Infrastructure Enabling Broad Adoption of New Methods That Yield Orders-of-Magnitude Speedup of Molecular-Simulation Averaging

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INTRODUCTION

Mapped averaging is a recently published scheme for the reformulation of ensemble averages. The framework uses approximate results from statistical mechanical theory to derive new ensemble averages (mapped averages) that represent exactly the error in the theory. Well-conceived mapped averages can be computed by molecular simulation with remarkable precision and efficiency, and in favorable cases the speedup factors are several orders of magnitude.

Harmonically mapped averaging (**HMA**) is the application of mapped averaging to crystalline systems. It enables simulation to compute directly the anharmonic contribution to the properties, without noise contributed by harmonic behavior. The result is a technique for computing crystalline properties with unprecedented, transformative efficiency.

The aim of this project is to implement these methods on well-established and widely used software packages for simulation of crystalline systems, and furthermore to develop mapped averages for new applications of interest to the users of these systems.

REFERENCES

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MAPPED-AVERAGING EQUATIONS

Targeted perturbation (Jarzynski)

$$\exp\left[-\left(A(\lambda')-A(\lambda)\right)\right]\equiv\exp\left[-\Delta A\right]=\left\langle\exp\left[-\left(U(\mathbf{r},\lambda')-U(\mathbf{r},\lambda)\right)\right]\right\rangle_{\lambda}$$

Coordinate transformation $\mathbf{r}\rightarrow\mathbf{r}'$

$$\exp\left[-\Delta A\right]=\left\langle J\exp\left[-\left(U(\mathbf{r}',\lambda')-U(\mathbf{r},\lambda)\right)\right]\right\rangle_{\lambda}$$

$$A_{\nu}=-\left\langle J_{\nu}\right\rangle+\left\langle U_{\nu}\right\rangle;\quad A_{\mu\nu}=-\left\langle J_{\mu\nu}-J_{\mu}J_{\nu}\right\rangle+\left\langle U_{\mu\nu}\right\rangle-\mathrm{Cov}\left[J_{\mu}-U_{\mu},J_{\nu}-U_{\nu}\right]$$

$$U_{\nu}=\partial_{\nu}U-\mathbf{F}\cdot\mathbf{r}_{\nu};\quad U_{\mu\nu}=\partial_{\mu\nu}U-\mathbf{F}\cdot\mathbf{r}_{\mu\nu}+\mathbf{r}_{\mu}\cdot\Phi\cdot\mathbf{r}_{\nu}$$

Mapping function

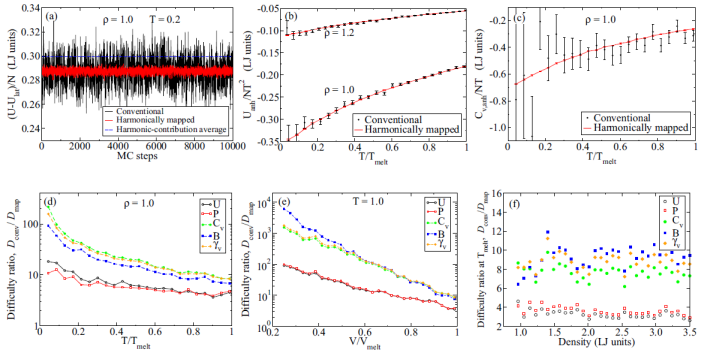
$$\Delta\mathbf{r}'=f(\beta',V')\Delta\mathbf{r};\qquad f(\beta',V')\equiv\left(\frac{V}{V'}\right)^{1/3}\left(\frac{\beta}{\beta'}\right)^{1/2}\left(\frac{V}{V'}\mathrm{e}^{-\beta'\left[\delta A-\delta U_{\mathrm{lat}}\right]}\right)^{\frac{1}{3(N-1)}}$$

