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and GeTe at 300 K: Ge-Te and Sb-Te bond lengths (r_0) and the first minima (r_{\min}) of the partial RDF, atomic coordination numbers (n_x , cutoff distance 3.2 Å) and order parameters (α_x), and the total volume of cavities (V_v).

	$a\text{-Ge}_2\text{Sb}_2\text{Te}_5$		$c\text{-Ge}_2\text{Sb}_2\text{Te}_5$		$a\text{-GeTe}$		$c\text{-GeTe}$	
	Calculated	Expt.	Calculated	Expt.	Calculated	Expt.	Calculated	Expt.
r_0 (Å)	2.78/2.93	2.61/2.85 ^a 2.63/2.83 ^c	2.92/3.02	2.83/2.91 ^a 3.0 \pm 0.3 ^a	2.78	2.65 ^b	3.00	3.00 ^b 2.80, 2.84 ^b
r_{\min} (Å)	3.84/3.88				3.68			
n_{Ge}	4.2	3.9 \pm 0.8 ^c	6		4.2	3.7 ^b	3+3	
n_{Sb}	3.7	2.8 \pm 0.5 ^c	6					
n_{Te}	2.9	2.4 \pm 0.8 ^c	4.8 ^d		3.3	2.5 ^b	3+3	
α_{Ge}	0.77		1		0.56		1	
α_{Sb}	0.61		1					
α_{Te}	0.75		1		0.94		1	
V_v (%)	11.8		\sim 10		6.4		\sim 0	

^aEXAFS and XRD (Ref. 9).

^bEXAFS and XRD (Ref. 30), and ND (Ref. 31). c -GeTe structures: rhombohedral (shorter bonds, coordination 3+3) and fcc (longer bonds, coordination 6).

^cEXAFS (Ref. 12).

^dVacancies reduce the value below 6.

Summary

- Ab-initio MD flexible, can simulate many systems accurately.
- Very expensive, can (mostly) study bulk-like properties.
- GeTe Amorphous/Liquid phase total RDF shows (much) shorter overall bonding than crystal.
- This is due (primarily) to Ge-x bonding which prefers tetrahedral. Very difficult to capture this with force-field potential!