2008 Solar Annual Review Meeting

Session: Thermal Storage - Advanced Fluid Development
Company or Organization: NREL
Funding Opportunity: Concentrating Solar Program

Greg Glatzmaier, Dan Blake, Joongoo Kang

NREL/PR-550-43337
Presented at the Solar Energy Technologies Program (SETP) Annual Program Review Meeting held April 22-24, 2008 in Austin, Texas

Relationship to Solar Program Goals

"…to make CSP cost competitive in the intermediate power markets by 2015 (~7¢/kWh with 6 hours of storage) and in baseload power markets (~5¢/kWh with 16 hours of storage) by 2020."

1. Project Overview

a) Description

- near-term R&D activities that address current heat transfer fluid (HTF) issues
- long-term R&D activities that develop the next generation heat transfer fluids & thermal energy storage concepts

b) Major FY08 Activities

- preparation of advanced fluids & thermal storage solicitation
- long-term exploration of thermal storage properties of nanoscale particles
- near-term analysis and modeling of organic HTF decomposition within parabolic trough power plant
- testing & evaluation support of FOA award (Abengoa molten salt)

Relationship to Solar Program Goals

Project overview (continued)

c) Planned Milestones

- prepare & review advanced fluids/thermal storage solicitation, March 2008
- initiate nanofluids modeling studies & submit progress report, September 2008
- complete organic HTF decomposition modeling, September 2008

Agreement	**FTEs**	**$(K)**	**Subcontract $(K)**
Advanced fluids	1.6	169	0
HTF decomposition modeling	0.3	83	0
FOA storage support	1.0	300	0
HTF/TES solicitation	1.0	300	0

Relationship to Solar Program Goals

Project overview (continued)

e) Personnel

- solicitation support: Greg Glatzmaier, Mark Mehos, Chuck Kutscher, Tom Mancini
- Nanofluids R&D: Dan Blake, Yong-Hyun Kim, Calvin Curtis, Joongoo Kang (post-doc), Greg Glatzmaier and Luc Moens
- HTF decomposition modeling: Greg Glatzmaier

2. Relevance to Program Plans & Goals

MYPP & Program Goals

- Advanced fluids with enhanced heat capacities directly impact thermal storage costs ($20/kWh) and plant LCOE
- Higher temperature advanced fluids will increase turbine efficiency, annual solar efficiency and reduce LCOE

FY08 Progress Report

Nanofluids R&D

- **Goal:** develop a new class of heat transfer fluids and increase fluid heat capacities by a factor of five

- **Approach**: use molecular modeling and directed synthesis to explore:
  - nanoscale "encapsulated" structures (50 – 500 atoms) capable of solid/solid, solid/liquid, or solid/gas phase transitions (nanoPCMs)
  - nanoparticles suspended in fluids (**nanoFLUIDs**) as heat transfer fluids

1. What has been accomplished thus far?
   - nanoscale fluids project started using internal NREL funding
   - Initial molecular modeling of thermal properties of aluminum clusters shows encouraging results

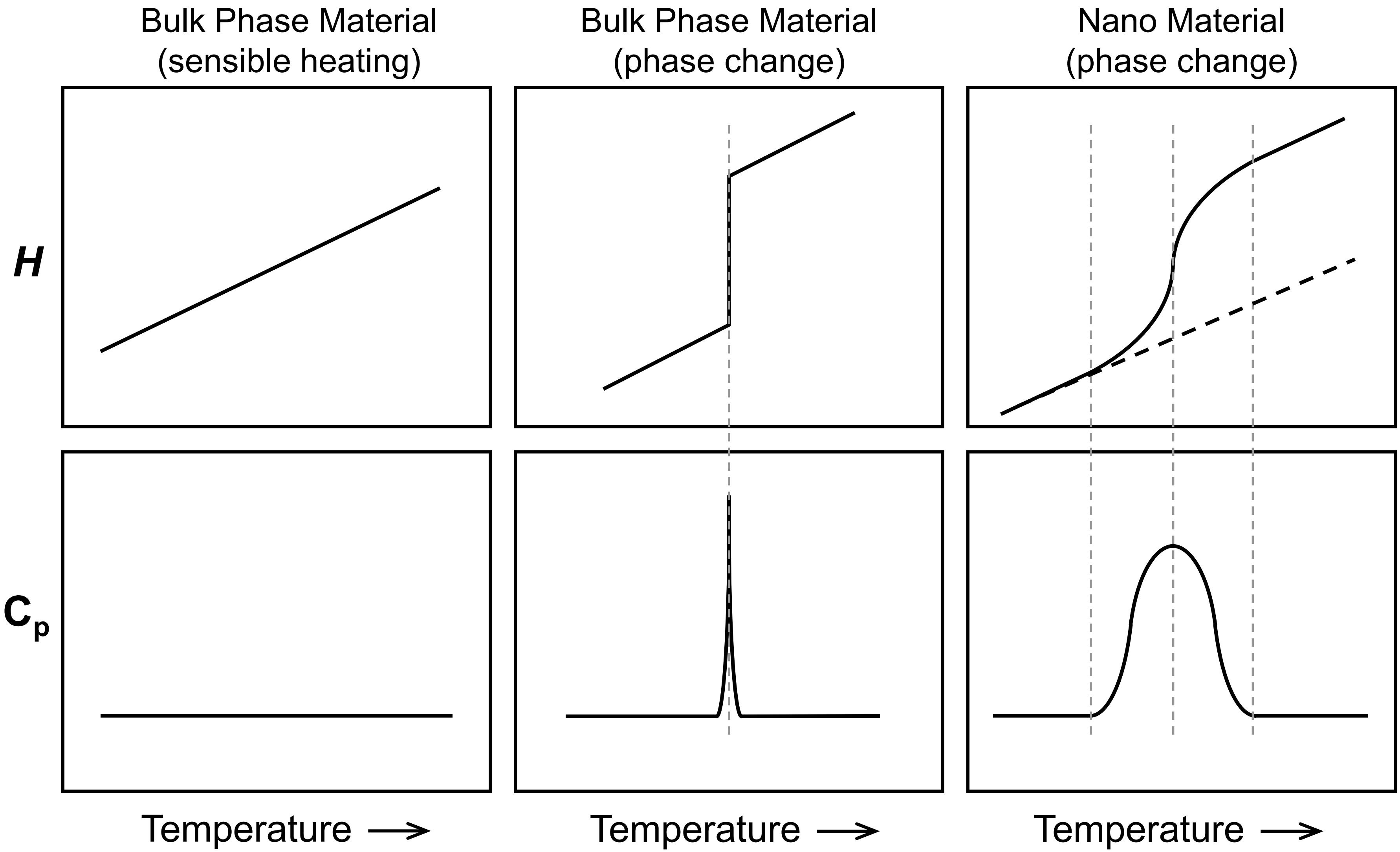
FY08 Progress Report

Nanofluids R&D

- Bulk materials:
  - sensible heating (ΔT = 100 ^{o}C): ΔH = 85-230 kJ/kg (VP-1, nitrates, concrete)
  - phase change: ΔH = 200-1400 kJ/kg (melting & sublimation)
  - phase change occurs at single temperature
- Nano particles:
  - encapsulated nanostructures change phase over a temperature range
  - fluid comprised of nanostructures does not have the same heat transfer limitations as the bulk material

