

Seebeck coefficient in classical fluids from equilibrium molecular dynamics

Enrico Drigo* and Stefano Baroni

SISSA - Scuola Internazionale Superiore di Studi Avanzati, Trieste

*endrigo@sissa.it



Introduction

The thermo-electric effect in ionic conductors describes the electric current induced by a temperature gradient. The computation of the corresponding off-diagonal Onsager coefficient is numerically ill-conditioned. We show how to calculate it as the numerically tractable product between a diagonal Onsager 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]:

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

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 electric polarization to the temperature gradient reads [5]:

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

where ρ is the charge density.

Bayesian inference

We fitted the Seebeck \mathbf{k} -dispersion as:

$$S(\mathbf{k}) \approx w_0 + w_1 k^2 + w_2 k^4 \dots$$

The M parameters, \mathbf{w} , maximize the posterior distribution function, $p(\mathbf{w}, \alpha | \{S(\mathbf{k}_i)\}, M)$, computed from the Bayes Theorem

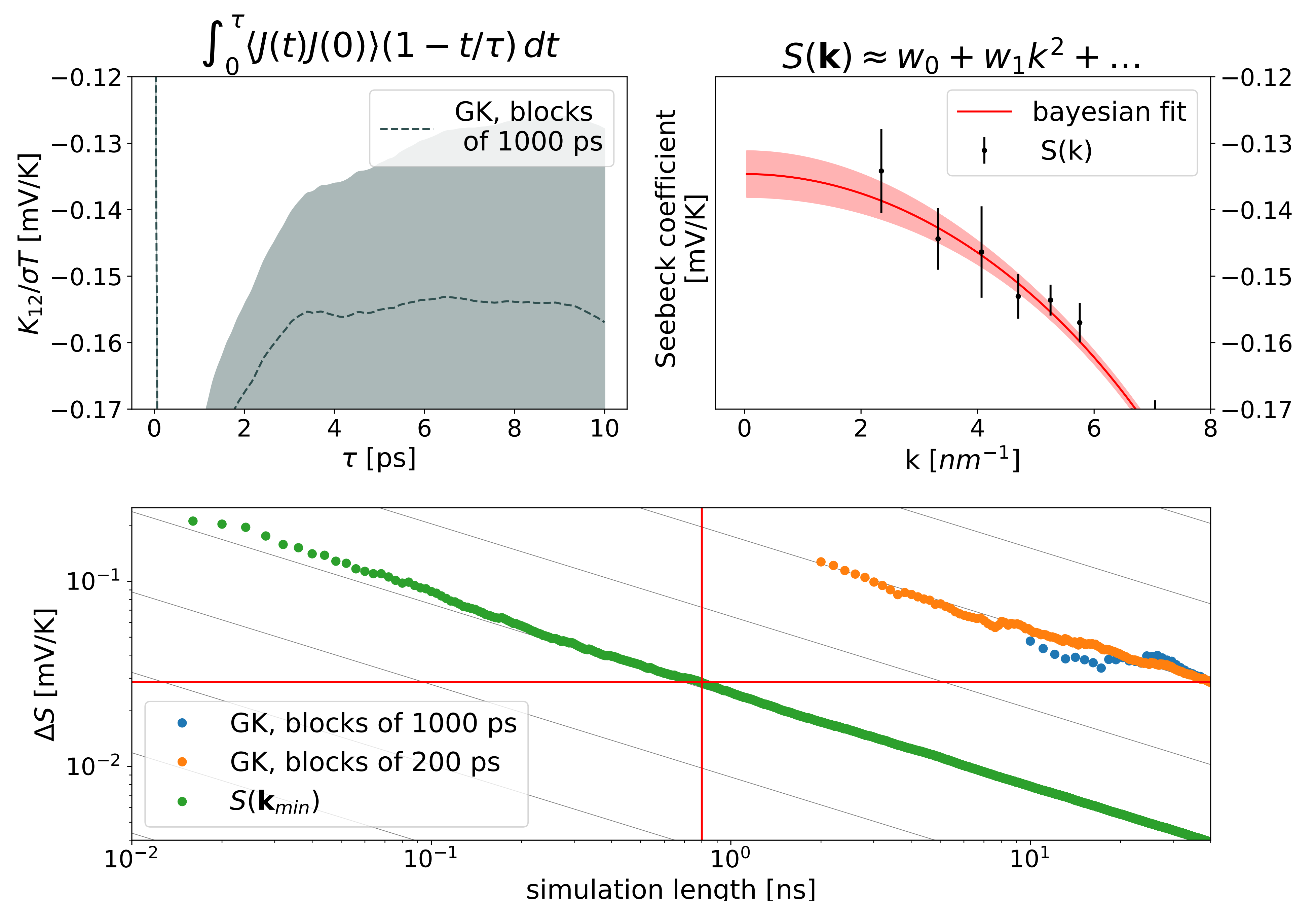
$$p(A|B)p(B) = p(B|A)p(A),$$

where α is the regularization hyper-parameter. We evaluate the optimal number of parameters, M , maximizing the *evidence* function [6]:

