

Calculating heat of fusion of polyethylene using Polymer Modeler at nanoHUB

In this tutorial:

- Setup MD simulations of polyethylene (PE), both amorphous and crystalline configurations
- Determine the heat of fusion of PE

Lorena Alzate, Ben Haley, Ale Strachan

strachan@purdue.edu

School of Materials Engineering & Birck Nanotechnology Center

Purdue University

West Lafayette, Indiana USA

Step 1: Launch Polymer Modeler tool

In your nanoHUB dashboard you will see MYTOOLS Module, if not you can get it in the Add Modules box

The screenshot shows the nanoHUB dashboard interface. At the top right, there is a blue button labeled "Add Modules". Below it, the "MY TOOLS" module is open, displaying a search bar with "Polymer" entered. The search results list several tools, with "Polymer Modeler" highlighted by a blue arrow. The "MY COURSES" module is also visible, showing a list of courses. The "UPLOADS IN PROGRESS" module shows a contribution named "struct2lammps" with a status of "published".

- All tools tab
- Search *Polymer Modeler*
- Launch tool (click in small box)

Step 2: Select the polyethylene structures

- Select **Use pre-built polymers** in the Structure options menu
- Select **Polyethylene (amorphous)** in the Prebuilt

Polymer Modeler (9:44 am) [Settings] [Terminate] [Keep for later]

1 Structure → 2 Simulation → 3 Simulate

Structure options: Build polymer

Build polymer: Build polymer

Use pre-built polymers

Monomer struct: Upload LAMMPS data file from previous run

Polymer: PMMA (isotactic)

Monomer

Number of monomer types: 1

Monomer format: zm

Monomer atoms: 4 # Number of backbone atoms

H_	1	1.09							
C_3	2	1.53	1	112					
H_	3	1.09	2	112	1	180			
H_	2	1.09	1	112	3	240			
H_	2	1.09	1	112	3	120			
C_2	3	1.53	2	112	1	60			
C_3	3	1.53	2	112	1	300			
H_	8	1.09	3	112	2	300			

Right click to upload

Head atom: 1

Tail atom: 4

Specify monomer arrangements: yes

Monomer arrangements

Simulation >

Storage (manage) 45% of 10GB [Lightning bolt] [Refresh] [780 x 600]

Polymer Modeler (9:44 am) [Settings] [Terminate] [Keep for later]

1 Structure → 2 Simulation → 3 Simulate

Structure options: Use pre-built polymers

Pre-built polymers

Prebuilt Structures: New

New

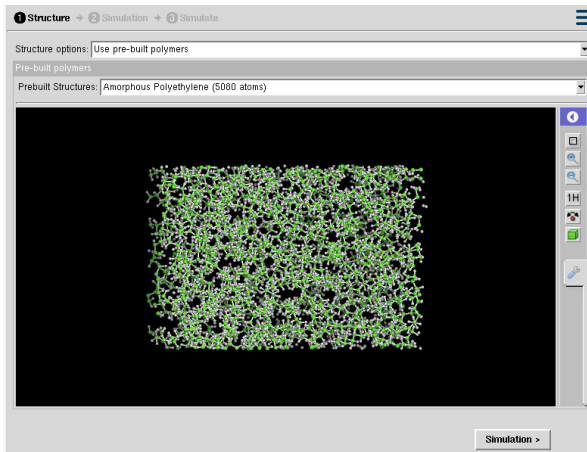
- Amorphous Polyethylene (5080 atoms)
- EPON825 (1028 atoms)
- EPON862 (15118 atoms)
- EPON862 (15344 atoms)
- EPON862 (16000 atoms)
- Polyethylene crystal (5040 atoms)

Simulation >

Storage (manage) 45% of 10GB [Lightning bolt] [Refresh] [780 x 600]

