

# MedeA Software Environment Overview

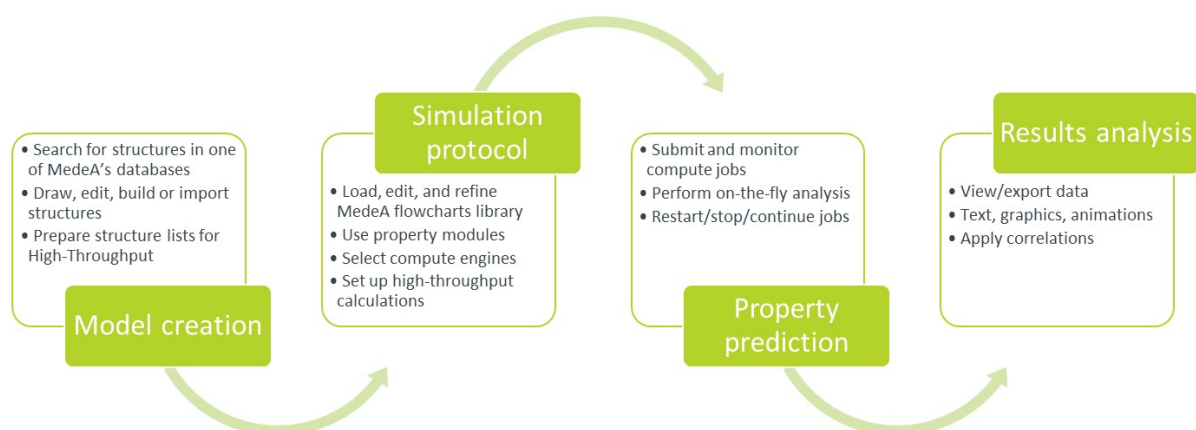
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## 1 Introduction

The *MedeA* software platform offers materials modeling capabilities ranging from the electronic structure to meso-scale phenomena. The core module of *MedeA*, the *MedeA Environment*, includes a comprehensive simulation environment for molecular dynamics (MD) with LAMMPS as a compute engine. *MedeA*'s add-on modules offer property prediction using density functional theory with VASP, quantum chemistry with Gaussian and MOPAC, statistical mechanics with the Monte-Carlo code GIBBS, and even correlation methods.

In addition, *MedeA* offers experimental structure databases, special builders, graphical analysis, a QSPR toolkit, and many other tools to generate materials property data. *MedeA*'s graphical flowchart editor helps simplifying and optimizing multi-stage calculations. In the *MedeA* flowchart library, Materials Design provides a growing set of validated workflows to standardize and automate simulation protocols.



## 2 All MedeA modules at a glance

Here's a list of all modules with links to the corresponding documentation section:

## 2.1 The *MedeA* Environment

Structure builders and database access, flowchart editor, forcefield library, job control and LAMMPS executables, along with many analysis tools make this module a comprehensive simulation environment for classical molecular dynamics.

Module name and link	Short description
MedeA Graphical Environment	Graphical workspace providing structure data and structure builders, a work flow editor and job control, and analysis tools.
MedeA InfoMaticA	Graphical user interface for searching, visualizing, and retrieving crystal structure data and structure models from <i>MedeA</i> 's structure databases.
MedeA Builders and Structure Editors	Basic builders and structure editors for crystals and molecules.
MedeA Advanced Builders	Advanced builders for supercells, surfaces, layers, polymers, point defects and nanoparticles, conformer search.
MedeA Flowchart Editor	Graphical editor for building workflows, and for accessing the <i>MedeA</i> workflow library and JobServer-side workflows.
MedeA Analysis	Geometry, symmetry, trajectories, electronic structure, spectroscopy, and many other tools for visualizing and analyzing simulation results.
MedeA LAMMPS	MD engine using NVT, NVE, and NPT ensembles
MedeA Forcefields	<i>MedeA</i> 's core forcefields library of validated forcefields for organic and inorganic materials.

In the following, we list all *MedeA* add-on modules.

## 2.2 *MedeA* databases

Module name and link	Short description
MedeA COD GUI	COD (Crystallography Open Database, University of Cambridge, UK) contains close to 500,000 structure entries
ICSD	Inorganic Crystal Structure Database by FIZ Karlsruhe, Leibniz Institute for Information Infrastructure, Germany
NCD	NIST Crystal Data by National Institute of Standards and Technology, USA
Pearson's Crystal Data	Pearson's Crystal Data: Crystal Structure Database for Inorganic Compounds® by ASM International, USA
MSIEureka	Dynamic Virtual Knowledgebase of Critically Evaluated Phase Constitution of Inorganic Materials by Materials Science International (MSI)

## 2.3 MedeA special builders

Module name and link	Short description
MedeA Amorphous Materials Builder	Generates equilibrated models of disordered or partially ordered organic or inorganic materials.
MedeA Thermoset Builder	Generates individual and batches of crosslinked structures based on amorphous input structures and user-defined reaction sites. Requires the <i>MedeA Amorphous Materials Builder</i> .
MedeA Mesoscale Builder	Generates mesoscale structures and polymer repeat units and lets you combine them with bulk or surface systems.
MedeA Docking	Determines preferred orientations of molecules within a host structure, typically either a surface or a microporous system.
MedeA Interface Builder	Generates heterogeneous interfaces and twist grain boundaries by combining two surface structures into a commensurate unit cell while minimizing the lattice mismatch.
MedeA Morphology	Simulates the morphology of a crystal using empirical or computed surface stability criteria.

