Seebeck coefficient in classical fluids from equilibrium molecular dynamics

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Introduction

The thermo-electric effect in ionic conductors refers to the electric current induced by a temperature gradient. The computation of this off-diagonal Onsager coefficient is numerically ill-conditioned. We show how to calculate it as the numerically tractable product between a diagonal coefficient and an off-diagonal static susceptibility, both computed from equilibrium molecular dynamics. This static susceptibility is well defined even in the insulating case, where it provides a theoretically sound and numerically tractable formulation of the thermo-polarization coefficients, which have so far been computed only through cumbersome non-equilibrium simulations [1, 2].

Theory

The Seebeck coefficient, S, is defined as the ratio between the electric field and the temperature difference inducing it when no electric curret flows (open circuit) [3]:

$$S = \left.\frac{\boldsymbol{E}}{\nabla T}\right|_{\boldsymbol{J}=0}$$

The Onsager equations for the electric and heat currents read:

$$\boldsymbol{J} = \sigma \boldsymbol{E} - (K_{12}/T)\nabla T,$$
$$\boldsymbol{J}^q = K_{12}\boldsymbol{E} - (L_{qq}T)\nabla T.$$

The mechanical perturbation describing the temperature gradient is written as:

$$\mathcal{H}' = \int \frac{-1}{k_B T^2} \int \nabla T(\boldsymbol{r})\cdot\boldsymbol{r}\left(\epsilon(\boldsymbol{r}) - \sum_i h_i n_i(\boldsymbol{r})\right) d\boldsymbol{r},$$

where ϵ is the energy density, n_i is the particle density, h_i is the partial enthalpy, $q = \epsilon - \sum_i h_i n_i$ is the heat density [4]. The static response of the polarization to the temperature gradient reads: [5]:

$$S = \frac{K_{12}}{\sigma T} = \lim_{\boldsymbol{k}\to 0}\lim_{\omega\to 0}\frac{1}{T}\frac{\chi_{q\rho}}{k^2},$$

where ρ is the charge density.

Bayesian inference

Given a dataset $\{S(\boldsymbol{k}_i)\}$ and a basis function set $\boldsymbol{\Phi} = \{1, k^2 \dots k^{2M}\}$ of $M+1$ elements, we find the parameters $\boldsymbol{w}$ and the regularization parameter, α, that maximize the posterior distribution function, $p(\boldsymbol{w}, \alpha | \{S(\boldsymbol{k}_i)\}, M)$.
We evaluate the optimal number of parameters maximizing the *evidence* function

$$p(\{S(\boldsymbol{k}_i)\}|M) = \int d\boldsymbol{w} d\alpha\, p(\{S(\boldsymbol{k}_i)\}|\boldsymbol{w})\, p(\boldsymbol{w}|\alpha)\, p(\alpha|\{S(\boldsymbol{k}_i)\}),$$

where we approximate the posterior distribution function of α with a delta function centered at its maximum [6].