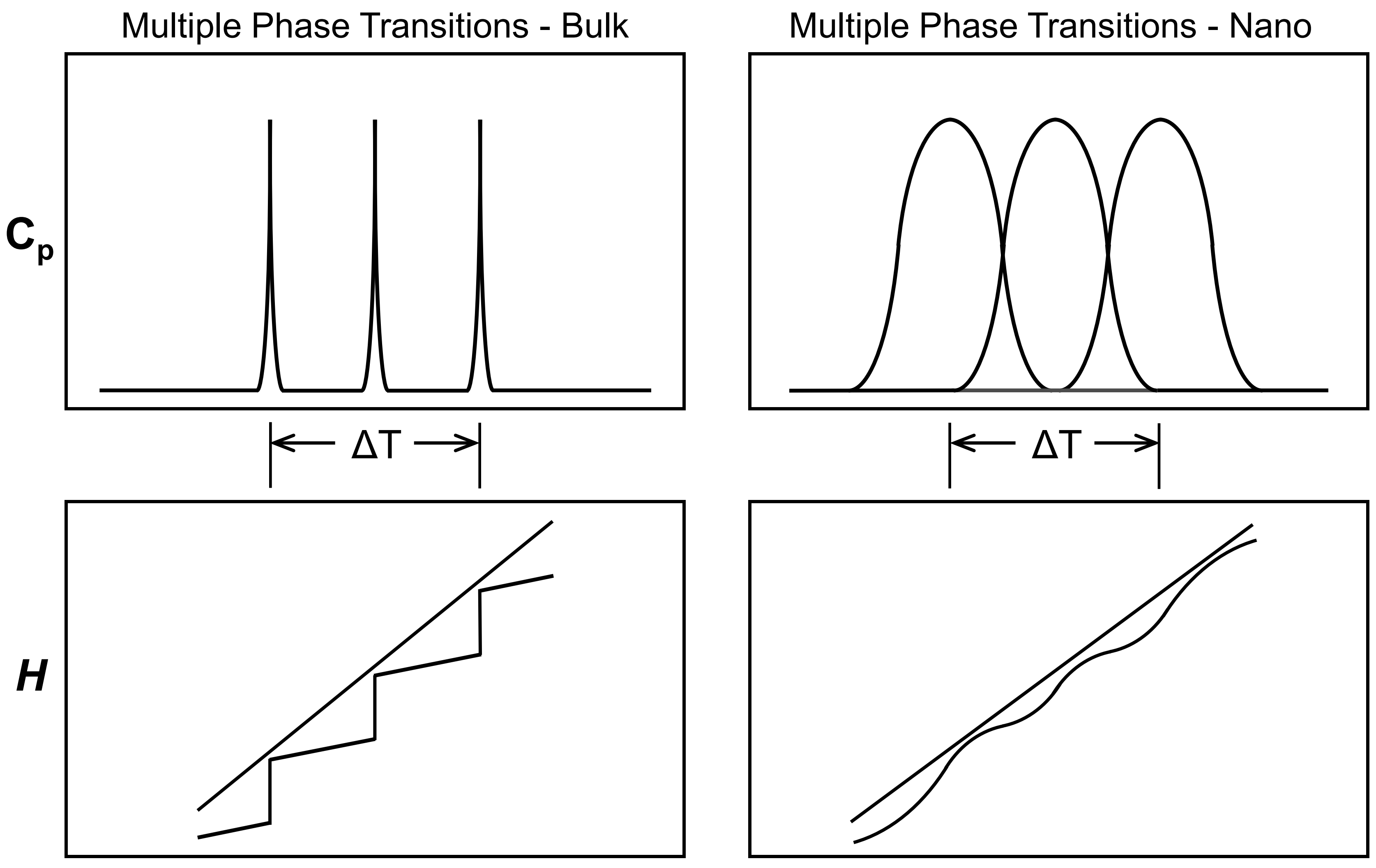
FY08 Progress Report

Nanofluids R&D



FY08 Progress Report

Nanofluids R&D



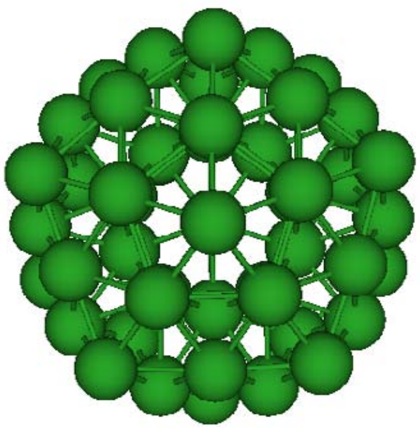
FY08 Progress Report

Nanoparticle Experimental Results

G.A. Breaux *et al.*, PRL (2005)

55 Atom Aluminum Clusters

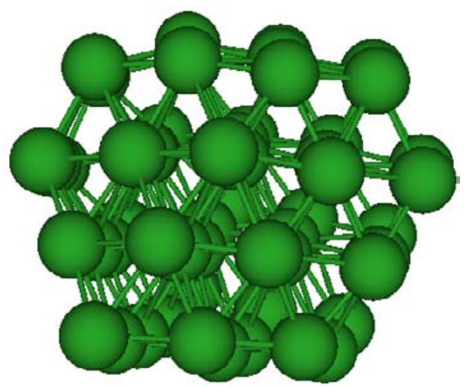
icosahedron (I_h)



