

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. In insulators 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 current flows (open circuit) [3]:

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

The Onsager equations for the electric and heat currents read:

$$\begin{aligned} \mathbf{J} &= \sigma \mathbf{E} - (K_{12}/T) \nabla T, \\ \mathbf{J}^q &= K_{12} \mathbf{E} - (L_{qq}/T) \nabla T. \end{aligned}$$

The mechanical perturbation describing the temperature gradient is written as:

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

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]:

$$S = \frac{K_{12}}{\sigma T} = \lim_{\mathbf{k} \rightarrow 0} \lim_{\omega \rightarrow 0} \frac{1}{T} \frac{\chi_{qp}}{k^2},$$

where ρ is the charge density.

Bayesian inference

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

We evaluate the optimal number of parameters maximizing the *evidence* function

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

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

References

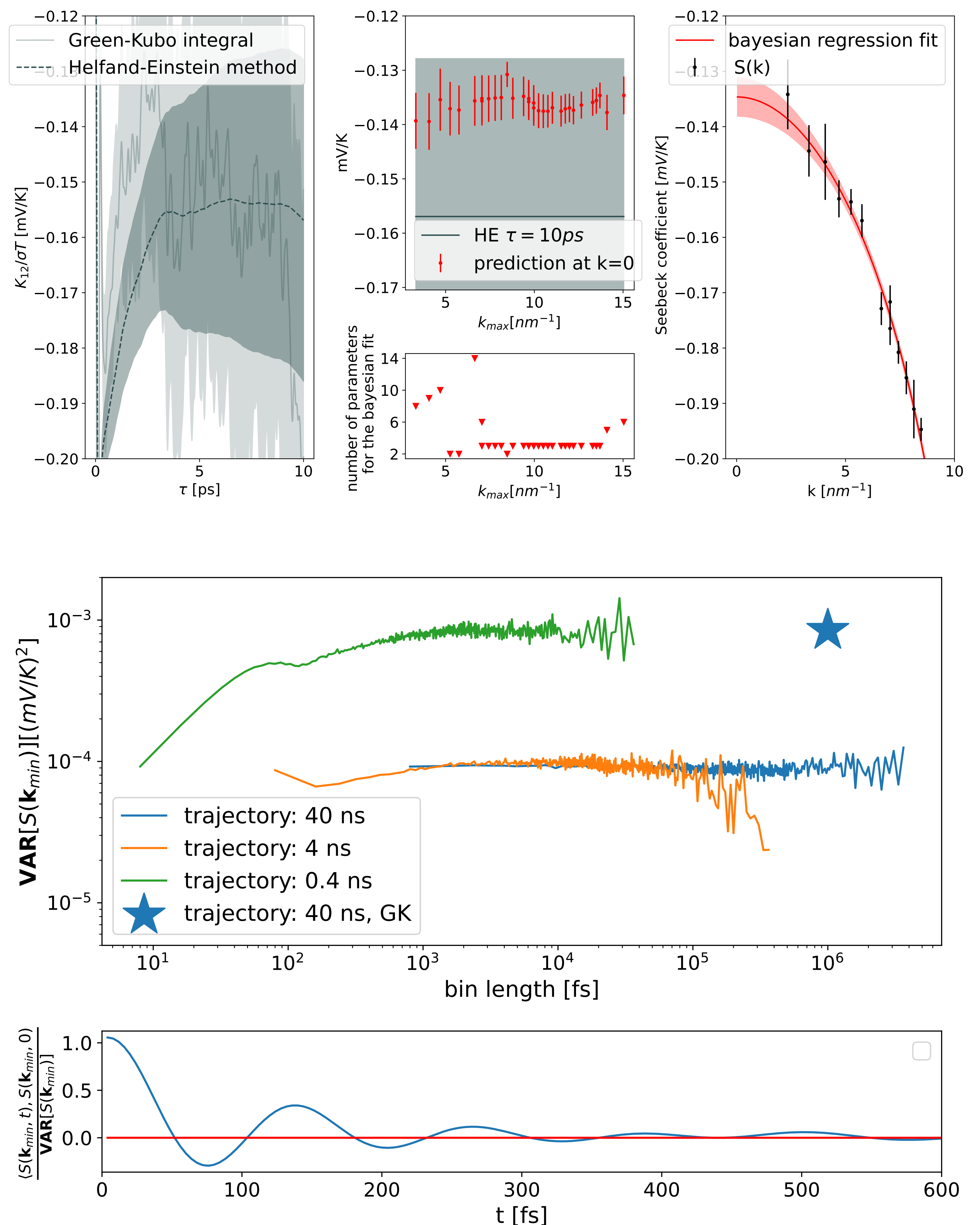
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Test cases: ionic conductor, molten salt Cs F