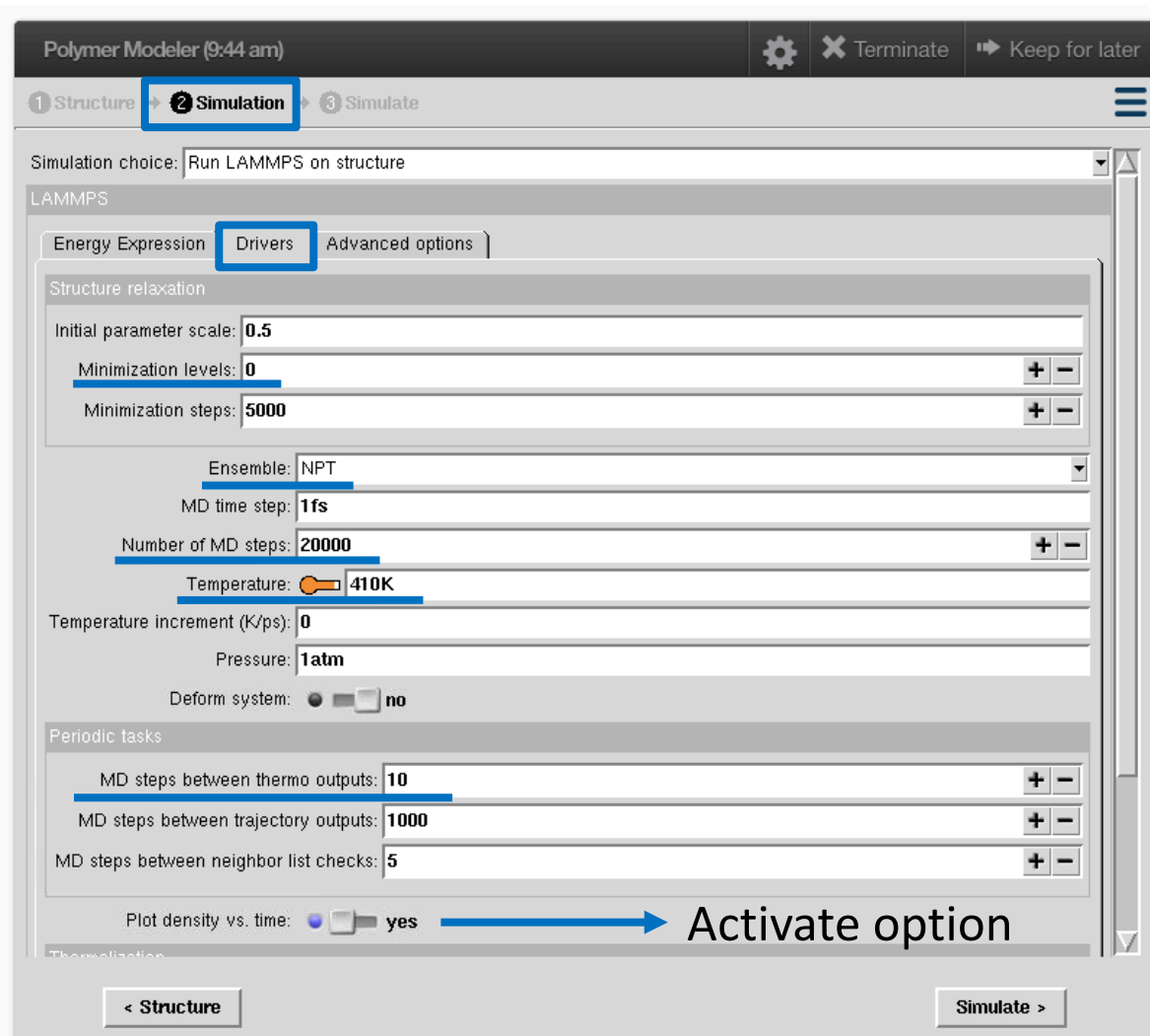
Step 3: Set up the simulation

Once the structure is selected you can visualize it



- Change **Minimization levels** to zero
- Change **Ensemble** to NPT
- Increase **Number of MD steps** to **20000** (20 ps)
- Change **Temperature** to **410K**

- Select **Simulation** tab and **Drivers** menu

A screenshot of the Polymer Modeler software interface, specifically the 'Simulation' tab. The 'Drivers' menu is selected, showing various simulation parameters. The 'Structure relaxation' section includes fields for 'Initial parameter scale' (0.5), 'Minimization levels' (0), and 'Minimization steps' (5000). The 'Ensemble' is set to 'NPT', 'MD time step' is '1fs', 'Number of MD steps' is '20000', 'Temperature' is '410K', 'Temperature increment (K/ps)' is '0', and 'Pressure' is '1atm'. The 'Deform system' is set to 'no'. The 'Periodic tasks' section includes 'MD steps between thermo outputs' (10), 'MD steps between trajectory outputs' (1000), and 'MD steps between neighbor list checks' (5). The 'Plot density vs. time' option is set to 'yes' and is highlighted with a blue arrow pointing to the text 'Activate option'. The interface includes a '< Structure' button and a 'Simulate >' button.