E = +3.95 eV

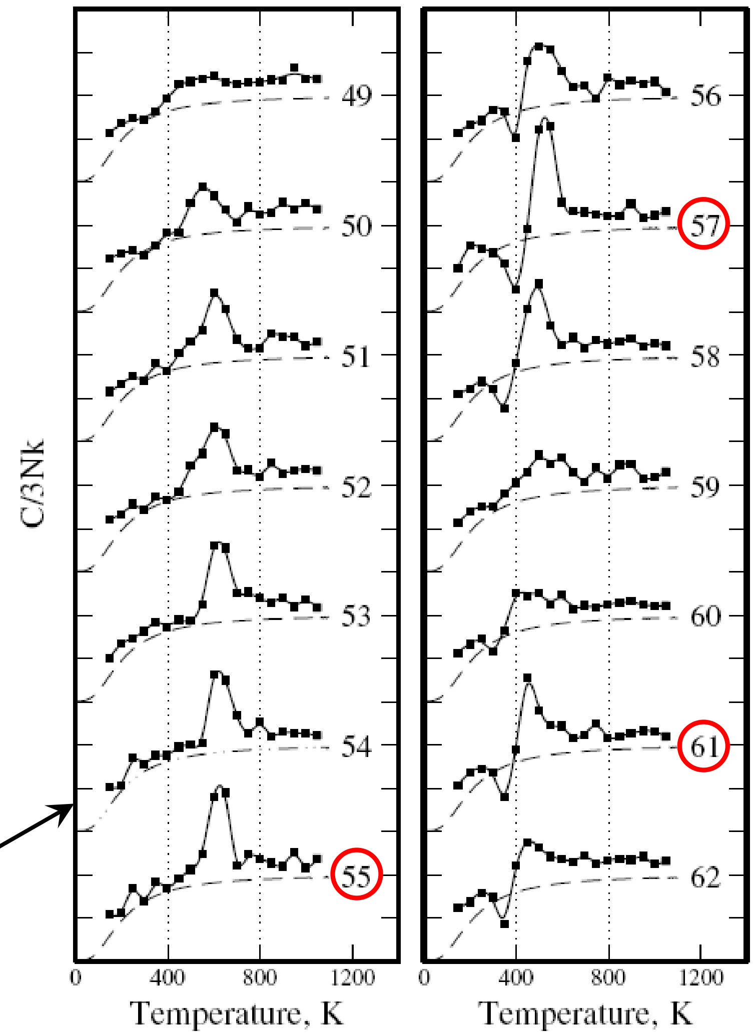
Z. H. Li *et al.*, JACS (2007)

ordered structure



E = 0 (most stable)

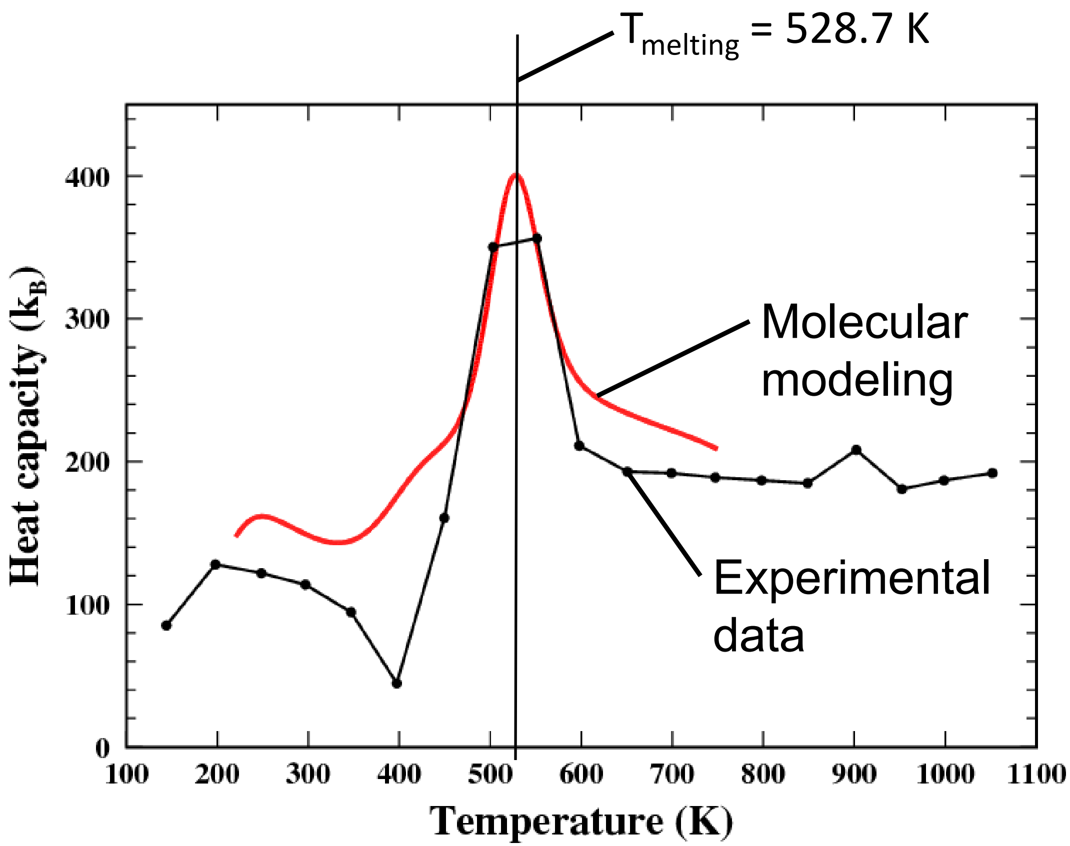
- melting phase transitions
- variation in aluminum nanoclusters' T_{melt}
- bulk aluminum T_{melt} = 933 K



FY08 Progress Report

Nanofluids R&D

Al 57



FY08 Progress Report

Nanofluids R&D

c) Costing (funding on track)

NREL			
Project Beginning Date	**FY07 Budget**	**FY08 Budget**	**Total Budget**
10/1/2008	59K	110K	169K

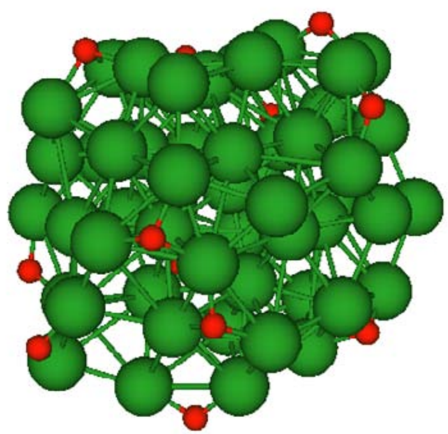
FY08 Progress Report

Nanofluids R&D

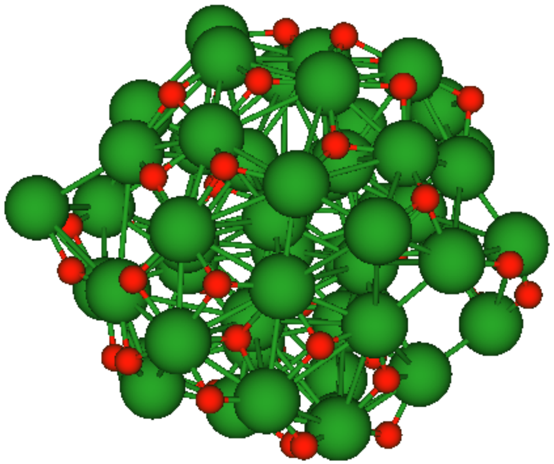
2. Plans for the 3rd and 4th Quarters

- Encapsulate nanostructure to stabilize particles using partial oxidation to form core-shell structures