## 2.4 MedeA compute engines and their GUI's

Module name and link	Short description
MedeA GIBBS	Monte Carlo engine for fluids and for adsorption of fluids in solids with statistical ensembles NVT, NPT, osmotic, GEMC, GCMC.
MedeA GIBBS GUI	Graphical user interface for <i>MedeA GIBBS</i> . Requires GIBBS.
MedeA VASP 6	The electronic structure <i>Vienna Ab-Initio Simulation Package</i> , version 6.3.2.
MedeA VASP 5.4	The electronic structure <i>Vienna Ab-Initio Simulation Package</i> , version VASP 5.
MedeA VASP GUI	Graphical user interface for <i>MedeA VASP</i> . Requires VASP 5 or VASP 6.
MedeA MOPAC	Electronic structure engine using semiempirical Hamiltonians.
MedeA MOPAC GUI	Graphical user interface for <i>MedeA MOPAC</i> . Requires MOPAC.
MedeA Gaussian GUI	Graphical user interface for <i>MedeA Gaussian</i> . Requires Gaussian.

## 2.5 MedeA Forcefields and Forcefield Generators

Module name and link	Short description
MedeA Embedded Atom Method (EAM) forcefields	The <i>MedeA</i> Embedded Atom Forcefield library for metallic systems.
MedeA Reaxff forcefields	The <i>MedeA ReaxFF</i> library to simulate complex chemical reactions and charge transfer.
MedeA Forcefield Optimizer	Determines optimum forcefield parameters for energy minimization (EM), MD simulations, and Monte Carlo (MC) simulations.

## 2.6 MedeA Machine-Learned Potentials

Module name and link	Short description
MedeA Machine Learned Potentials (MLP)	Provides support for machine-learned potential in MD simulations with <i>MedeA LAMMPS</i> .
MedeA Machine Learned Potential Generator (MLPG)	Generates machine-learned potentials for an input training-set of structures.

## 2.7 MedeA property modules

Module name and link	Short description
MedeA Diffusion	Automated diffusion calculations with <i>MedeA LAMMPS</i> .
MedeA Viscosity	Automated viscosity calculations with <i>MedeA LAMMPS</i> : Green-Kubo (GK), Müller-Plathe NEMD.
MedeA Thermal Conductivity	Automated thermal conductivity simulations with <i>MedeA LAMMPS</i> : Green-Kubo (GK), Müller-Plathe NEMD.
MedeA Surface Tension	Determines surface tension and interfacial tension with <i>MedeA LAMMPS</i> .
MedeA Deposition	Simplifies atomic-scale simulations with <i>MedeA LAMMPS</i> , for deposition, growth, oxidation, and etching.
MedeA MT - Elastic Properties	Automated calculation of mechanical and thermal properties with <i>MedeA LAMMPS</i> and <i>MedeA VASP</i> . Requires <i>MedeA VASP</i> .
MedeA Deformation	Simplifies exploring deformation and fracture beyond the elastic regime with <i>MedeA VASP</i> or <i>MedeA LAMMPS</i> . Requires <i>MedeA VASP</i> .
MedeA Cohesive Energy Density (CED)	Calculates the cohesive energy density, solubility parameter, and heat of vaporization for molecular systems using <i>MedeA LAMMPS</i> .
MedeA Transition State Search	Simplifies the prediction of reaction and diffusion pathways, transition states, and activation barriers with <i>MedeA VASP</i> . Requires <i>MedeA VASP</i> .
MedeA Phonon	Automated calculation of lattice dynamics and vibrational properties with <i>MedeA VASP</i> or <i>MedeA LAMMPS</i> . Requires <i>MedeA VASP</i> .
MedeA UNCLE	Explores phase stability and performs Monte Carlo Simulations for crystals containing millions of atoms by determining a simplified Hamiltonian based on a cluster expansion of the input crystal structure.
MedeA Electronics	Automated calculation of advanced electronic properties including Fermi surfaces, transport and effective masses with <i>MedeA VASP</i> . Requires <i>MedeA VASP</i> .

## 2.8 MedeA high-throughput computing, correlations, and descriptors

Module name and link	Short description
MedeA P3C	Property prediction for thermoplastic polymers using empirical correlations
MedeA QSPR Toolkit (QT)	Toolbox for deriving Quantitative Structure Property/Activity Relationship (QSPR/QSAR)
MedeA High-Throughput Launchpad	Enables high-throughput calculations for large sets of systems using a single computational protocol.
MedeA High-Throughput Descriptors	Helps to define, compute, exploit, and organize materials descriptor within the <i>MedeA Environment</i> .

## 3 Computing solid-state properties with MedeA

The following table provides a selection of solid-state properties accessible in *MedeA* together with the relevant *MedeA* modules.