HMA – KEY EQUATIONS

Property	Definition	Conventional average	Harmonically mapped average
Configurational energy	$U=\mathcal{A}_{\beta}$	$\langle U\rangle$	$\frac{d(N-1)}{2\beta}+\langle U+\frac{1}{2}\mathbf{F}\cdot\Delta\mathbf{r}\rangle$
Pressure	$P=-\frac{\mathcal{A}_V}{\beta}$	$\frac{\rho}{\beta}+\langle P_{\mathrm{vir}}\rangle$	$\Delta\hat{P}+\langle P_{\mathrm{vir}}+f_V\mathbf{F}\cdot\Delta\mathbf{r}\rangle$
Isochoric Heat capacity	$TC_V=-\beta\mathcal{A}_{\beta\beta}$	$\beta\mathrm{Var}[U]$	$\frac{d(N-1)}{2\beta}+\beta\,\mathrm{Var}[U_{\mathrm{anh}}]-\frac{1}{2}\langle\mathbf{F}\cdot\Delta\mathbf{r}+\Delta\mathbf{r}\cdot\Phi\cdot\Delta\mathbf{r}\rangle$
Isothermal bulk modulus	$\frac{B}{V}=\frac{\mathcal{A}_{VV}}{\beta}$	$\frac{\rho}{\beta V}-\langle\partial_V P_{\mathrm{vir}}\rangle-\beta\mathrm{Var}[P_{\mathrm{vir}}]$	$\frac{1}{V}\Delta\hat{B}-\beta\,\mathrm{Var}[P_{\mathrm{anh}}]-\langle\partial_V P_{\mathrm{vir}}+f_{VV}\mathbf{F}\cdot\Delta\mathbf{r}+2f_V\,\partial_V\mathbf{F}\cdot\Delta\mathbf{r}-f_V^2\,\Delta\mathbf{r}\cdot\Phi\cdot\Delta\mathbf{r}\rangle$
Isochoric thermal pressure coefficient	$T\gamma_v=\mathcal{A}_{\beta V}-\frac{\mathcal{A}_V}{\beta}$	$\frac{N}{V\beta}+\beta\mathrm{Cov}[U,P_{\mathrm{vir}}]$	$\Delta\hat{P}+\beta\,\mathrm{Cov}[U_{\mathrm{anh}},P_{\mathrm{anh}}]+\frac{1}{2}\langle f_V\,\mathbf{F}\cdot\Delta\mathbf{r}+\partial_V\mathbf{F}\cdot\Delta\mathbf{r}-f_V\,\Delta\mathbf{r}\cdot\Phi\cdot\Delta\mathbf{r}\rangle$

$U_{\mathrm{anh}}\equiv U-U_{\mathrm{lat}}+\frac{1}{2}\mathbf{F}\cdot\Delta\mathbf{r}$; $P_{\mathrm{anh}}\equiv P_{\mathrm{vir}}+f_V\,\mathbf{F}\cdot\Delta\mathbf{r}-P_{\mathrm{lat}}$; $P_{\mathrm{vir}}=-\partial_V U$; $P_{\mathrm{lat}}=-\partial_V U_{\mathrm{lat}}$; $B_{\mathrm{lat}}=-V\,\partial_V P_{\mathrm{lat}}$; $\rho\equiv N/V$;
$f_V=\frac{\beta\Delta\hat{P}-\rho}{d(N-1)}$; $f_{VV}=f_V^2-\frac{1}{V}\frac{\beta\Delta\hat{B}-\rho}{d(N-1)}$; $\Delta\hat{P}\equiv\hat{P}-P_{\mathrm{lat}}$; $\Delta\hat{B}\equiv\hat{B}-B_{\mathrm{lat}}$; $\partial_V\mathbf{F}=\frac{1}{Vd}(\mathbf{F}-\mathbf{r}\cdot\Phi)$

HMA PERFORMANCE



OBJECTIVES

DEVELOPMENT

- Develop HMA formulas for other properties (e.g. elastic moduli)
- Form expressions for 1st and 2nd derivatives for model classes:
  - rigid-bond constraints
  - multibody potentials
  - polarizable potentials
  - ab initio potentials

IMPLEMENTATION

- Implement HMA in some widely used molecular simulation packages
  - LAMMPS, HOOMD, VASP, Cassandra, Etomica
  - Classes to calculate HMA properties
  - Codes to implement Hessian, etc.
- Documentation and training

IMPACT

- Development of powerful new tools for the Materials Genome Initiative
- Tools will be distributed as part of five robust and sustainable molecular simulation packages enabling researchers to easily exploit the remarkable capabilities of harmonically mapped averaging
- Provide better methods for elastic constants (required in LAMMPS)

TIMELINE

Year 1

- Implement existing HMA formulas in LAMMPS and VASP
- Develop HMA elastic moduli and implement in Etomica, LAMMPS & VASP

Year 2

- Implement in HOOMD & Cassandra
- Beta test- LAMMPS and VASP
- Develop for molecular crystals and implement in Etomica
- Formulate tools for FE calculation

Year 3

- Implement HMA for molecular crystals in simulation packages
- Beta test - HOOMD and Cassandra

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