Al 55 + 12 O



Al 55 + 42 O



a) Status of milestone: R&D on track

Future Activities

Nanofluids R&D

1. FY09 Planned Activities

   a) Follow-on efforts
      - continue work on modeling, synthesis, and characterization of nanocluster storage materials
      - tunability of phase transition temperature as a function of material and cluster size
      - evaluate other elements (metals, carbon)

   b) New directions
      - model larger metal atom clusters (>200 atoms)
      - requires significantly more computing power

   c) Budget
      - 2.2 FTEs (1 post doc), $360K

   d) Projected Milestones
      - progress report on modeling & directed synthesis of phase-change materials

Future Activities

Nanofluids R&D

2. FY10 and Beyond Ideas

   a) Future Project: complementary work effort using nanoscale particle features & properties to develop a metal-based fluid with a proper liquid-phase temperature range (10 ^{o}C – 500 ^{o}C), consider elemental mercury as a model

   b) Outside the Box: tune nanoscale properties to develop a set of nanofluids that has an effective phase transition over a 100 ^{o}C ΔT

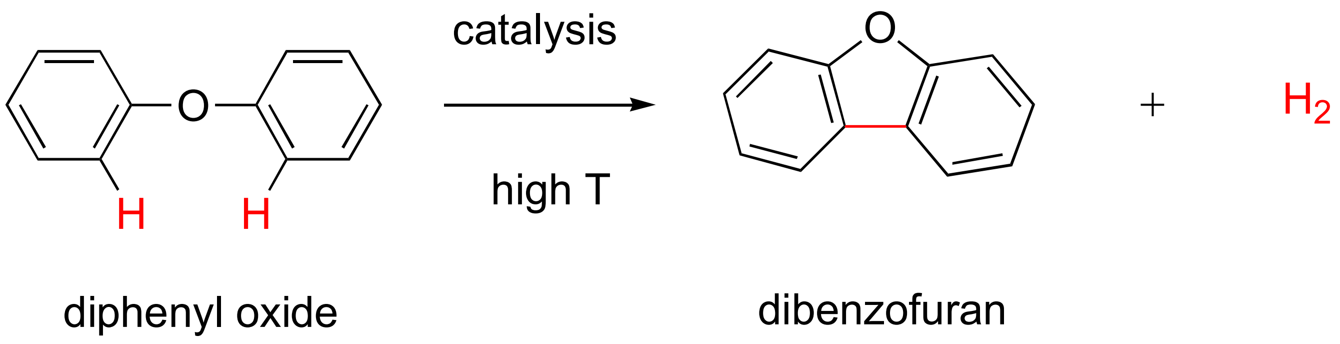
   c) Vision: an inexpensive, noncorrosive combined HTF/storage fluid with a 10 ^{o}C – 500 ^{o}C liquid temperature range

FY08 Progress Report

Organic HTF decomposition: mechanisms

1. What has been accomplished thus far?

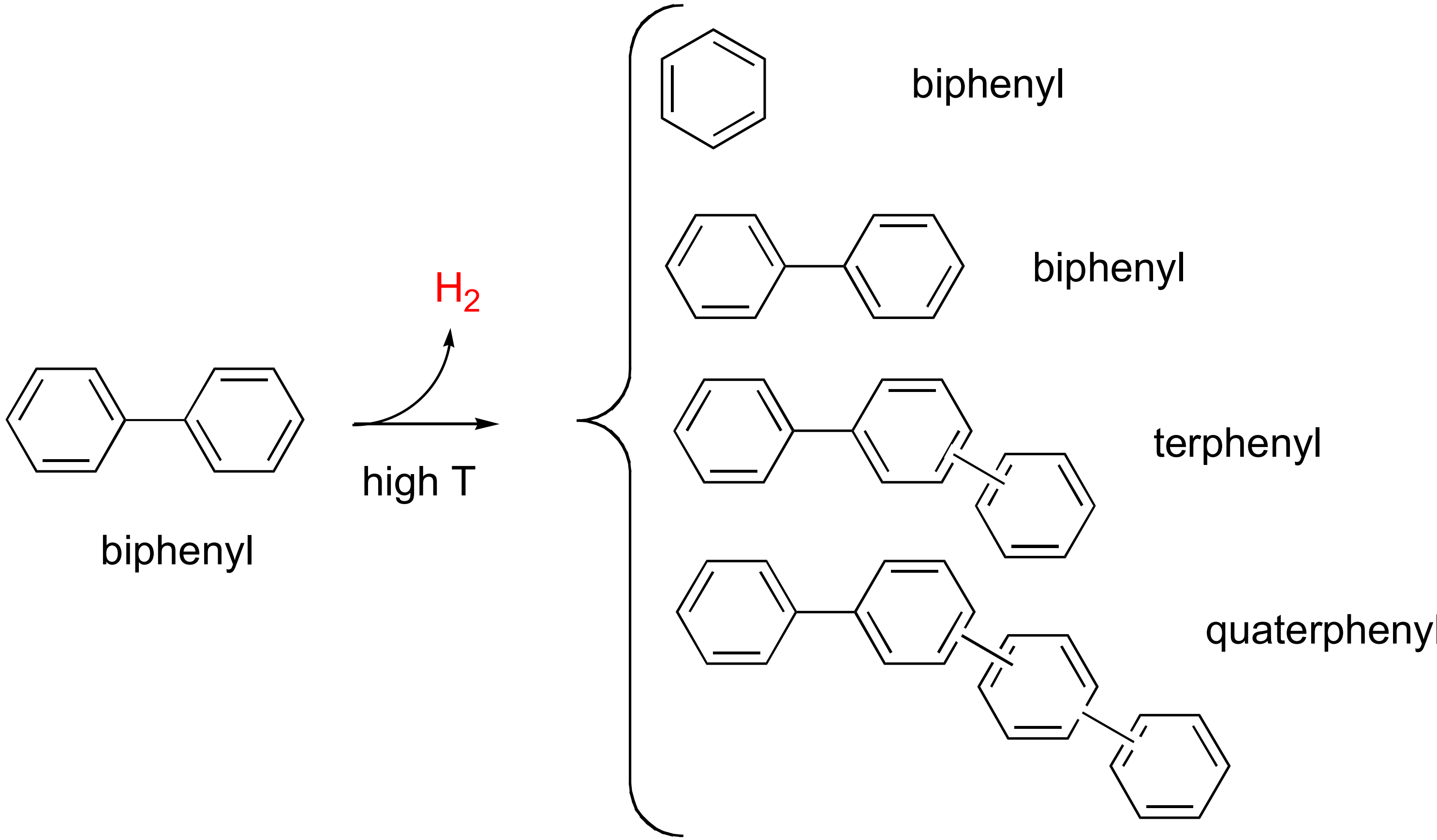
- **Goal:** determine organic HTF decomposition reaction mechanisms
- **Status**
  - work on reaction mechanisms complete
  - results published in NREL technical report **TP-510-42468**