Property ID	Property type	Property	Observable, symbol, descriptor	Computational Method
[1]	<b>Structural</b>	Crystal structure	Lattice parameters $(a, b, c)$ , $(\alpha, \beta, \gamma)$ , Powder pattern	<i>MedeA</i> VASP, LAMMPS
[2]	<b>Structural</b>	Surface relaxation, reconstruction	Lattice parameters $(a, b, c)$ , $(\alpha, \beta, \gamma)$ , atomic position	<i>MedeA</i> VASP, LAMMPS
[3]	<b>Structural</b>	Adsorption (chemisorption)	Bond length	<i>MedeA</i> VASP, LAMMPS
[4]	<b>Structural</b>	Point defects	Atomic positions	<i>MedeA</i> VASP, LAMMPS
[5]	<b>Structural</b>	Powder diffraction pattern	Lattice parameters $(a, b, c)$ , $(\alpha, \beta, \gamma)$	<i>MedeA Environment</i>
[6]	<b>Structural</b>	Amorphousness	Total-, atomic pair correlation function plot	<i>MedeA</i> VASP, LAMMPS
[7]	<b>Thermo-mechanical</b>	Density	Composition, unit cell volume, crystal structure: $(a, b, c)$ , $(\alpha, \beta, \gamma)$	<i>MedeA</i> VASP, LAMMPS
[8]	<b>Thermo-mechanical</b>	Elastic moduli	Strain-stress analysis, Hill-Walpole analysis	<i>MedeA MT</i> , VASP, LAMMPS
[9]	<b>Thermo-mechanical</b>	Thermal Expansion	Lattice constants, Free energy $A(T)$	<i>MedeA Phonon</i> , VASP, LAMMPS
[10]	<b>Thermo-mechanical</b>	Fracture	Strain-stress analysis	<i>MedeA Deformation</i> , LAMMPS, VASP
[11]	<b>Thermo-mechanical</b>	Non-elastic regime, plasticity	Strain-stress analysis	<i>MedeA Deformation</i> , LAMMPS, VASP
[12]	<b>Thermodynamic</b>	Thermodynamic potentials	Internal energy $\Delta U$ , Enthalpy $\Delta H$ , Entropy $\Delta S$ , Gibbs Free energy $\Delta G$	<i>MedeA Phonon</i> , <i>MedeA MT</i> , <i>MedeA VASP</i> , LAMMPS
[13]	<b>Thermodynamic</b>	Thermodynamic properties	Heat capacity $c_v$ , $c_p$ , isothermal compressibility, linear volumetric thermal expansivity, velocity of sound	<i>MedeA Phonon</i> , <i>MedeA MT</i> , <i>MedeA VASP</i> , LAMMPS
[14]	<b>Thermodynamic</b>	Solubilities	Solubility energy $E_{Sol}$	<i>MedeA Phonon</i> , VASP
[15]	<b>Thermodynamic</b>	Adsorption (physisorption)	Adsorption isotherm $\Theta_A(P)$	<i>MedeA GIBBS</i>
[16]	<b>Thermodynamic</b>	Transition temperatures	Solid $\leftrightarrow$ transition, melting temperature $T_m$	<i>MedeA LAMMPS</i> , VASP
[17]	<b>Thermodynamic</b>	Mass diffusion coefficient	Diffusion coefficient $D$	<i>MedeA Diffusion</i> , LAMMPS, TSS, VASP
[18]	<b>Thermodynamic</b>	Permeability	Solubility $S$ , diffusion coefficient $D$	<i>MedeA GIBBS</i> , <i>Diffusion</i> , LAMMPS
[19]	<b>Thermodynamic</b>	Thermal conductivity	Thermal conductivity coefficient $\kappa$	<i>MedeA Thermal Conductivity</i> , LAMMPS
[20]	<b>Thermodynamic</b>	Mixing Enthalpy, Formation enthalpy	Enthalpy of formation of solid solution ( $\Delta H_{SS}$ )	<i>MedeA Phonon</i> , UNCLE, VASP
[21]	<b>Thermodynamic</b>	Phase stability	Free energy $\Delta A(T)$	UNCLE, Phonon, VASP

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Property ID	Property type	Property	Observable, symbol, descriptor	Computational Method
[22]	<b>Thermodynamic</b>	Cohesive energy/Binding energies	$E_{coh}$	MedeA CED, VASP, LAMMPS
[23]	<b>Vibrational Analysis</b>	Phonon Dispersion and Density of States	Phonon dispersion relation $\omega(\vec{q})$ , Global and atom-resolved phonon density of state, $n(\vec{q})$	MedeA Phonon, VASP, LAMMPS
[24]	<b>Vibrational Analysis</b>	Spectrometry	Infrared/Raman spectrum Transmittance $T(\nu)$	MedeA Phonon, MedeA VASP
[25]	<b>Chemical</b>	Reaction mechanisms and reaction rates	Reaction barrier, reaction pathway	MedeA TSS, MedeA Phonon, MedeA VASP
[26]	<b>Chemical</b>	Reactivity on surfaces	Binding energies, reaction barriers	MedeA VASP, LAMMPS
[27]	<b>Chemical</b>	Solid-solid reactions	Heat of formation $\Delta H_f$ , heat of reaction $\Delta H_r$	MedeA VASP, Phonon
[28]	<b>Electronic, optical, magnetic</b>	Photochemical	Electronic structure, conduction bands, excited states	MedeA VASP
[29]	<b>Electronic, optical, magnetic</b>	Electrical conductivity	Electrical conductivity $\sigma$ , resistivity $\rho$	MedeA Electronics, VASP
[30]	<b>Electronic, optical, magnetic</b>	Electronic density	Electronic density function $\rho$	MedeA VASP
[31]	<b>Electronic, optical, magnetic</b>	Electrostatic potential	Electrostatic potential $\Phi$ , electronic density function $\rho$	MedeA VASP
[32]	<b>Electronic, optical, magnetic</b>	Dielectric properties	Dielectric tensor $\epsilon$	MedeA VASP
[33]	<b>Electronic, optical, magnetic</b>	Piezoelectric properties	Piezoelectric tensor $\delta$	MedeA VASP
[34]	<b>Electronic, optical, magnetic</b>	Spin density distribution, magnetic moments	$\mu_B$ , electronic density function $\rho$	MedeA VASP
[35]	<b>Electronic, optical, magnetic</b>	Energy band structure - metal, semiconductor, insulator	Electronic dispersion $\epsilon(\vec{k})$	MedeA VASP
[36]	<b>Electronic, optical, magnetic</b>	Band gaps, band offsets at heterojunctions	Electronic dispersion $\epsilon(\vec{k})$	MedeA VASP
[37]	<b>Electronic, optical, magnetic</b>	Ionization energies and electron affinities	Electronic dispersion $\epsilon(\vec{k})$	MedeA VASP

