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 is 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 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 electric polarization to the temperature gradient reads [5]:

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

where ρ is the charge density.

Bayesian inference

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

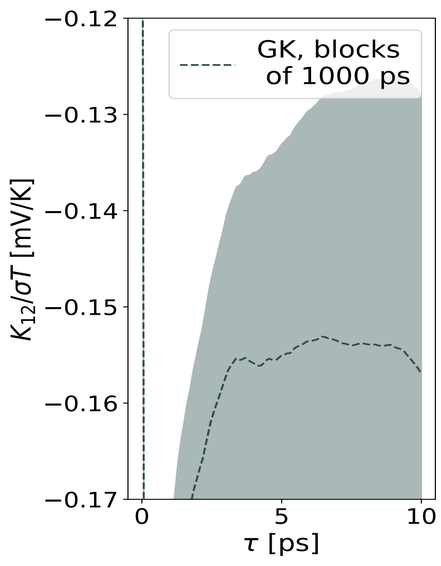
$$S(\mathbf{k}) \approx w_0 + w_1 k^2 + w_2 k^4 \ldots$$

The M parameters, $\boldsymbol{w}$, maximize the posterior distribution function, $p(\boldsymbol{w}, \alpha|\{S(\boldsymbol{k}_i)\}, M)$, 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]:

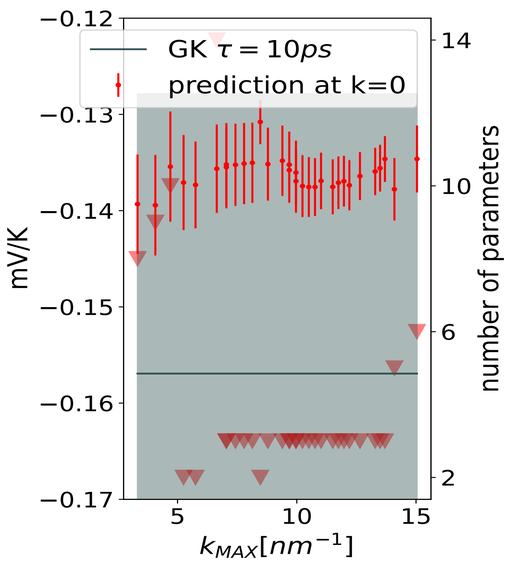
$$p(\{S(\boldsymbol{k}_i)\}|M) = \int d\boldsymbol{w} d\alpha\, p(\{S(\boldsymbol{k}_i)\}|\boldsymbol{w})\, p(\boldsymbol{w}|\alpha)\, p(\alpha|\{S(\boldsymbol{k}_i)\})\,.$$

Test case: ionic conductor, molten salt Cs F

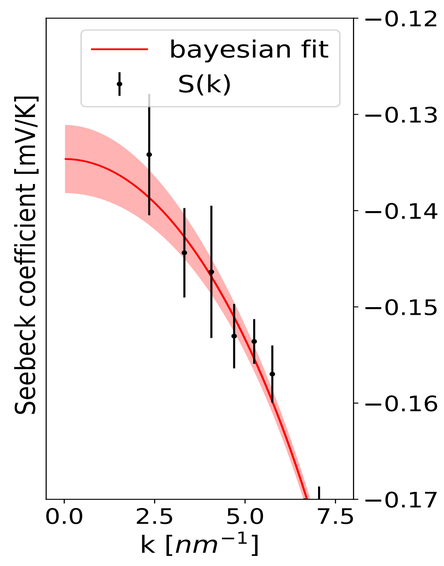
We performed a 40 ns-long classical MD simulation of 512 atoms of the molten salt Cs F at density $3.37 g/cm^3$ and 1000K, we modeled the system with the Fumi-Tosi potential. The Seebeck coefficient computed as a static quantity from a 0.8 ns trajectory is as accurate as the Green-Kubo integral evaluated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



