Green-Kubo and Einstein-Helfand Expressions for Transport Properties from Dissipative Particle Dynamics Simulations

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The application of Green-Kubo and Einstein-Helfand expressions for transport coefficients from dissipative particle dynamics simulations has been recently subject of debate. In this presentation, we demonstrate that the classic Green- Kubo and Einstein-Helfand formulas are also valid for DPD, DPDE and other generalized models, provided that (i) the dynamic model conserves the physical property whose transport is studied (e.g. momentum, energy, etc.), (ii) the dissipative and random terms are included, and (iii) the fluctuations satisfy Detailed Balance. However, while Einstein-Helfand relations do not present numerical issues, some problems arise with the statistical significance of the correlations leading to the Green-Kubo calculations. Effectively, taking shear viscosity as a paradigmatic example, a random contribution, whose strength scales as $1/dt^{1/2}$, with dt being the time-step, can cause difficulties if the latter is not separated from the total stress tensor and calculated analytically. As an example, in Fig. 1, we show the stress tensor correlation for the same model with two different values of the time-step. With this procedure, we produce an alternative although equivalent expression, which overcomes such a statistical inconvenience and allows for accurate prediction of the transport coefficients. We compare our expression to the extant formula proposed by Ernst and Brito (M.H. Ernst and R. Brito, *Europhys. Lett.*, 2006, 73, 183–189), whose alternative derivation seemed to cast doubts on the validity of the traditional formulas in DPD systems. However, we demonstrate that the two expressions are completely equivalent and find exactly the same result both analytically and numerically. We show that the differences are not due to the lack of time-reversibility in the Langevin-like dynamics inherent in DPD methods, but instead from a pre-averaging of the random contributions. Despite the overall validity of Green-Kubo expressions, we find that the Einstein-Helfand relations (D.C. Malaspina *et al.*, *Phys. Chem. Chem. Phys.*, 2023, 25, 12025-12040) do not suffer from the need to decompose the stress tensor and can readily be used.

The result of our analysis provides a strong foundation for the use of equilibrium expressions in the calculation of transport coefficients in stochastic DPD-like models.

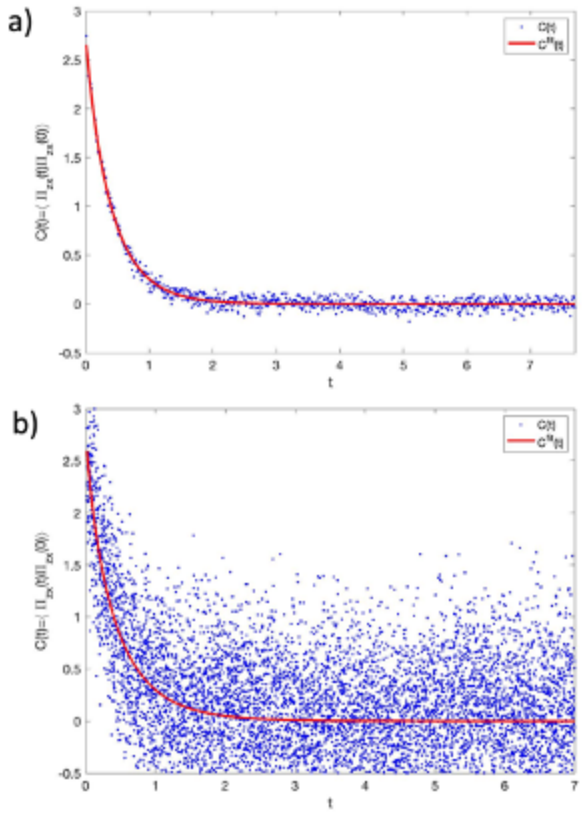

Fig. 1 Stress tensor correlation as a function of time along with the regression curve. a) Decay of the stress tensor correlation for $dt = 0.01$. b) Decay of the stress tensor correlation for $dt = 0.001$.