Step 4: Click simulate, wait for results

The screenshot shows the 'Simulate' tab of the Polymer Modeler software. The 'Simulation choice' is set to 'Run LAMMPS on structure'. The 'LAMMPS' section is active, showing 'Energy Expression', 'Drivers', and 'Advanced options' tabs. Under 'Structure relaxation', the 'Initial parameter scale' is 0.5, 'Minimization levels' is 0, and 'Minimization steps' is 5000. The 'Ensemble' is set to NPT, 'MD time step' is 1fs, and 'Number of MD steps' is 20000. The 'Temperature' is 410K, 'Temperature increment (K/ps)' is 0, and 'Pressure' is 1atm. The 'Deform system' is set to 'no'. Under 'Periodic tasks', 'MD steps between thermo outputs' is 10, 'MD steps between trajectory outputs' is 1000, and 'MD steps between neighbor list checks' is 5. A 'Simulate >' button is highlighted with a blue box.

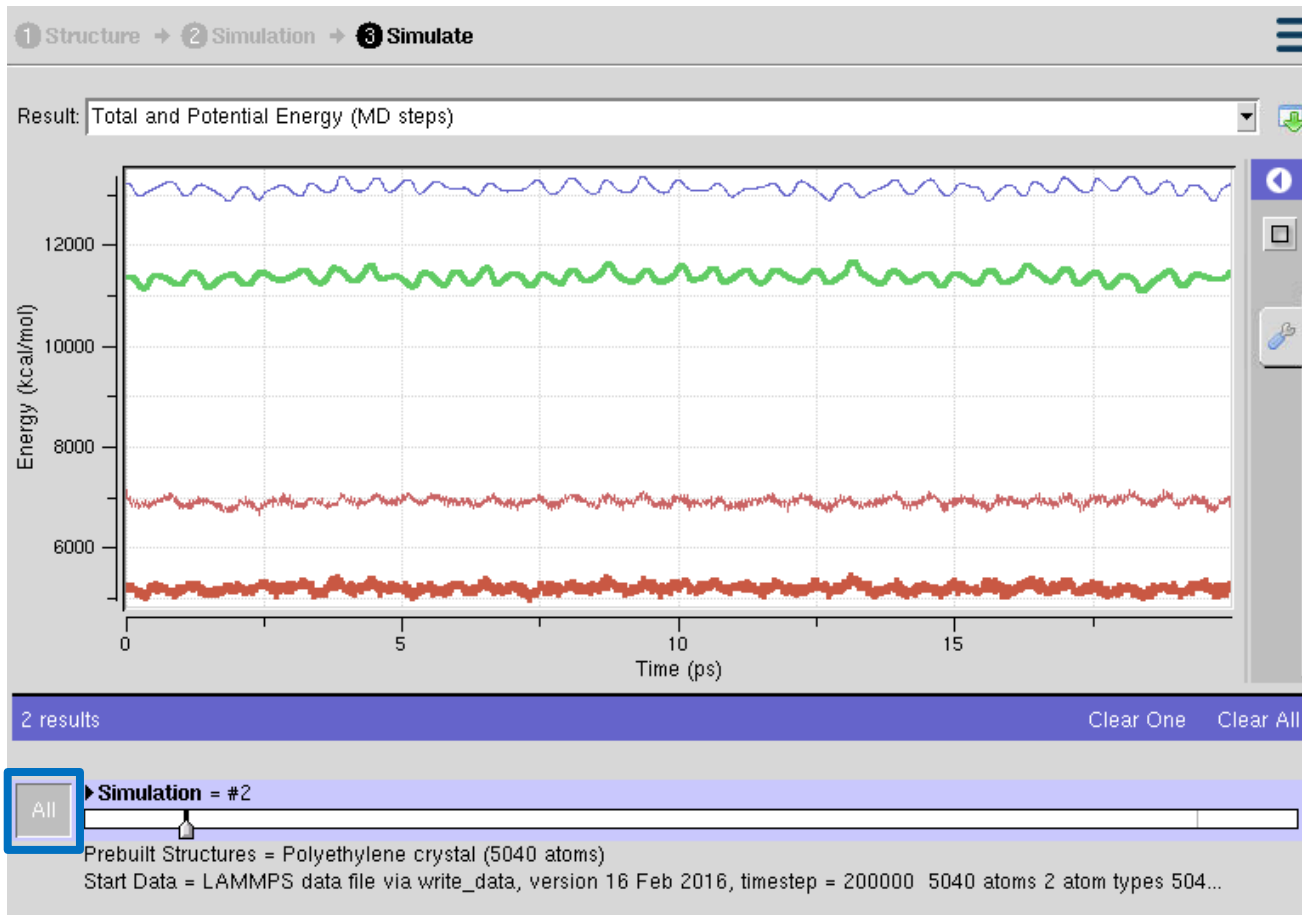
The screenshot shows the LAMMPS simulation output window. It displays 'Neighbor list info ...' and 'Setting up run ...'. A warning message states: 'WARNING: Inconsistent image flags (.../domain.cpp:682)'. Below this, a table shows simulation data for 31 processors. The table has columns for Step, TotEng, KinEng, Temp, PotEng, E_bond, E_angle, E_dihed, E_impro, E_vdwl, E_coul, E_long, Press, Pxx, Pyy, Pzz, and Pxy. A progress bar at the bottom indicates 10% completion, and the text 'Running LAMMPS (this may take some time...)' is displayed. An 'Abort' button is visible at the bottom right.