Diphenyl oxide ring closure

FY08 Progress Report

Organic HTF decomposition: mechanisms



Free-radical polymerization of biphenyl

FY08 Progress Report

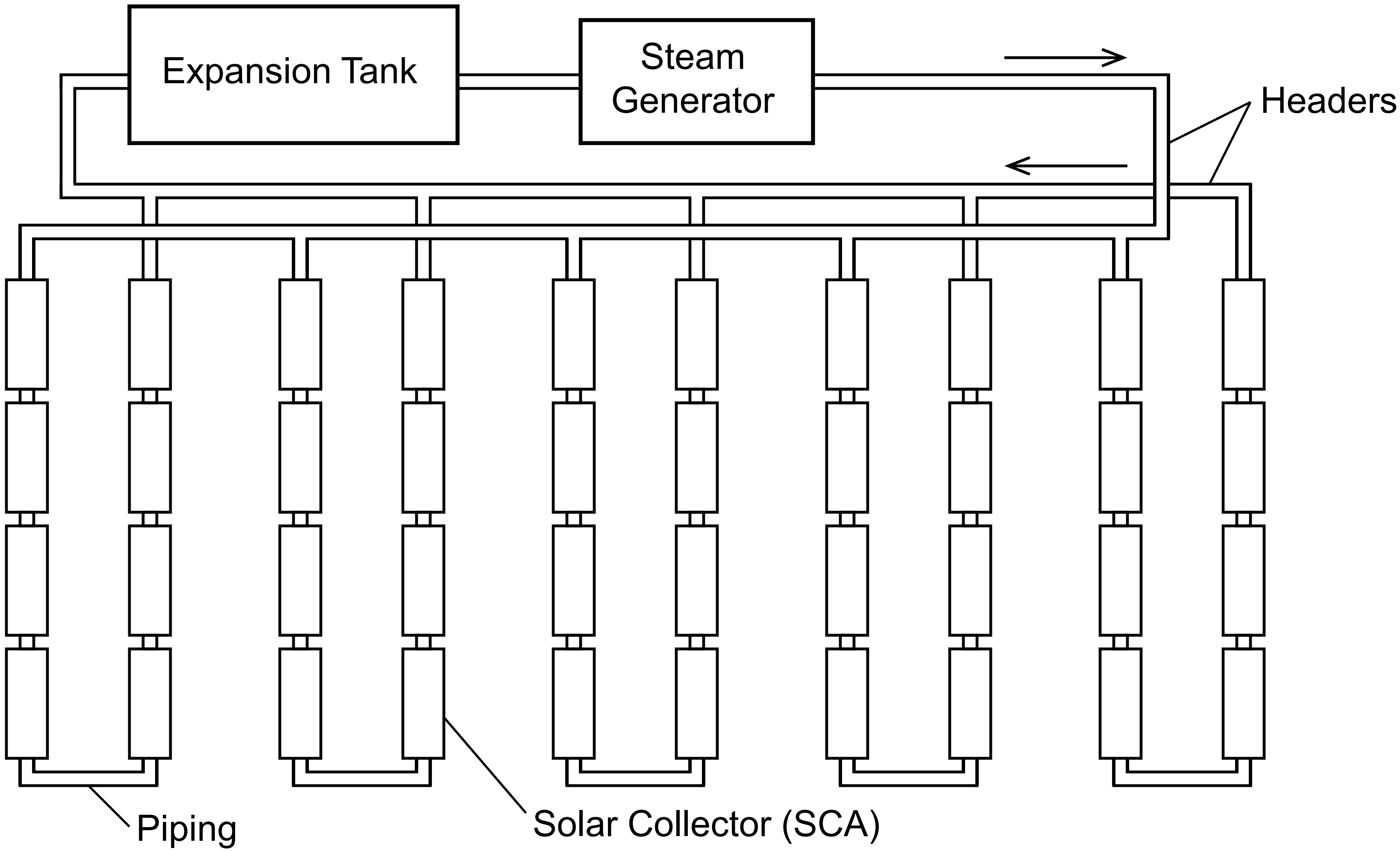
Organic HTF decomposition: modeling

1. What has been accomplished thus far?

- **Goals**
  - understand the occurrence of hydrogen within parabolic trough power plants due to organic HTF decomposition
  - evaluate promising mitigation methods
- **Approach**
  - model hydrogen generation and transport within a parabolic trough power plant
  - develop a steady-state hydrogen material balance within each major plant component including expansion tank, steam generator, headers, solar collectors and piping connections

