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

Contents

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]*:

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

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:

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

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

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

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.

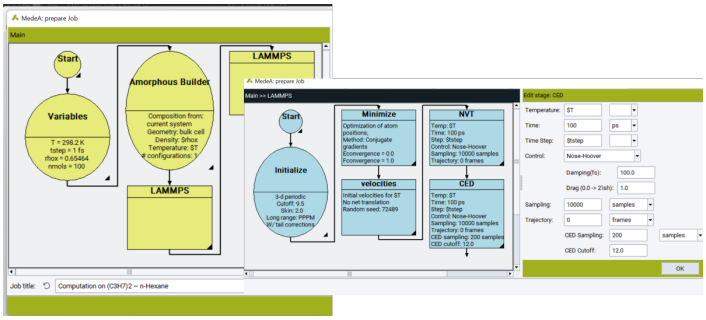
DOCUMENTATION

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 $\mathrm{\AA}$ 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%
                    Ecoul:     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%
                  CEDcoul:     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, “Capter 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