Step	TotEng	KinEng	Temp	PotEng	E_bond	E_angle	E_dihed	E_impro	E_vdwl	E_coul	E_long	Press	Pxx	Pyy	Pzz	Pxy
0	13229.699	6207.209				410		7022.49	2313.8472	3689.5817			625.12085			
10	13228.58	6286.8949				415.26343		6941.6854	2351.7647	3571.9872			623.70534			
20	13230.119	6183.8364				408.45618		7046.2827	2429.6809	3598.2753			632.61893			
30	13231.247	6108.8144				403.50082		7122.4326	2396.7955	3669.7316			644.15247			
40	13226.089	6201.6685				409.63403		7024.421	2296.1544	3661.4093			645.46903			
50	13220.348	6241.091				412.23798		6979.2572	2323.5365	3611.1322			633.47979			
60	13212.233	6218.8291				410.76753		6993.4037	2322.1656	3627.0771			631.34358			
70	13204.825	6282.9607				415.00356		6921.8647	2276.9687	3596.3139			637.07307			
80	13198.617	6163.8277				407.13457		7034.7889	2297.706	3665.2215			637.09123			
90	13189.878	6174.5662				407.84387		7015.3114	2319.7195	3650.5499			632.14834			
100	13181.577	6193.2954				409.08098		6988.2811	2351.4338	3589.4407			639.48665			
110	13168.2	6192.8229				409.04976		6975.3768	2357.6827	3562.6694			631.23653			
120	13149.856	6206.3913				409.94599		6943.4643	2271.3327	3672.2458			624.71518			
130	13132.616	6267.5583				413.9862		6865.0579	2265.6663	3590.5442			624.08712			
140	13117.197	6235.0065				411.83608		6882.19	2239.668	3613.2284			633.66817			
150	13102.518	6139.1638				405.50546		6963.3543	2342.2667	3613.3638			635.82593			
160	13086.223	6140.091				405.5667		6946.1319	2343.97	3594.4117			626.86491			
170	13066.502	6105.7335				403.29731		6960.7683	2290.8773	3629.8292			627.67018			
180	13046.929	6199.1059				409.46477		6847.8227	2289.4274	3549.9892			629.41284			
31	-138.62824	527.82659	954.92261			1015.081		-386.52387	-936.70003	-505.95496			40.09811			

Step 5: Once it finishes, repeat same procedure for prebuilt Crystal Polyethylene
Just go back to the **Structure** tab, no need to open a new Polymer Modeler