FY08 Progress Report

Organic HTF decomposition: modeling



FY08 Progress Report

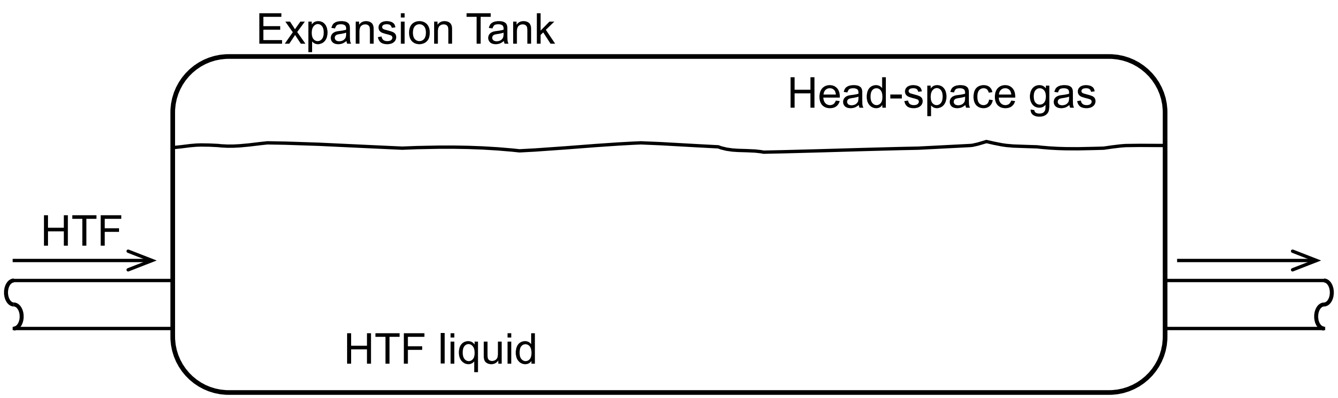
Organic HTF decomposition: modeling

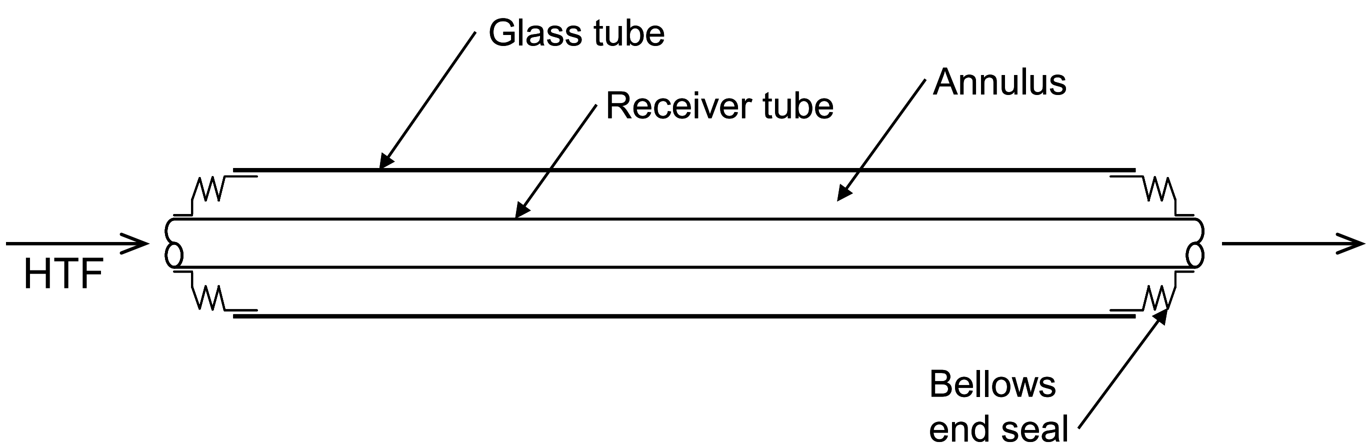
1. What has been accomplished thus far?

- each material balance accounts for hydrogen generation & transport into and out of the component due to HTF flow & permeation
- material balances on HCEs model hydrogen concentrations in both the receiver tube and the annulus
- material balance on the expansion tank models gas-phase & liquid-phase hydrogen concentrations

FY08 Progress Report

Organic HTF decomposition: modeling





FY08 Progress Report

Organic HTF decomposition: modeling

1. What has been accomplished thus far?

- **Status**
    - software was written in Engineering Equation Solver (EES)
    - software is functioning, modeling work is next

c) Costing (spending on track)

NREL			
Project Beginning Date	**FY07 Budget**	**FY08 Budget**	**Total Budget**
10/1/2008	83K	0	83K

FY08 Progress Report

Organic HTF decomposition: modeling

2. Plans for the 3rd and 4th Quarters

- analyze generation and transport of hydrogen in typical parabolic trough power plant
- use model to evaluate promising methods to reduce or remove hydrogen from HTF loop and the HCE annulus

a) Status of milestone: on track

Future Activities

Organic HTF decomposition: modeling

1. FY09 Planned Activities

   a) Follow-on efforts

      - Implement and test a promising method to remove hydrogen at a SEGS plant
      - FPL/Kramer Junction expressed much interest in this work

   c) Budget Table (FTEs, $FTE, Subcontract Info)

      - 0.75 FTEs, 225K $FTE

   d) Projected Milestones

      - complete field test of hydrogen mitigation method

Future Activities

Organic HTF decomposition: modeling

2. FY10 and Beyond Ideas

   a) Future Projects

      - follow-on implementation & testing at other parabolic trough power plants
      - on-going monitoring and modeling of hydrogen mitigation field tests

   c) Vision: a parabolic trough power plant with no hydrogen

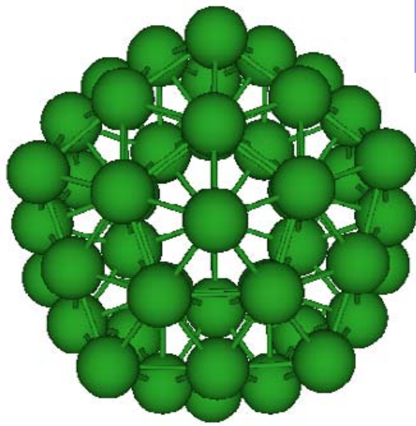
FY08 Progress Report

Nanofluids R&D

Low-energy structures of 55 atom aluminum clusters

icosahedron (I_h)

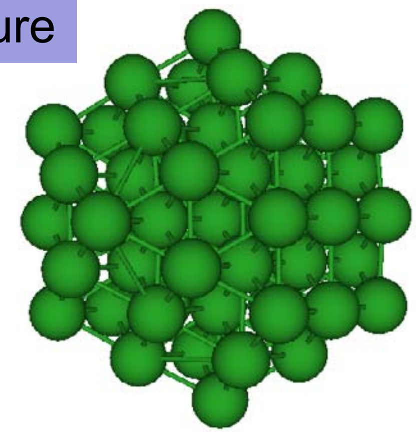
Z. H. Li *et al.*, JACS (2007)



E = +3.95 eV

fcc-based structure

D ~ 1 nm

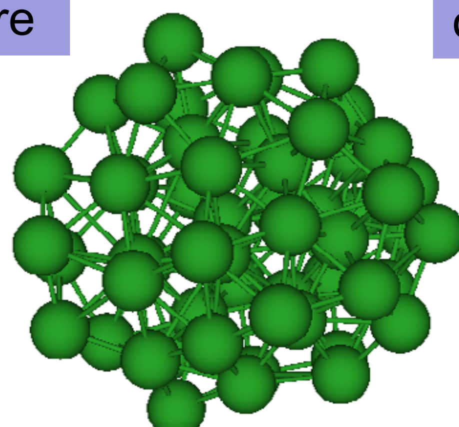


E = +2.36 eV

disordered structure

(simulated annealing)