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Table 1 – continued from previous page

Property ID	Property type	Property	Observable, symbol, descriptor	Computational Method
[38]	<b>Electronic, optical, magnetic</b>	Work function	Work function $W$ , Electrostatic Potential $\Phi$ , Fermi level $E_F$	<i>MedeA VASP</i>
[39]	<b>Solid Characterization</b>	X ray diffraction pattern	Powder pattern	<i>MedeA VASP</i>
[40]	<b>Solid Characterization</b>	Vibrational spectra	IR/Raman spectrum	<i>MedeA Phonon, VASP</i>
[41]	<b>Solid Characterization</b>	NMR spectra	Chemical shift, electric field gradients, quadrupolar coupling constant	<i>MedeA Phonon, VASP</i>
[42]	<b>Solid Characterization</b>	Optical spectra	Optical transmission absorption, reflection spectra, spectral emissivity, color space	<i>MedeA VASP</i>
[43]	<b>Solid Characterization</b>	Photoelectron spectra	Bandstructure, electronic dispersion $\epsilon(\vec{k})$	<i>MedeA VASP</i>
[44]	<b>Solid Characterization</b>	Inelastic x-ray scattering angles	Phonon dispersion relation $\omega(\vec{q})$ , Global and atom-resolved phonon density of state, $n(\vec{q})$	<i>MedeA Phonon, VASP</i>
[45]	<b>Solid Characterization</b>	Brillouin light-scattering data	Single-crystal elastic constants	<i>MedeA MT, VASP</i>
[46]	<b>Solid Characterization</b>	Differential scanning calorimetry (DSC)	Thermodynamic potentials: Internal energy $\Delta U$ , Enthalpy $\Delta H$ , Entropy $\Delta S$ , Gibbs Free energy $\Delta G$	<i>MedeA Phonon, VASP</i>

## 4 MedeA fluid properties

The following table shows selected fluid properties and a short description of the computational protocol.



Property ID	Property name	Symbol	Computational Method
[1]	Vapor-Liquid Equilibrium	VLE	MedeA GIBBS
[2]	Critical Temperature	$T_c$	MedeA GIBBS
[3]	Critical Pressure	$P_c$	MedeA GIBBS
[4]	Critical Volume	$V_c$	MedeA GIBBS or MedeA LAMMPS
[5]	Acentric Factor	$\omega$	MedeA GIBBS
[6]	Vaporization Enthalpy	$\Delta H_{vap}(T)$	MedeA GIBBS
[7]	Normal Boiling Point	$T_b$	MedeA GIBBS
[8]	Saturation Pressure	$P_{sat}(T)$	MedeA GIBBS
[9]	Saturated Liquid Density	$\rho(T)$	MedeA LAMMPS or MedeA GIBBS
[10]	Compressibility Factor	Z	MedeA GIBBS
[11]	Henry Constant	$K_H$	MedeA GIBBS
[12]	Apparent Liquid Density	mv15	MedeA LAMMPS
[13]	Viscosity	$\eta$	MedeA Viscosity, LAMMPS
[14]	Self-diffusivity	D	MedeA Diffusion, LAMMPS
[15]	Thermal Conductivity	$\lambda$	MedeA Thermal Conductivity, LAMMPS
[16]	Joule-Thomson Coefficient	$\mu_{JT}$	MedeA GIBBS or MedeA LAMMPS
[17]	Heat Capacity	$C_P(T)$	MedeA Gaussian or MedeA MOPAC with MedeA GIBBS or MedeA LAMMPS
[18]	Isobaric Thermal Expansivity	$\alpha$	MedeA GIBBS or MedeA LAMMPS
[19]	Isothermal Compressibility	$\beta_T$	MedeA GIBBS or MedeA LAMMPS
[20]	Speed of Sound	$U_s$	MedeA GIBBS
[21]	Dielectric Constant	$\epsilon$	MedeA Gaussian or MedeA MOPAC , MedeA LAMMPS
[22]	Surface Tension	$\gamma(T)$	MedeA Surface Tension, LAMMPS

### Vapor-liquid equilibrium

Monte Carlo simulations with *MedeA GIBBS* in the isochoric Gibbs ensemble can be employed to calculate vapor-liquid equilibria (VLE) properties of pure compounds. In the isochoric Gibbs ensemble simulation (GEMC, NVT) there are two (or more) coexisting phases. The coexisting phases are not in direct contact, there is one simulation box for each phase. The total number of molecules, the total volume and the temperature of each phase is kept constant. However, the molecules are allowed to transfer between phases, therefore switch simulation boxes. Also, the volume of each phase is allowed to change, while the total volume is kept constant. This ensemble allows the study of multi-phase systems, without dealing explicitly with the interface(s).