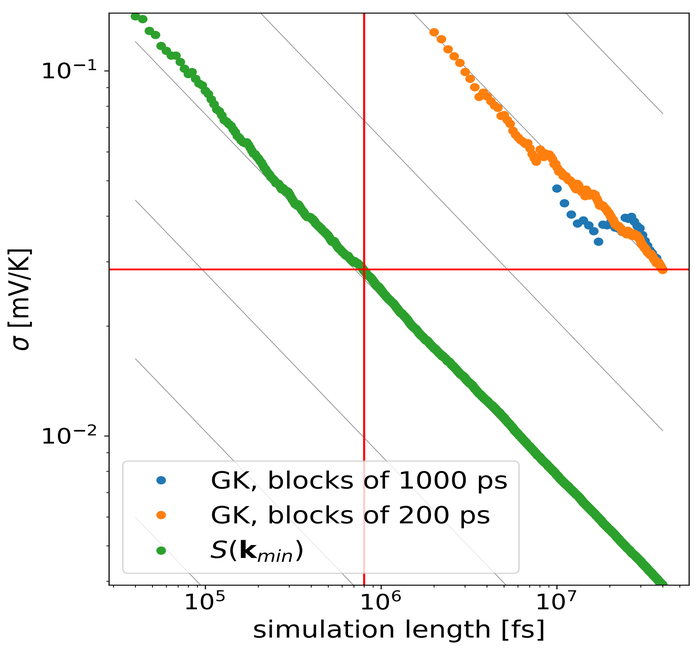
$\int_0^\tau \langle J(t)J(0)\rangle(1 - t/\tau)\,dt$