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

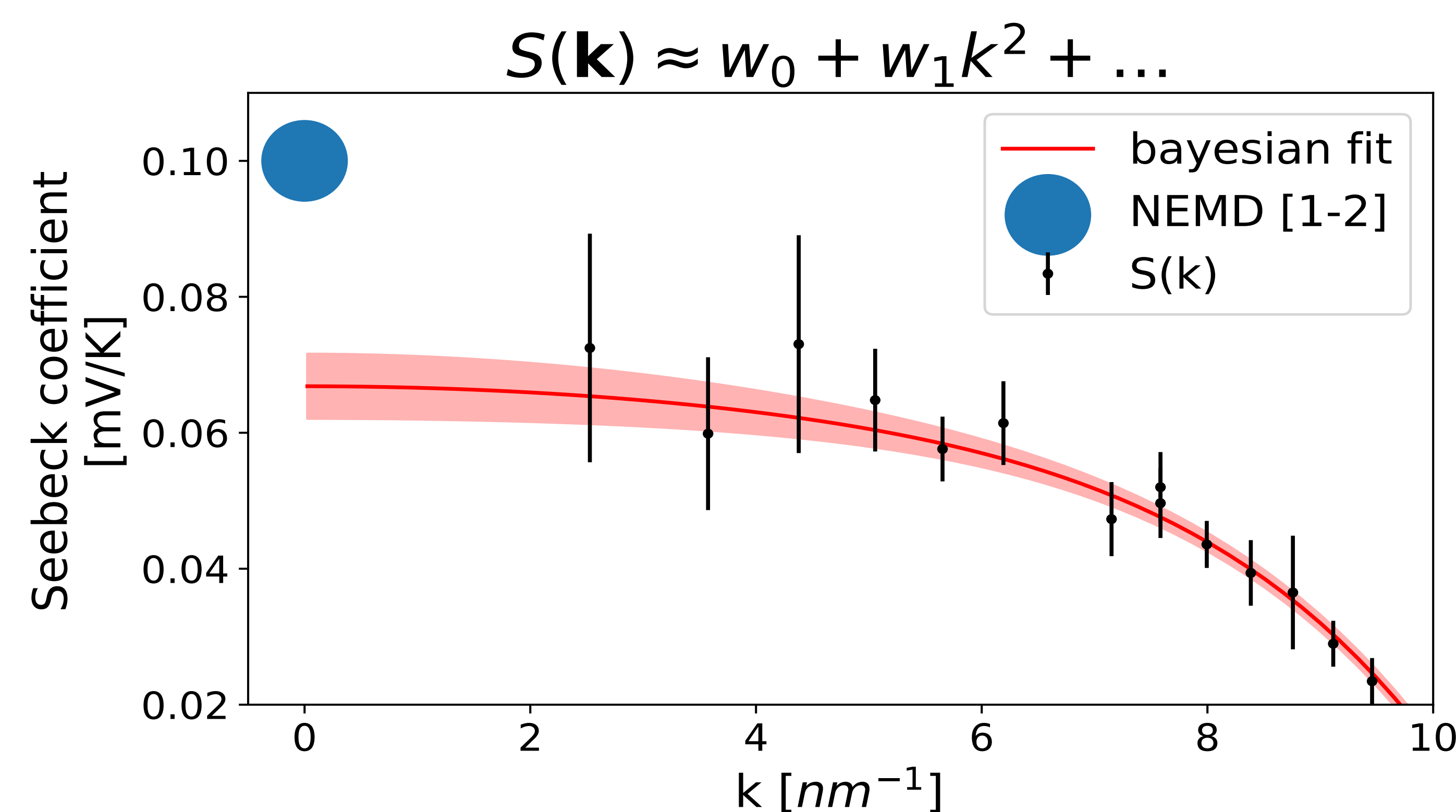
Test case: ionic conductor, molten salt Cs F

We performed a 40 ns-long classical MD simulation of 512 atoms of the molten salt Cs F at density 3.37 g/cm^3 and 1000K, we modeled the system with the Fumi-Tosi potential. The Seebeck coefficient computed as a static quantity from a 0.8 ns trajectory is as accurate as the Green-Kubo integral evaluated from a 40 ns simulation. **The static estimator is about one order of magnitude more efficient than the bare Green-Kubo (GK) calculation.**



Test case: insulating liquid, water

We performed a 1 ns-long classical MD simulation of 512 molecules of SPC/E water at room conditions. In the insulating case the two transport coefficients are 0 and their ratio would be numerically ill-conditioned.



References

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Conclusions

- The off-diagonal Onsager coefficient in classical fluids is readily available from equilibrium molecular dynamics.
- The static thermo-polarization coefficient is readily available from equilibrium molecular dynamics via long-wavelength extrapolation of static response functions obtained through bayesian inference.