The Coming of Age of Nonlinear Response Theory: Rheology and Tribology at Experimentally Accessible Rates of Strain

Billy Todd[1, S, C], Luca Maffioli[1], James Ewen[2], Edward Smith[3], Peter Daivis[4] and Daniele Dini[2]

[1]*Mathematics, Swinburne University of Technology, Hawthorn, Victoria, Australia*
[2]*Mechanical Engineering, Imperial College London, London, United Kingdom*
[3]*Mechanical and Aerospace Engineering, Brunel University, Uxbridge, United Kingdom*
[4]*Physics, RMIT University, Melbourne, Victoria, Australia*
btodd@swin.edu.au

Nonlinear response theory is an exceptionally powerful but largely untapped methodology that combines nonequilibrium statistical mechanics to nonequilibrium molecular dynamics (NEMD) [1-3]. In particular, the so-called transient-time correlation function methodology (TTCF) is especially amenable to simulation. Its immense potential lies in the impressive statistical accuracy achievable at external field strengths arbitrarily close to zero. This means that, in principle, it allows one to simulate actual rheological and tribological systems at experimentally accessible strain rates at the molecular level. While there have been a few studies on this technique demonstrating its power and effectiveness, it remains relatively obscure for two primary reasons: (1) the high computational overhead, and (2) the lack of available free or commercial software to allow convenient use.

In this presentation, we demonstrate that both bottlenecks that previously restricted the use of TTCF are now removed. The TTCF methodology will be explained, and its applications to rheology and tribology highlighted. We will show how the gap between NEMD simulation and experimental measurement can be eliminated and highlight recent simulations of elastohydrodynamic lubrication (EHL) down to experimental rates of strain [4-6]. These simulations on complex molecular fluids under high nanoscale confinement are shown to be feasible on high performance supercomputers. Furthermore, we note the accessibility of our Python scripts for general use with the freely available and popular LAMMPS software package [5,7], so that anyone can set up and run their own simulations to take advantage of this state-of-the-art simulation methodology.

References:

1. D.J. Evans and G.P. Morriss, *Statistical Mechanics of Nonequilibrium Liquids*, Cambridge (2008).
2. D.J. Evans, D.J. Searles and S.R. Williams, *Fundamentals of Classical Statistical Thermodynamics: Dissipation, Relaxation and Fluctuation Theorems*, John Wiley & Sons (2016).
3. B.D. Todd and P.J. Daivis, *Nonequilibrium Molecular Dynamics: Theory, Algorithms and Applications*, Cambridge (2017).
4. L. Maffioli, E.R. Smith, J.P Ewen, P.J. Daivis, D. Dini and B.D. Todd, J. Chem. Phys. **156**, 184111 (2022)
5. L. Maffioli, J.P Ewen, E.R. Smith, S. Varghese, P.J. Daivis, D. Dini and B.D. Todd, Comput. Phys. Commun. (submitted, 2023)
6. L. Maffioli, J.P Ewen, E.R. Smith, P.J. Daivis, D. Dini and B.D. Todd (in preparation).
7. A. P. Thompson, H. M. Aktulga, R. Berger, D. S. Bolintineanu, W. M. Brown, P. S. Crozier, P. J. in't Veld, A. Kohlmeyer, S. G. Moore, T. D. Nguyen, T. D. Nguyen, R. Shan, M. J. Stevens, J. Tranchida, C. Trott, S. J. Plimpton, Comput. Phys. Commun. 271, 108171 (2022).