

MedeA: Cohesive Energy Density: Compute Key Thermodynamic Characteristics of Molecular Systems

Contents

- [Introduction](#)
- [CED Usage](#)
- [CED Output](#)

1 Introduction

MedeA CED computes the cohesive energy density (CED) and the solubility parameter, δ , from a LAMMPS molecular dynamics simulation in the canonical (NVT) ensemble.

The CED is defined as the increase in internal energy, U , per mole of a substance when all intermolecular forces are eliminated [[vanKrevelen2009](#)]:

$$e_{coh} \equiv E_{coh}/V \quad (\text{at } 298 \text{ K}) \text{ in: } J/cm \text{ or } MJ/m \text{ or } MPa \quad (1)$$

MedeA CED provides an indication of a system's polarity and binding energy. For example, in a polymer, the higher the CED is the harder it is for guest molecules to permeate the polymer.

The solubility parameter is defined as:

$$\delta = (E_{coh}/V)^{1/2} \equiv e_{coh}^{1/2} \quad (\text{at } 298 \text{ K}) \text{ in: } (J/cm)^{1/3} \text{ or } (MJ/m)^{1/2} \text{ or } MPa^{1/2} \quad (2)$$

For liquids of low molecular weight, the CED is equivalent to the heat of vaporization divided by the molar volume in the condensed phase.

$$E_{coh} = \Delta U_{vap} = \Delta H_{vap} - p\Delta V \approx \Delta H_{vap} - RT \quad (3)$$

Key Benefits

- Automated setup, execution, and analysis of LAMMPS molecular dynamics simulations for cohesive energy density, solubility parameters, and interfacial tension calculations
- Handles model construction and assignment of forcefield atom types and charges in one unified environment so that there is no need to use external tools
- Provides formatted output

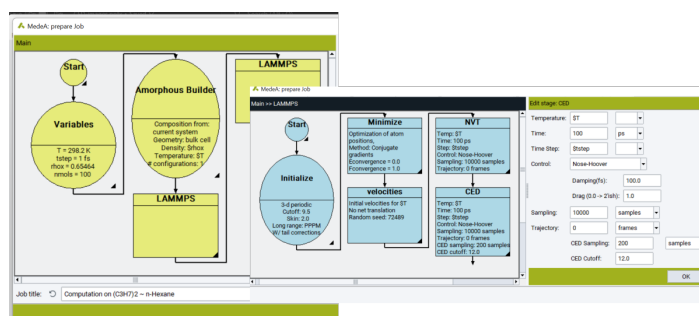
Hint: The *MedeA CED* module works with molecular dynamics simulations using LAMMPS. Ab initio MD trajectories are not currently supported with the *CED* module.

2 CED Usage

The **CED** stage computes the cohesive energy density during a molecular dynamics simulation in the canonical (NVT) ensemble.

Hint: To start with, you need to set up a fluid or polymer model. When starting from a molecular system, use the *MedeA Amorphous Materials Builder* to generate an appropriate input structure. The *MedeA* flowchart library contains template workflows for building amorphous systems.

You can load the **CED** stage into any *MedeA LAMMPS* Flowchart. To do so, click on the structure window containing your system and select **New Job...** from the **Jobs** menu. In the below screenshot, the **Amorphous Builder** stage is followed by two **LAMMPS** stages. The second **LAMMPS** stage includes a **Minimize** stage, an equilibration run using an **NVT** stage, and finally the **CED** stage.



The parameters of the **CED** stage are:

- *Temperature*: The temperature at which to equilibrate the system and compute the interface tension.
- *Time*: The simulation time.
- *Time Step*: The time step size employed in solving the equations of motion.
- *Control*: The thermostat used for the NVT ensemble.
- *Sampling*: Number of samples, steps, or length of time from which to compute the CED.
- *Trajectory*: Write the configuration to a trajectory file with a frequency specified in frames, steps, or time.
- *Cutoff*: Cutoff in Å for the sampling used when computing the CED.

3 CED Output

After completing a *CED* simulation, results are written to *Job.out* and a results table is produced.

Stage 4.5: Cohesive energy density using NVT integration
for 100 ps with a timestep of 1 fs, T is 298.2 K

Property	Value	+/- Uncertainty	Units	After Steps	% Run
t:	100000		fs		
T:	298.214	+/- 0.022	K	0	0.0%
P:	-29	+/- 49	atm	0	0.0%
V:	21859.4	+/- 3.8e-10	Ang^3	0	0.0%
rho:	0.65465	+/- 0	g/mL	0	0.0%
Etotal:	6758	+/- 21	kJ/mol	0	0.0%
Epot:	-677	+/- 21	kJ/mol	0	0.0%
Ekin:	7434.76	+/- 0.54	kJ/mol	0	0.0%
Evdw:	-2452	+/- 6.5	kJ/mol	0	0.0%
Ecou1:	658.3	+/- 2.2	kJ/mol	1000	10.0%
CED:	221.76	+/- 0.45	J/cm^3	0	0.0%
CEDvdw:	221.5	+/- 0.45	J/cm^3	0	0.0%
CEDcou1:	0.254	+/- 0.01	J/cm^3	0	0.0%
dHvap_ideal:	31.671	+/- 0.06	kJ/mol	0	0.0%

LAMMPS stage successfully completed on 12 core(s) on Thu 24 November 2022 at 17:15:52 CET after 387 s (0:06:27)

The output table lists the CED, and a split of the CED into van der Waals and Coulombic distributions. The output also provides the ideal heat of vaporization.

References

[vanKrevelen2009] D.W. Van Krevelen, "Chapter 7 - Cohesive Properties and Solubility", *Properties of Polymers (Fourth Edition) Their Correlation with Chemical Structure; Their Numerical Estimation and Prediction from Additive group Contributions* 2009, Pages 189-227, <https://doi.org/10.1016/B978-0-08-054819-7.00007-8>