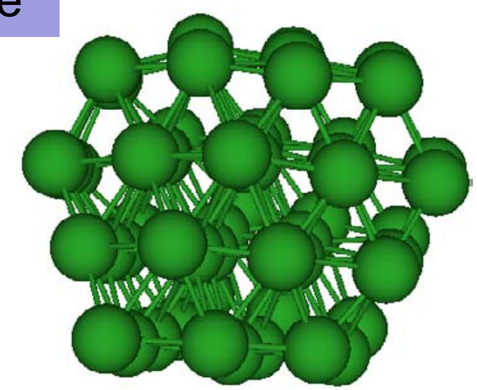
J.-Y. Yi *et al.*, PRL (1991)



E = +0.08 eV

ordered structure

(simulated annealing)

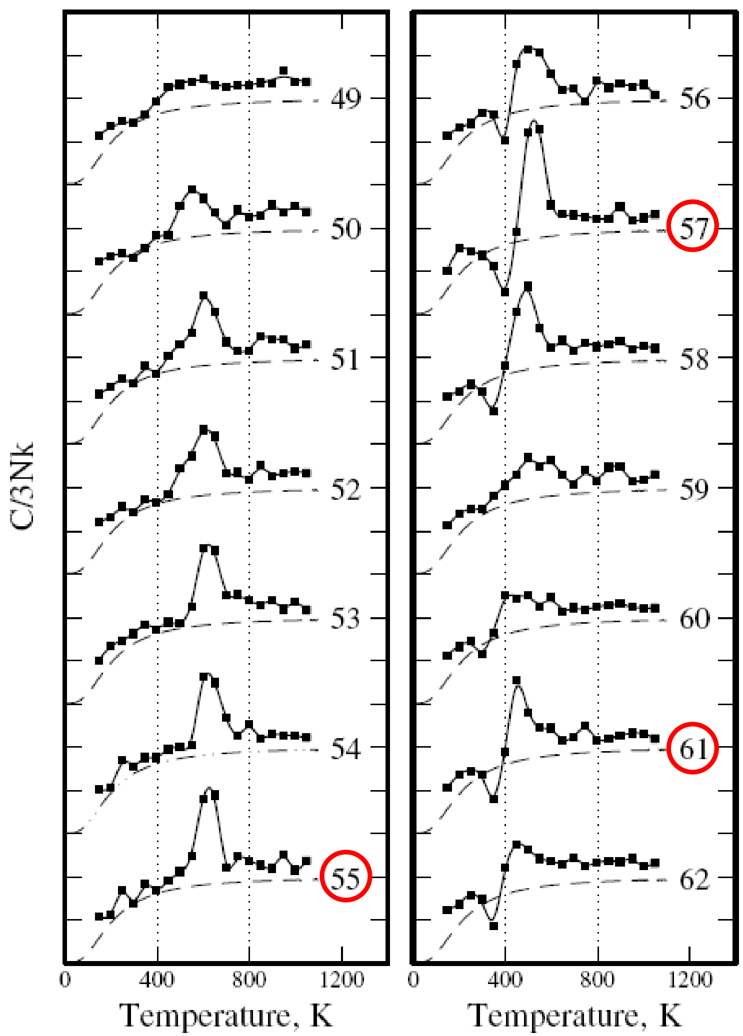


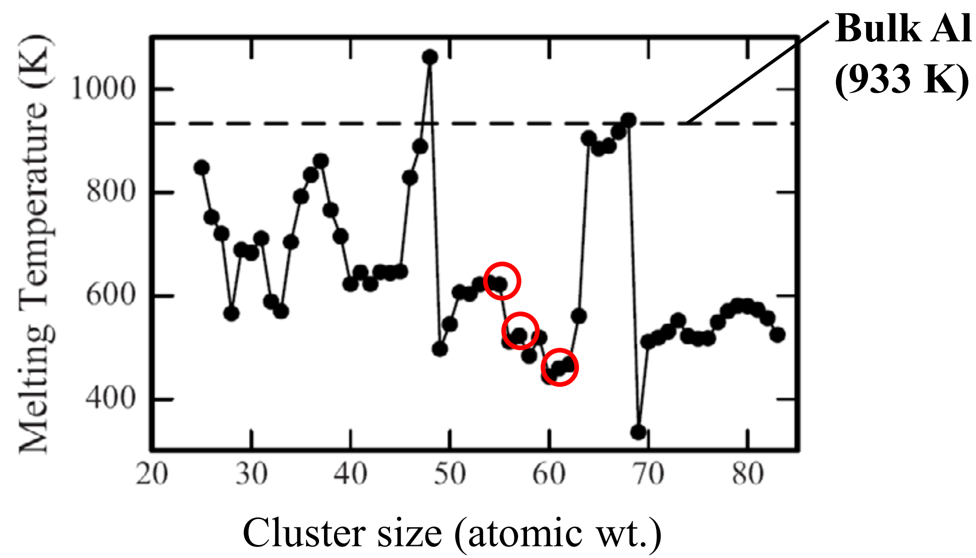
E = 0 (most stable)

FY08 Progress Report

Nanoparticle Experimental Results

G.A. Breaux *et al.*, PRL (2005)