### Critical temperature

The critical temperature  $T_c$  refers to the liquid-vapor critical point. It is obtained from Gibbs Ensemble Monte Carlo two-phase simulations at subcritical temperatures with *MedeA GIBBS*. The extrapolation to  $T_c$  relies on non-classical scaling laws as described by [1]: [2]. The accuracy depends on the forcefield, but for large molecules, accuracy is also affected by statistical uncertainties.

### Critical pressure

- [1] P. Ungerer, B. Tavittian and A. Boutin, "Applications of molecular simulation in the oil and gas industry - Monte Carlo methods", Editions Technip (2005)
- [2] D. Frenkel and B. Smit, "Understanding molecular simulation: from algorithms to applications", Academic press (2002)



The critical pressure  $P_c$  corresponds to the liquid-vapor critical point. It is obtained by extrapolating the saturation pressure line obtained with *MedeA GIBBS* from GEMC simulations up to the critical point in a Clapeyron plot, i.e.,  $\ln(P_{sat})$  over  $1/T$ . The relative uncertainty on  $P_c$  is thus equivalent to  $P_{sat}$  or slightly larger.

### Critical volume

The critical volume  $V_c$  is the molar volume of the compound at the liquid-vapor critical point. It is the inverse of the critical density. It can be determined together with the critical temperature by extrapolation from data on 4-5 pairs of coexistence densities below the critical temperature. The coexisting densities can be determined with *MedeA GIBBS* or *MedeA LAMMPS*.

### Acentric factor

The acentric factor ( $\omega$ ) is a dimensionless parameter defined via the saturated vapor pressure at  $T = 0.7T_c$ :

$$\omega = 1 - \log_{10} \frac{P_{sat}(T=0.7T_c)}{P_c}$$

The uncertainty follows the uncertainties on  $P_{sat}$ ,  $P_c$  and  $T_c$

### Vaporization enthalpy

At a given temperature, the vaporization enthalpy  $\Delta H_{vap}$  is the difference between the molar enthalpy of the liquid phase and the molar enthalpy of the vapor phase in equilibrium conditions. It is determined from Gibbs Ensemble Monte Carlo (GEMC) simulations using *MedeA GIBBS* together with coexisting densities at 4-5 temperatures [1]. At lower temperatures,  $\Delta H_{vap}$  is approximated with the cohesive energy of the liquid phase by doing single phase *MedeA GIBBS* or *MedeA LAMMPS* simulations.

### Normal boiling point

The normal boiling temperature  $T_b$  is defined as the temperature for which the saturated vapor pressure is equal to 1 atmosphere (1.0125 bar). It is obtained by interpolating the saturated vapor pressures determined from GEMC simulations with *MedeA GIBBS*.

### Saturation pressure

The saturated vapor pressure,  $P_{sat}(T)$  is the gas phase pressure of a pure component in equilibrium with the pure liquid at T. This property is determined by *MedeA GIBBS* from a combination of two-phase GEMC simulations imposing a global volume [2] [3].

### Saturated liquid density

For a pure compound the saturated liquid density  $\rho(T)$  depends on the temperature only. It is determined from GEMC or single phase NPT simulations with *MedeA GIBBS*.

### Compressibility factor

The compressibility factor  $Z = PV/RT$ , where  $V$  is the molar volume, serves to quantify the degree of deviation from the ideal gas law ( $Z=1$ ) which is observed at low pressure.  $Z$  is determined for saturated vapor densities collected during GEMC simulations with *MedeA GIBBS*.

### Henry constant

At the limit of infinite dilution, the Henry constant  $K_{H,ij}$  of a solute  $i$  in a solvent  $j$  may be calculated through the expression :

$$K_{(H,ij)} = \frac{f_i}{c_i}$$

with  $f_i$  being the fugacity of component  $i$  and  $c_i$  the concentration of  $i$  in the liquid solvent. A concentration of 1 molecule of  $i$  per 200 molecules of solvent can be used to model an infinite dilution. The fugacity is directly evaluated from NPT calculation performed with *MedeA GIBBS*.

### Apparent liquid density

The purpose of the apparent liquid density mv15 is to estimate the liquid density of a mixture at 15°C by adding contributions of each component. From this definition it follows that mv15 is not a pure component

[3] A.Z. Panagiotopoulos, "Direct determination of phase coexistence properties of fluids by Monte Carlo simulation in a new ensemble", *Mol. Phys.* **61** (4), p. 813 (1987)

property. It is rather the inverse of the partial molar volume  $(\frac{\partial v}{\partial n_i})_{P,T,n_j}$ . Thus, mv15 depends on the composition of the liquid mixture in which an additional molecule is added. Mv15 can be computed using *MedeA LAMMPS*. Small variations of the number of molecules  $n_i$  in the reference mixture(s) are generally considered.

### Viscosity

Here, by viscosity  $\eta$  we refer to the zero-shear viscosity in a Newtonian fluid, where the shear rate is proportional to the shear stress. For pure compounds, the Green Kubo expressions in equilibrium MD (D Dysthe 1999) or the Muller-Plathe method (F Müller-Plathe 1999) in non-equilibrium MD can be applied using *MedeA Viscosity*. Viscosity predictions are limited to conditions where approximately  $\eta < 20$  cP (20 mPa.s). Outside this range, or in the case of high molecular-weight polymers, we need to apply other methods, such as extrapolation from higher temperatures, using the relation to the easier-to-calculate self-diffusion coefficient or QSPR.