References

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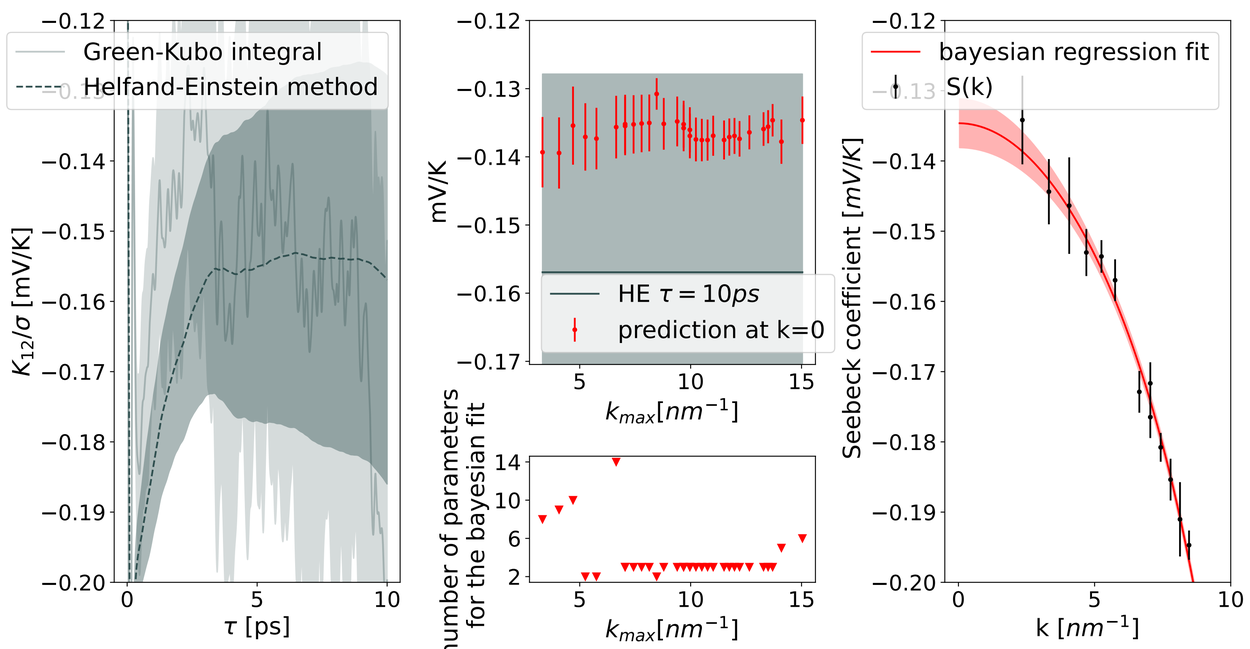
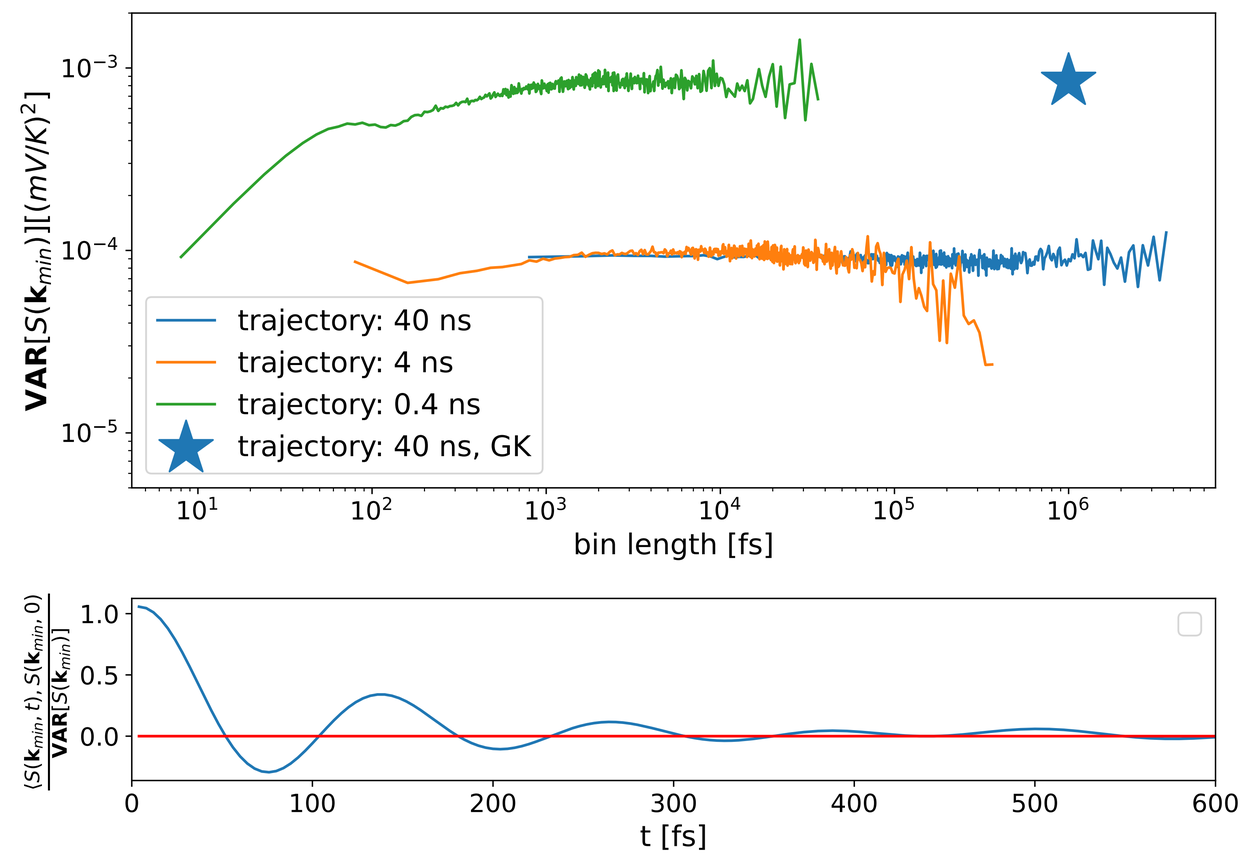
Test cases: ionic conductor, molten salt Cs F