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. **On the 40 ns trajectory, the static estimator is 10 times more efficient than the Green-Kubo integral.**

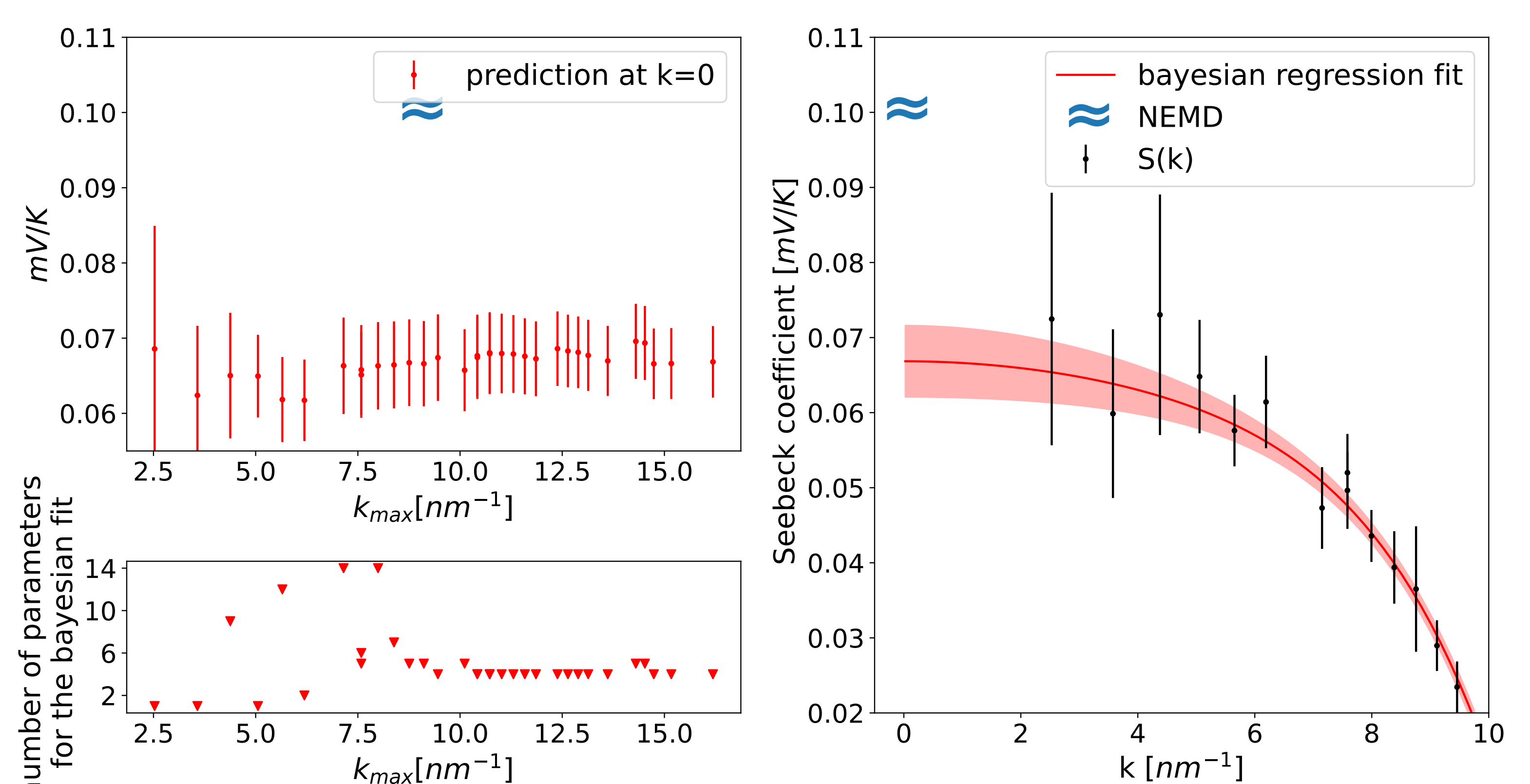
The Seebeck coefficient computed as a static quantity on the 0.4 ns trajectory is as accurate as the Green-Kubo integral evaluated on the 40 ns simulation.

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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