Step 6: Analyze data

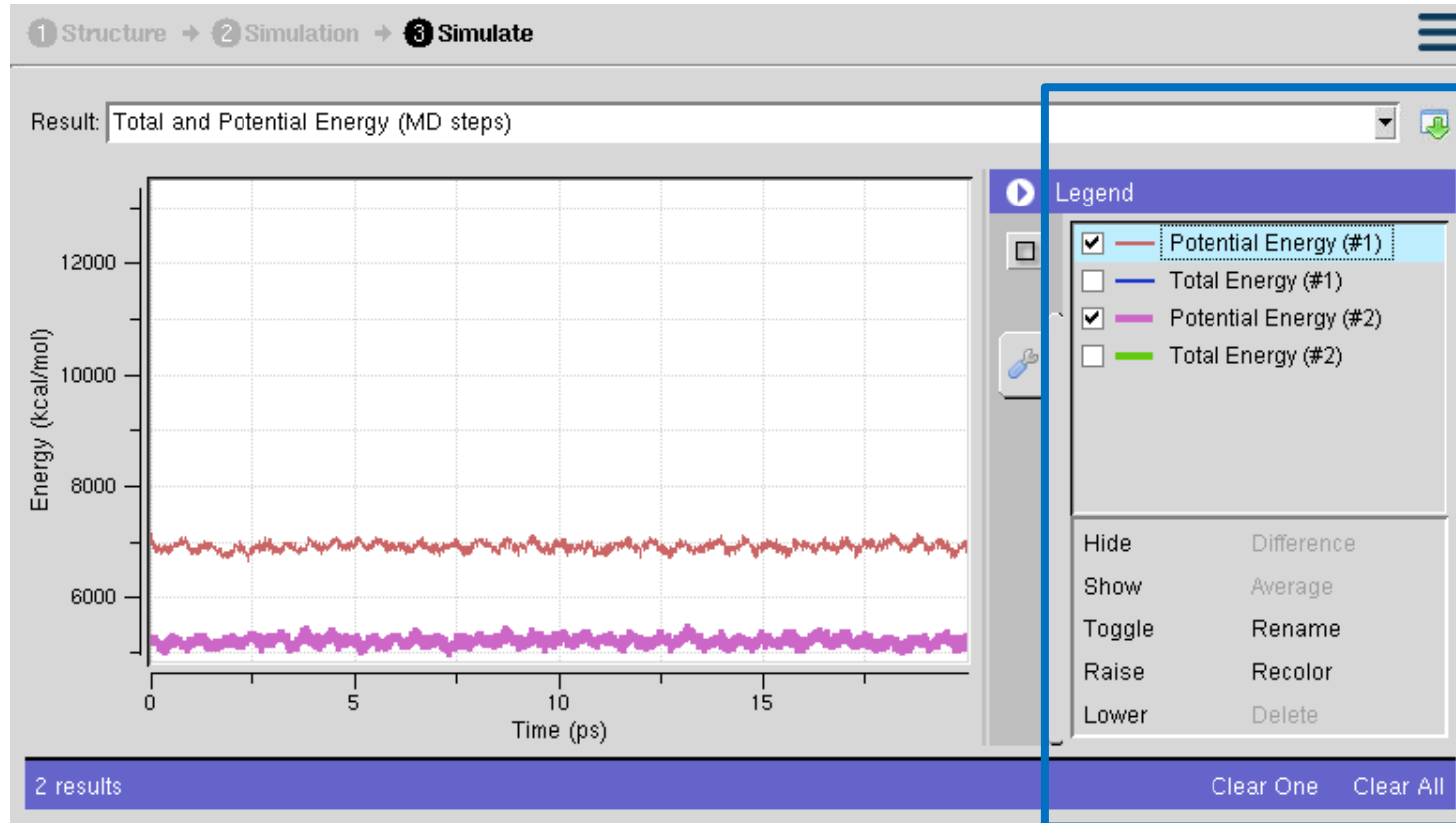
■ Select result: **Total and Potential Energy**



- Click **here** to recolor and rename data
- We will also unselect the Total Energy output

- Click **All** and you can visualize both results in the same screen

Step 6: Analyze data (Continuation)



- Once unselect the Total Energy output
- Click in the download bottom (right corner) and save file. It will contain the time and Potential Energy for each simulation case in order of simulation, for this case #1 is Amorphous PE and #2 Crystal PE