### Self-diffusivity

The self-diffusivity (D) quantifies the rate of diffusion of a molecule in a condensed phase. It is determined directly in *MedeA Diffusion* by analyzing the mean squared displacement during a *LAMMPS* molecular dynamics run. For molecules with very long relaxation time at the temperature of interest, the self-diffusivity can be obtained by extrapolating from higher temperatures, or by QSPR.

### Thermal Conductivity

The thermal conductivity  $\lambda$  describes the linear relation between the conductive heat transfer and the temperature gradient. It is determined directly using *MedeA Thermal Conductivity* using the Green Kubo method or the Müller-Plathe method.

### Lower Heat of Combustion

The lower heat of combustion PCI in standard conditions (25 °C, 1 bar) is computed as the enthalpy change during complete combustion, when all reaction products are supposed to be in the gas state. With *MedeA MOPAC*, the predicted accuracy is of 20 kJ/mol for e.g. gasoline or gasoil-range hydrocarbons, or 3% for heavy compounds.

### Upper Heat of Combustion

The upper heat of combustion PCS is obtained from the lower heat of combustion by adding the enthalpy of vaporization of water among the products. With *MedeA MOPAC*, the average deviation with experimental values will be similar (20 kJ/mol on light compounds, 3% on heavier ones).

### Ideal Gas Heat Capacity

the ideal gas capacity  $C_{P,id}(T)$  can be predicted as a function of temperature with *MedeA MOPAC* or *MedeA Gaussian* for a reference pressure of 1 bar. From our experience, the expected average accuracy obtained with *MedeA MOPAC* is lower than 4% (AAD) for organic molecules and 10% for inorganic molecules in the temperature range 300 – 1000 K [4]. For mixtures of known composition,  $C_{P,id}(T)$  is the molar average of pure component ideal heat capacities.

### Ideal Gas Enthalpy of Formation

The ideal gas enthalpy of formation, or standard heat of formation, is predicted by *MedeA MOPAC* (PM7) as this semi-empirical method has been parameterized based on a large number of evaluated data. The expected accuracy is approximately 20 kJ/mol on light compounds, 3% on heavier ones. *MedeA Gaussian* can also be used for this purpose.

### Ideal Gas Gibbs Free Energy of Formation

The Gibbs free energy of formation at 25 °C and 1 bar in the ideal gas state can be computed from *MedeA MOPAC* using corrections for the entropy of elements in the standard state. The expected accuracy is approximately 20 kJ/mol on light compounds, 3% on heavier ones. *MedeA Gaussian* can also be used for this purpose

[4] X. Rozanska, J.J.P. Stewart, P. Ungerer, B. Leblanc, C. Freeman, P. Saxe and E. Wimmer., "High-Throughput Calculations of Molecular Properties in the MedeA Environment: Accuracy of PM7 in Predicting Vibrational Frequencies, Ideal Gas Entropies, Heat Capacities, and Gibbs Free Energies of Organic Molecules", *J. Chem. & Eng. Data* **59** (10), p. 3136 (2014)

### Joule-Thomson Coefficient

The Joule Thomson coefficient is determined in high-pressure conditions from classical Monte Carlo using *MedeA GIBBS* or molecular dynamics with *MedeA LAMMPS*.

### Heat Capacity

The heat capacity of a fluid (pure or mixture) at T, P is obtained by summing up its ideal heat capacity  $C_{P,id}(T)$  and its residual heat capacity  $C_{P,res}(T, P)$ . The latter is determined from energy fluctuations in *MedeA GIBBS* or by finite differences or fluctuations in *MedeA LAMMPS*.

### Isobaric Thermal Expansivity

The isobaric thermal expansion coefficient  $\alpha$  (or expansivity) is obtained with *MedeA GIBBS* from volume and energy fluctuations in the NPT ensemble (M Lagache 2001) (P. U. M Lagache 2004) or by finite differences or fluctuations using *MedeA LAMMPS*.

### Isothermal Compressibility

The isothermal compressibility,  $\beta_T$ , is obtained with *MedeA GIBBS* from volume fluctuations in the NPT ensemble (M Lagache 2001) (P. U. M Lagache 2004) or by finite differences or fluctuations using *MedeA LAMMPS*.

### Speed of Sound

The speed of sound  $U_s$  of a fluid – either liquid or gas, pure or mixture - is computed in *MedeA GIBBS* from the isentropic compressibility coefficient and the molar volume. It is applicable to high pressure (up to 10-1,000 bar) and high temperature (up to 1,000 K).

### Electronegativity

Electronegativity,  $\chi$ , is a chemical property describing the tendency of an atom or a functional group to attract electrons. The Mulliken electronegativity, i.e. the arithmetic mean of the first ionization energy and the electron affinity, also called “absolute electronegativity” can be calculated with *MedeA MOPAC* and *MedeA Gaussian* (performing a geometry optimization with *MedeA MOPAC* and then an energy calculation with *MedeA Gaussian*).