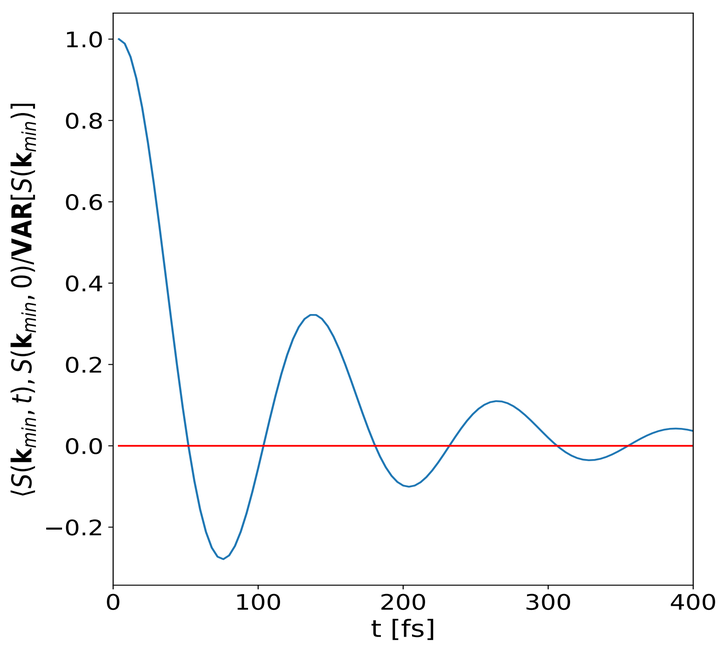


$\lim_{\mathbf{k}\to 0}\chi_{q,\rho}(\mathbf{k})/Tk^2$



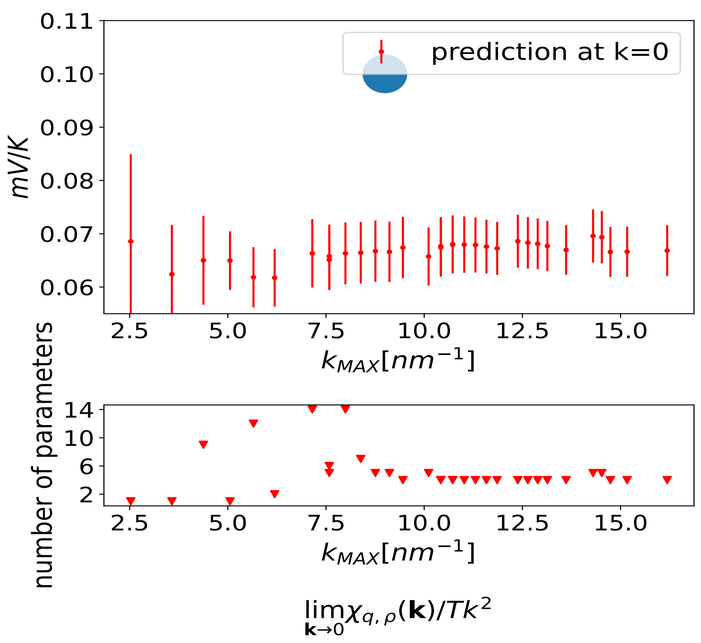
$S(\mathbf{k}) = \chi_{q,\rho}(\mathbf{k})/Tk^2 \approx w_0 + w_1 k^2 + \ldots$



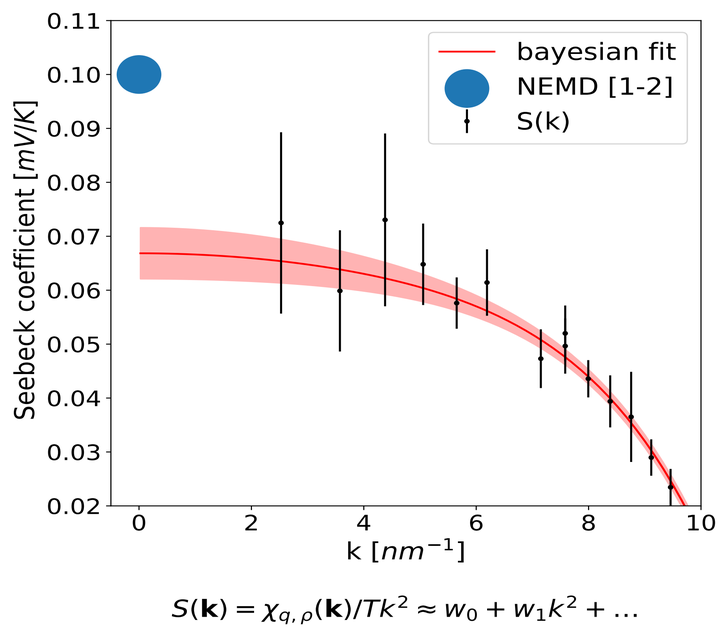


Test case: insulating liquid, water

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.



$\lim_{\mathbf{k}\to 0}\chi_{q,\rho}(\mathbf{k})/Tk^2$



$S(\mathbf{k}) = \chi_{q,\rho}(\mathbf{k})/Tk^2 \approx w_0 + w_1 k^2 + \ldots$

References

[1] P. Wirnsberger, D. Fijan, R. A. Lightwood, A. Šarić, C. Dellago, and D. Frenkel. Numerical evidence for thermally induced monopoles. *Proc Natl Acad Sci U S A*, 114(19):4911–4914, April 2017.

[2] Jeff Armstrong and Fernando Bresme. Temperature inversion of the thermal polarization of water. *Phys. Rev. E*, 92:060103, Dec 2015.

[3] H. B. Callen. The application of onsager's reciprocal relations to thermoelectric, thermomagnetic, and galvanomagnetic effects. *Phys. Rev.*, 73:1349–1358, Jun 1948.

[4] D. Forster. *Hydrodynamic Fluctuations, Broken Symmetry, and Correlation Functions*. CRC Press, mar 2018.

[5] P. C. Martin. Sum rules, kramers-kronig relations, and transport coefficients in charged systems. *Phys. Rev.*, 161:143–155, Sep 1967.

[6] C. M. Bishop. *Pattern Recognition and Machine Learning*. Springer, 1 edition, 2006.

This work was partially funded by the EU through the MaX Centre of Excellence for supercomputing applications, grant No. 824143.