Step 7: Calculate heat of fusion

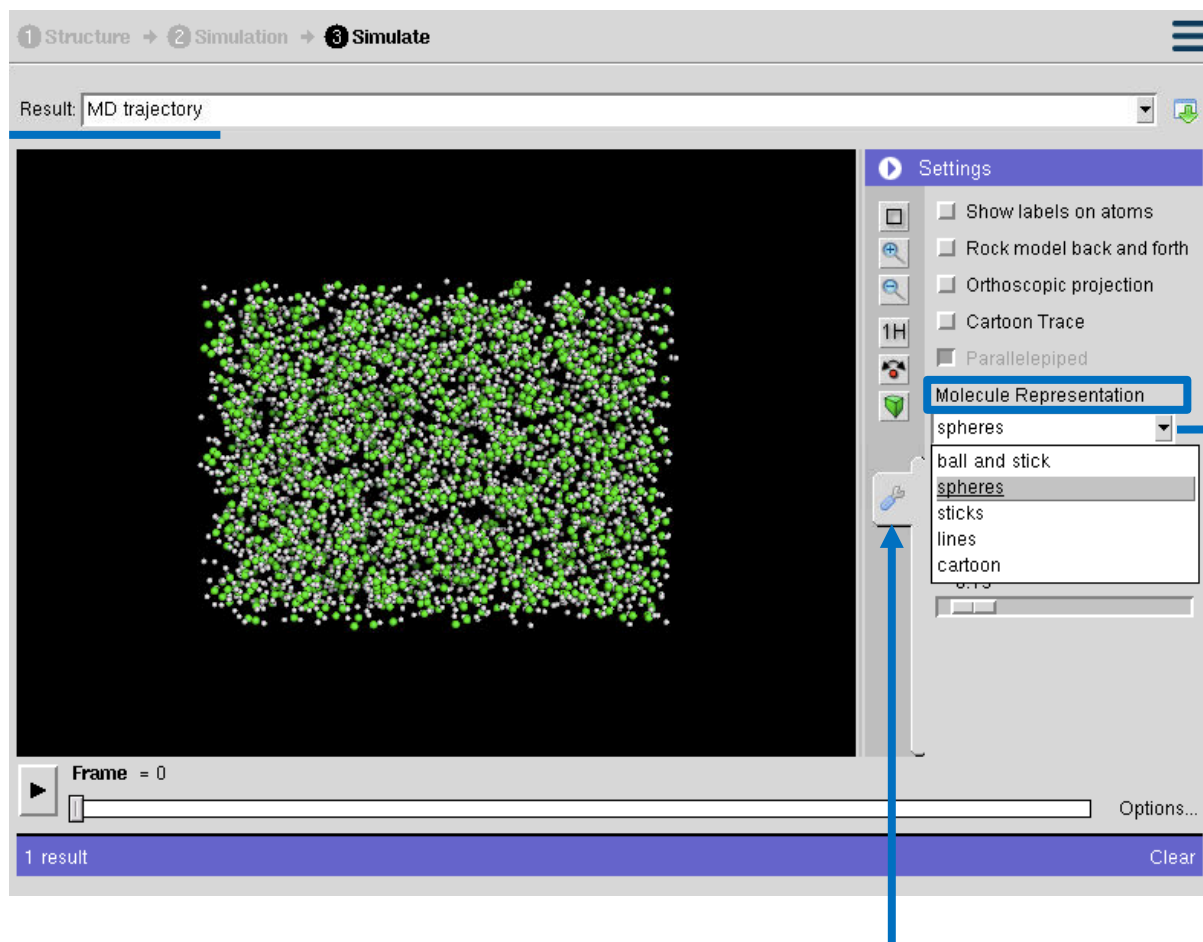
- Get an average of the Potential Energy for each simulation (you can import the data to Excel for example)
- Parameters of interest:
 - Number of Monomers in simulated PE = 840
 - Molecular weight monomer (MW_m) = 28 g/mol
 - Conversion 1 Kcal/mol = 4.184 KJ/mol

$$\langle dH \rangle = \left(\frac{\langle PE(\text{Amorphous}) \rangle - \langle PE(\text{Crystal}) \rangle}{\text{Monomers}} \right) * \frac{1}{MW_m} \text{ [Kcal/g]}$$

$$\langle dH \rangle = \langle dH \rangle \text{ [Kcal/g]} \times 4.184 \times 1000 \text{ [J/g]}$$

MD trajectory visualization

- To visualize the MD trajectory select this option in the Result menu



2. Change Molecule Representation to **spheres**

1. Open the Settings option clicking here

Heat of fusion (example)

- We have obtained the averaged potential energies for a simulation of crystal PE:

$$\langle PE(\text{Crystal}) \rangle = 5205.6 \pm 72.6 \text{ [Kcal/g]}$$

$$\langle dH \rangle = \left(\frac{\langle PE(\text{Amorphous}) \rangle - [5205.6 \pm 72.6]}{840} \right) * \frac{1}{28} \text{ [Kcal/g]}$$

$$\langle dH \rangle = [X \pm \text{error}] \text{ [Kcal/g]}$$

$$\langle dH \rangle = [X \pm \text{error}] \times 4.184 \times 1000 \text{ [J/g]}$$