Vibrational Entropy of Crystalline Solids from Covariance of Atomic Displacements

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1 Purpose

This archive contains tools to calculate entropy from covariance matrix based on method describe in Huang, Y.; Widom, M. Vibrational Entropy of Crystalline Solids from Covariance of Atomic Displacements. Entropy 2022, 24, 618. `https://doi.org/10.3390/e24050618`. These tools are designed especially for output from MD simulation implemented in VASP. You are free to modify and redistribute the code for general purpose.

2 Contents

Following list of files should be contained in the directory:

- README

- install.sh
- src

  Contain source files.
- example

  Contain examples
- bin

  Contain compiled binaries.

3 Required packages

1. GSL - GNU Scientific Library

   The GNU Scientific Library (GSL) is a numerical library for C and C++ programmers. It is free software under the GNU General Public License. It is installed on most linux systems. To install it, check `https://www.gnu.org/software/gsl/`.

2. Aflow [optional]

   The aflow-sym.sh requires AFLOW codes in order to run properly. To install it, check `http://aflow.org/install-aflow/`.

3. pos2xyz and xyz2pos from euler

   The xdat-ent program is originally written on euler so that it utilizes certain mgtools on euler. Unfortunately the author is unwilling to modify these codes to make it more convenient for general users and you will have to ask for permissions to access these tools.

   The "pos2xyz" converts a POSCAR file to a XYZ file. The "xyz2pos" converts a XYZ file to a POSCAR file.

4 How to install

Go to the main directory and run "./install.sh". It will compile the source files and put binaries into the bin directory.

After you run the command, you run the test script "./test.sh" in the examples directory.

5 List of tools

[BEFORE YOU RUN]

- xdat-ent-init.sh
  - Description
    Preparing "Trun" and "Mass" input files for "xdat-ent-rhoALL_quantum_mod" commands.
  - Input:
    * INCAR
    * POTCAR
    * /home/Tools/src/mgtools/INFO/CHTAB.
  - Usage:
    xdat-ent-init.sh *Only work on euler.
  - Output:
    Generate "Trun" and "Mass".

- aflow-sym.sh
  - Description
    This script utilizes "aflow" tools to help find symmetry operations. It is recommended to run on a small cell for efficiency.
  - Input:
    POSCAR or XYZ file.
  - Usage:
    aflow-sym.sh [-x <xyz file>] [-p <POSCAR file>]
  - Output:
    A "symmetry_operation.dat " which contains number of operations N and N 3x3 operation matrix in direction space.

[WHEN YOU RUN]

- xdat-ent-rhoALL_quantum_mod tools
  - Description
    * xdat-ent-rhoALL_quantum_mod
      Pure element crystalline from NVT simulation

* xdat-ent-rhoALL_quantum_npt
  Pure element crystalline from NPT simulation
* xdat-ent-rhoALL_quantum_alloy
  Alloys from NVT simulation.

xdat-ent-rhoALL_quantum_mod has been tested to be robust while only a few examples have been performed with xdat-ent-rhoALL_quantum_npt and xdat-ent-rhoALL_quantum_alloy command. So be careful with these two commands!

– Input:

"example" directory provides examples of input files.

* Trun
  This file contains in value which is the temperature of MD simulation.
* Mass
  This file contains three rows:
  1. type of species.
  2. atomic numbers.
  3. atomic masses [a.u.] in atomic units.
* xyzfile
  This file contains the ideal structure of a crystal. The first three rows are lattice constants. The 4th row contains number of atoms N. The following N rows should obeys: dx,dy,dz,na ... where dx,dy,dz is directional vector and na is atomic number.
* symmetry-file
  This file contains symmetry operation matrices U. The first row is number of operations N and then it is followed by N 3x3 matrices U each of which is a operation matrix in directional space (b'=Ub).
* XDATCAR
  Output from VASP MD simulations.

- Usage:

  xdat-ent-rhoALL_quantum_mod -f xyzfile -s symmetry-file XDATCAR* > out

- Output:

- covariance_pair.dat

  3x3 covariance matrices in real space of all symmetry distinguishing pairs.

- density_matrix.dat

  See reference for more mathematical description. A 3Nx3N matrix.

- force_matrix.dat

  See reference for more mathematical description. A 3Nx3N force matrix.

- Eigenvalues.dat

  A 3Nx2 matrix. The first row are eigenvalues of density matrix. The second row are frequencies (hbar*omega [eV]) of eigen modes See reference for mathematical relation.

- "out":

  The last line of "out" reports calculated entropy with S_classic (classical entropy) and S_quantum (quantum entropy)

[AFTER YOU RUN]

- freq2quan.py

  - Description

    Calculate free energy F[eV/at], internal energy U [eV/at], entropy S [kB/at] and heat capacity Cv [kB/at] from Eigenvalues.dat

  - Input: "Trun", "Eigenvalues.dat"
  - Usage: freq2quan.py
  - Output: calculated quantities.

- force2dos

  - Description

    Calculate free energy F[eV/at], internal energy U [eV/at], entropy S [kB/at] and heat capacity Cv [kB/at] from Eigenvalues.dat

  - Input:
    - "Trun", "force_matrix.dat", xyzfile
    - KDim (an integer indicate kmesh KDimxKDimxKdim).

    - recip_vectors of a primitive cell
      3x3 matrix
  - Usage:
    force2dos xyzfile KDim > out;
  - Output:
    In "out" file, there are two columns of datas. The first column is hbar*omega [meV]. The second one is vibrational DOS [states/atom/meV].

- force2band
  - Description
    Calculate free energy F[eV/at], internal energy U [eV/at], entropy S [kB/at] and heat capacity Cv [kB/at] from Eigenvalues.dat
  - Input:
    - "Trun", "force_matrix.dat", xyzfile
    - KDim (an integer indicate kmesh KDimxKDimxKdim).
    - recip_vectors of a primitive cell
      3x3 matrix
    - kpath
  - Usage:
    force2band xyzfile > out;
  - Output:
    Eigenvalues along kpath.

6 Pay attention to

- symmetry operations:

  Symmetry operations will greatly improve precision of calculated entropy for a short run at a cost of calculation time. With symmetry operation turned on, each configuration will be process N times where N is the number of operations.

  This program is known to give incorrect results when applied to low-symmetry super cell from a highly symmetrical crystalline structure, e.g. a 5x5x5 primitive cell of BCC Li. Hence, it is recommended to run simulation at its high-symmetry unit cell. e.g. a super cell of a 2-atom BCC unit cell or a 4-atom FCC unit cell.

- Eigenvalues.dat:

  A reasonable calculation should give 3 zero eigenvalues in the first column in Eigenvalues.dat and correspondingly 3 nan or large number in the second column. So be careful with zero or nan values in Eigenvalues.dat.

  Imaginary modes may show up which are denoted as negative eigenvalues. As long as there are 3 zero eigenvalues, we think the program is doing its job.