### Dipole Moment

A molecule's dipole moment,  $\mu$ , is an electric dipole, which occurs when the atoms in a molecule have substantially different electronegativity. The dipole vector of a molecule in the gas state (calculated from atomic charges and the lone pairs), along with the net dipole moment, can be calculated with *MedeA MOPAC* and *MedeA Gaussian* (performing a geometry optimization with *MedeA MOPAC* and *MedeA Gaussian* and then an energy calculation with Gaussian). When molecules with many conformers are considered, the calculation of this property can take place after a conformer search is performed and an average (weighted) over the range of conformers can be calculated. This will increase the computational effort (larger number of simulations) analogously to the number of conformers identified for each compound.

### Quadrupole Moment

A molecule's quadrupole moment, Q, is an electric quadrupole, which is providing a measure of the charge distribution in a molecule. The quadrupole moment of a molecule (primitive and traceless matrixes and quadrupole magnitude) can be calculated with *MedeA MOPAC* and *MedeA Gaussian* (performing a geometry optimization with *MedeA MOPAC* and then an energy calculation with *MedeA Gaussian*).

### Polarizability

Neutral nonpolar species have spherically symmetric arrangements of electrons in their electron clouds. When in the presence of an electric field, their electron clouds can be distorted. The ease of this distortion is defined as the polarizability of a molecule. The polarizability,  $\alpha$ , of a molecule can be calculated with *MedeA MOPAC* and *MedeA Gaussian* (performing a geometry optimization with MOPAC and then an energy calculation with Gaussian).

When molecules with many conformers are considered, the calculation of this property can take place after a conformer search is performed and an average (weighted) over the range of conformers can be calculated. This will increase the computational effort (larger number of simulations) proportionally to the number of conformers identified for each compound.

## Acid Dissociation Constant

The acid dissociation constant,  $K_a$ , is a quantitative measure of the strength of an acid in solution. Each acid has a different  $pK_a$  ( $pK_a = -\log_{10}K_a$ ). This is the equilibrium constant for a chemical reaction known as dissociation in the context of acid-base reactions. The acid dissociation constant,  $pK_a$ , can be calculated with *MedeA MOPAC* and *MedeA Gaussian*. Using *MedeA MOPAC* PM6 for OH-group containing molecules, the expected absolute average deviation is of the order of  $\pm 0.3$   $pK_a$  units.

## Dielectric Constant

The dielectric constant is the ratio of the permittivity of a substance to the permittivity of free space. The dielectric constant affects the Coulomb forces between two point-charges in the material. This property can be estimated from molecular dynamics simulation using *MedeA LAMMPS* or *MedeA VASP*. *MedeA LAMMPS* efficiently samples the fluid's conformational contribution to the dielectric constant and *MedeA VASP* predicts the electronic contribution to the dielectric constant and its evolution under an external field.

## Surface Tension

Surface tension is defined as the free energy per unit area of interface between the liquid and the vapor phases. It is also the force exerted by the interface. For pure compounds and mixtures, this property will can be determined using the *MedeA Surface Tension* module.

## 5 MedeA molecular properties

Molecular properties are accessible through most *MedeA* engines including periodic DFT *VASP*, forcefield-based molecular dynamics with *LAMMPS*, and codes using localized basis sets (*Gaussian*) and semiempirical Hamiltonians (*MedeA MOPAC*). The quality of results will largely depend on the level of theory used, followed by how well a particular property is converged in terms of geometry, energy and -if applicable - electronic structure. Note that forcefield-based classical methods can provide very accurate results, provided the forcefield parametrization is suitable for the materials and properties of interest. Below, we list a selection of molecular properties conveniently obtained from *MedeA Gaussian* and *MedeA MOPAC*:

Property type ID	Property type	Property	Observable, symbol, descriptor	Computational Method
[1]	Structural	Cluster relaxation, reconstruction	Surface energy $\sigma$ , surface geometry	<i>MedeA Gaussian</i> or <i>MedeA MOPAC</i>
[2]	Structural	Adsorption	Geometry, binding energy, infrared spectrum, isotherms	<i>MedeA Gaussian</i> or <i>MedeA MOPAC</i>
[3]	Structural	Cluster and molecule defect	Geometry, site preference, enthalpy of formation $H_f(T)$	<i>MedeA Gaussian</i> or <i>MedeA MOPAC</i>
[4]	Structural	Geometry	Bond distance, angle, dihedral angle, rotational constants	<i>MedeA Gaussian</i> or <i>MedeA MOPAC</i>
[5]	Structural	Ground state	Composition, Free energy $A(T)$	<i>MedeA Gaussian</i> or <i>MedeA MOPAC</i>
[6]	Thermodynamic & Chemistry	Thermodynamic functions	Enthalpy $\Delta H$ , Internal energy $\Delta U$ , Entropy $\Delta S$ , Gibbs Free energy $\Delta G$ , specific heat $c_v$	<i>MedeA Gaussian</i> or <i>MedeA MOPAC</i>
[7]	Thermodynamic & Chemistry	Molecule ideal gas phase thermodynamic	<i>Ideal Gas Heat Capacity</i> $C_{P,id}(T)$ , Entropy $S(T)$ , vibrational, rotational, and translational partition functions	<i>MedeA Gaussian</i> or <i>MedeA MOPAC</i>
[8]	Thermodynamic & Chemistry	Solubilities	Solubility energy $E_{Sol}$ , Solvation energy, Henry constant	<i>MedeA Gaussian</i> or <i>MedeA MOPAC</i>