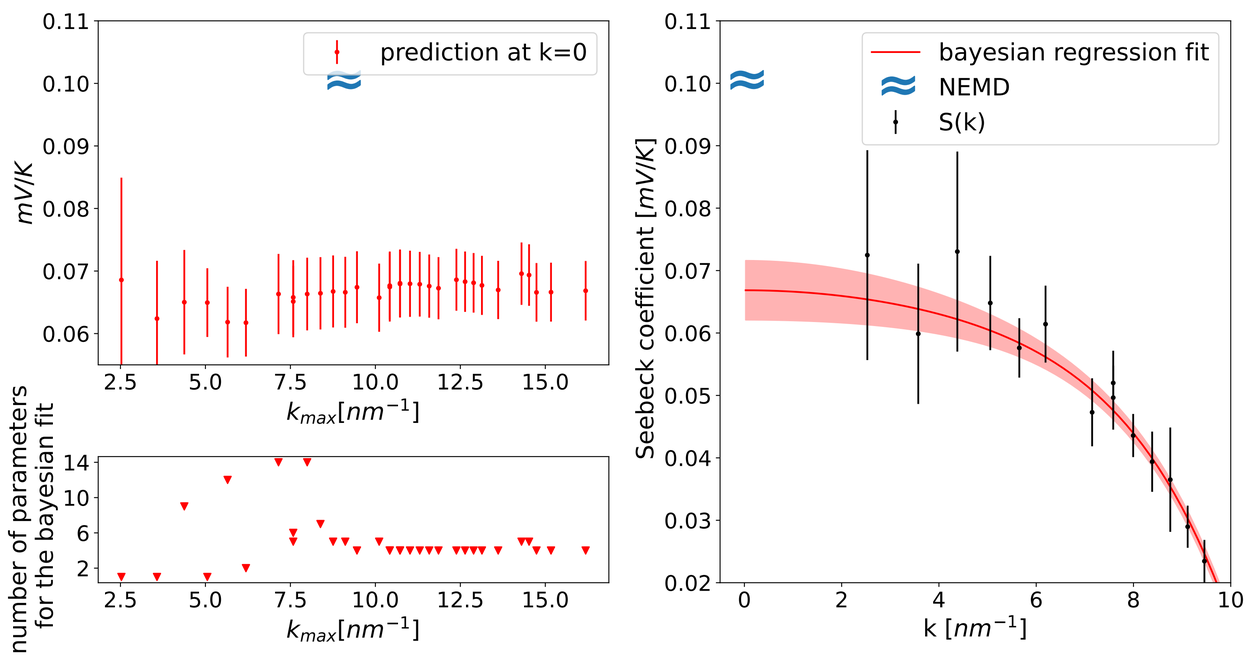
We performed classical simulations of 512 atoms of the molten salt Cs F at 1000K. The Green-Kubo integral has a very poor convergence, in order to obtain a reliable result we needed 40 ns-long trajectories. **In the 40 ns trajectory, the static estimator is 10 times more efficient than the Green-Kubo integral.**
In order to obtain the same accuracy as the one of the 40 ns trajectory, the static estimator needs 4 ns-long simulations. The Seebeck coefficient computed as a static quantity in the 0.4 ns trajectory is as accurate as the Green-Kubo integral evaluated in the 40 ns simulation. **Overall the static estimator is about 100 times more efficient than the bare Green-Kubo calculation.**





Test case: insulating liquid, SPC/E water

We performed $1\,ns$-long classical simulations of 512 molecules of SPC/E water at 300K. In the insulating case the electric conductivity and the thermo-electric transport coefficient are 0 by construction and their ratio would be numerically ill-conditioned.



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