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.

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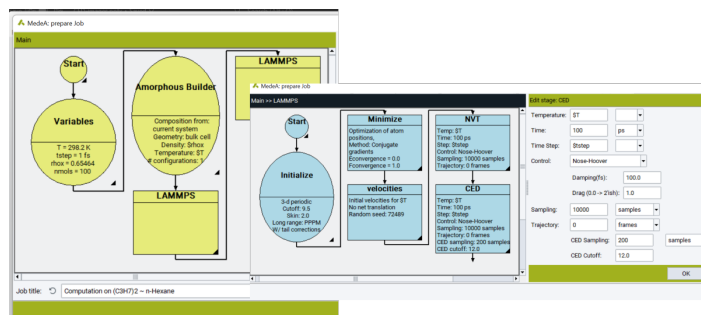
The parameters of the **CED** stage are:

- *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.

DOCUMENTATION

```
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