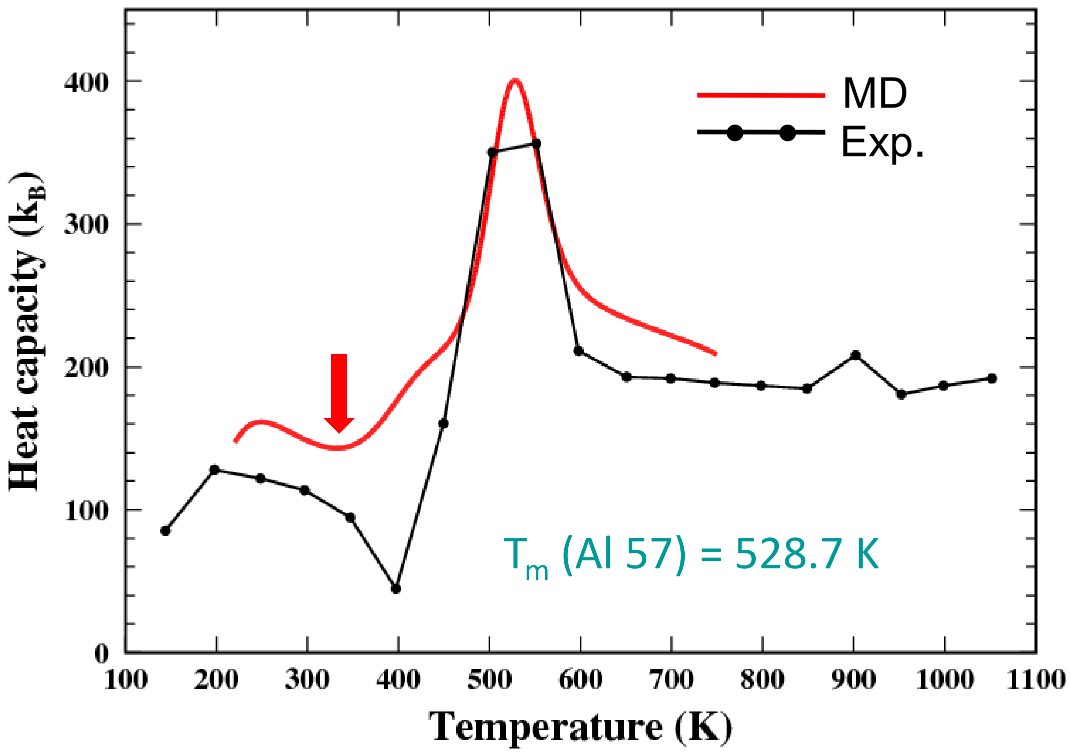


- Peaks in the heat capacities due to melting (latent heat)
- Sudden drop of T_m for clusters with n>55
- A dip in the heat capacities before the clusters melt
- Nanoscale clusters have a broad melting transition in contrast to bulk materials

FY08 Progress Report

Nanofluids R&D

Al 57



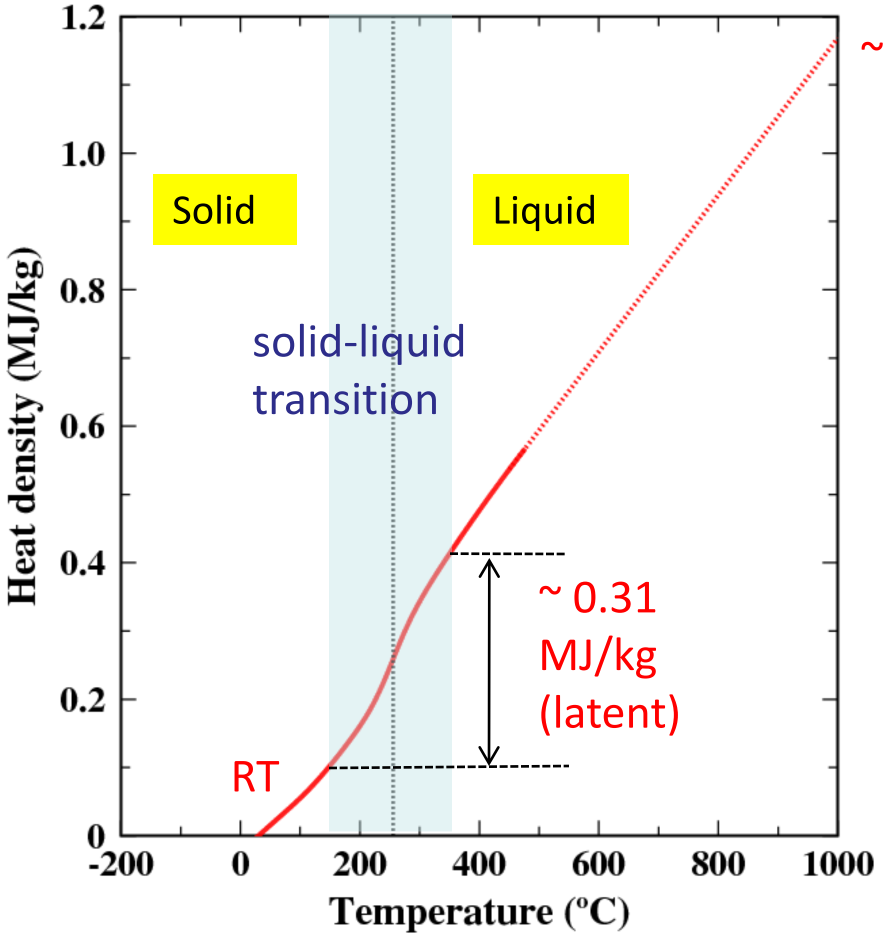
- We need more MD simulations to get a converged curve.
- Sudden drop of T_m for clusters with n>55
- A dip in the heat capacities before the clusters melt

Calculation gives good fit to experimental data.

FY08 Progress Report

Nanofluids R&D

Thermal storage (Al 57)



Bulk Al: T_m = 660 °C

latent heat = 0.397 MJ/kg

sensible heat = 0.0008MJ/kg °C

Nanoscale Al57:

$T_m \approx$ 180-280 °C

sensible heat ≈ 0.0013MJ/kg°C

The operating temperatures of the thermal storage system must match those of the power conversion process and therefore vary from **80-150°C** for low-temperature applications to **400-1000°C** for high-temperature systems.

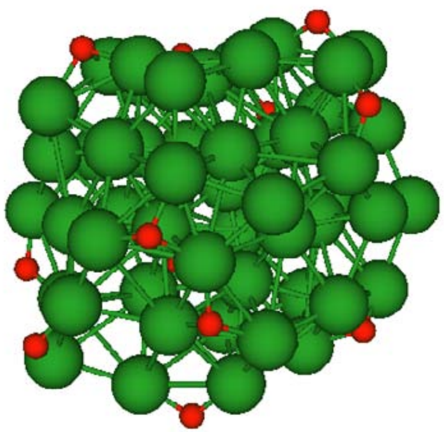
FY08 Progress Report

Nanofluids R&D

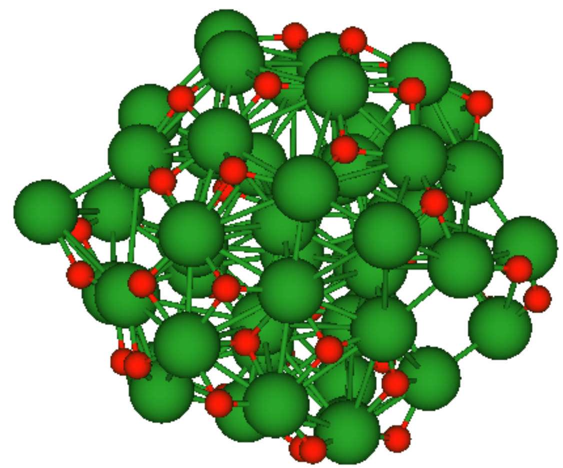
2. Plans for the 3rd and 4th Quarters

- Encapsulate nanostructure to stabilize particles using partial oxidation to form core-shell structures
- High thermal conductivity is needed for enhanced thermal energy charge/discharge processes

Al 55 + 12 O, T=150K, 7 ps



Al 55 + 42 O, T=400K, 12 ps



a) Status of milestone: R&D on track

FY08 Progress Report

Nanofluids R&D