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Property type ID	Property type	Property	Observable, symbol, descriptor	Computational Method
[9]	<b>Thermodynamic &amp; Chemistry</b>	Binding and interaction energies	Total electronic energy $E_{Tot,el}$	<i>MedeA Gaussian</i> or <i>MedeA MOPAC</i>
[10]	<b>Thermodynamic &amp; Chemistry</b>	Reaction mechanisms and rates	Reaction barrier, reaction pathway	<i>MedeA Gaussian</i> or <i>MedeA MOPAC</i>
[11]	<b>Thermodynamic &amp; Chemistry</b>	Reactivity on surfaces (cluster)	Binding energies, reaction barriers	<i>MedeA Gaussian</i> or <i>MedeA MOPAC</i>
[12]	<b>Thermodynamic &amp; Chemistry</b>	Reaction energies	Reaction energies, enthalpies, Gibbs free energies, and entropies	<i>MedeA Gaussian</i> or <i>MedeA MOPAC</i>
[13]	<b>Thermodynamic &amp; Chemistry</b>	Heat of formation	Heat of formation	<i>MedeA Gaussian</i> or <i>MedeA MOPAC</i>
[14]	<b>Thermodynamic &amp; Chemistry</b>	Photochemical	Electronic structure, excited states	<i>MedeA Gaussian</i> or <i>MedeA MOPAC</i>
[15]	<b>Thermodynamic &amp; Chemistry</b>	<i>Lower Heat of Combustion</i>	PCI	<i>MedeA Gaussian</i> or <i>MedeA MOPAC</i>
[16]	<b>Thermodynamic &amp; Chemistry</b>	<i>Upper Heat of Combustion</i>	PCS	<i>MedeA Gaussian</i> or <i>MedeA MOPAC</i>
[17]	<b>Thermodynamic &amp; Chemistry</b>	<i>Ideal Gas Enthalpy of Formation</i>	$\Delta H_f^0$	<i>MedeA Gaussian</i> or <i>MedeA MOPAC</i>
[18]	<b>Thermodynamic &amp; Chemistry</b>	<i>Ideal gas Gibbs Free Energy of Formation</i>	$\Delta G_f^0$	<i>MedeA Gaussian</i> or <i>MedeA MOPAC</i>
[19]	<b>Thermodynamic &amp; Chemistry</b>	<i>Acid Dissociation Constant</i>	pKa	<i>MedeA Gaussian</i> or <i>MedeA MOPAC</i>
[20]	<b>Spectroscopy</b>	Infrared/Raman spectra	Vibrational frequencies, intensities, force constants	<i>MedeA Gaussian</i> or <i>MedeA MOPAC</i>
[21]	<b>Spectroscopy</b>	UV-Vis absorption spectra	Wavelength, intensities, excitation energies, oscillator strength	<i>MedeA Gaussian</i> or <i>MedeA MOPAC</i>
[22]	<b>Spectroscopy</b>	UV-Vis emission spectra	Wavelength, de-excitation energy	<i>MedeA Gaussian</i> or <i>MedeA MOPAC</i>
[23]	<b>Spectroscopy</b>	NMR	Shielding constants	<i>MedeA Gaussian</i>
[24]	<b>Electronic, optical, magnetic</b>	Electron density	Electronic density function $\rho$	<i>MedeA Gaussian</i>
[25]	<b>Electronic, optical, magnetic</b>	Electrostatic potential	Electronic density function $\rho$	<i>MedeA Gaussian</i> or <i>MedeA MOPAC</i>
[26]	<b>Electronic, optical, magnetic</b>	Dielectric properties	Response tensors: Dielectric, piezoelectric, and Born effective charge	<i>MedeA Gaussian</i> or <i>MedeA MOPAC</i>
[27]	<b>Electronic, optical, magnetic</b>	Electron Paramagnetic Resonance (EPR, ESR)	EPR spectrum, ESR spectrum	<i>MedeA Gaussian</i>
[28]	<b>Electronic, optical, magnetic</b>	Piezoelectric properties	Response tensors: Dielectric, piezoelectric, and Born effective charge	<i>MedeA Gaussian</i>

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Property type ID	Property type	Property	Observable, symbol, descriptor	Computational Method
[29]	Electronic, optical, magnetic	Spin density distribution, magnetic moments	$\mu_B$ , electronic density function $\rho$	MedeA Gaussian or MedeA MOPAC
[30]	Electronic, optical, magnetic	Ionization energies and electron affinities	Electronic dispersion $\epsilon(\vec{k})$	MedeA Gaussian or MedeA MOPAC
[31]	Electronic, optical, magnetic	<i>Electronegativity</i>	$\chi$	MedeA Gaussian or MedeA MOPAC
[32]	Electronic, optical, magnetic	<i>Dipole Moment</i>	$\mu$	MedeA Gaussian or MedeA MOPAC
[33]	Electronic, optical, magnetic	<i>Quadrupole Moment</i>	Q	MedeA Gaussian or MedeA MOPAC
[34]	Electronic, optical, magnetic	<i>Polarizability</i>	$\alpha$	MedeA Gaussian or MedeA MOPAC
[35]	Electronic, optical, magnetic	molecular orbital energy gap	HOMO-LUMO gap	MedeA Gaussian or MedeA MOPAC
[36]	Electronic, optical, magnetic	molecular orbitals	3D isodensity maps	MedeA Gaussian