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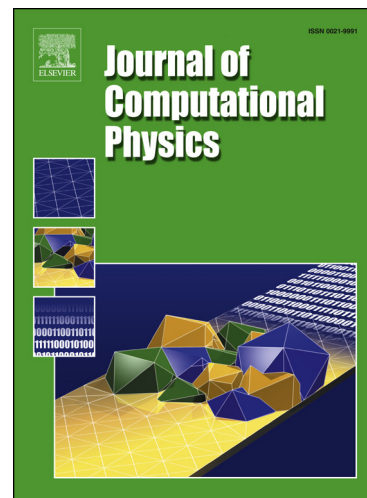
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Pseudospectral methods for density functional theory in bounded and unbounded domains

Andreas Nold^a, Benjamin D. Goddard^b, Peter Yatsyshin^a, Nikos Savva^c, Serafim Kalliadasis^{a,*}

^a*Department of Chemical Engineering, Imperial College London, London, SW7 2AZ, UK*

^b*School of Mathematics and Maxwell Institute for Mathematical Sciences, The University of Edinburgh, Edinburgh, EH9 3FD, UK*

^c*School of Mathematics, Cardiff University, Cardiff CF24 4AG, United Kingdom*

Abstract

Classical Density Functional Theory (DFT) is a statistical-mechanical framework to analyze fluids, which accounts for nanoscale fluid inhomogeneities and non-local intermolecular interactions. DFT can be applied to a wide range of interfacial phenomena, as well as problems in adsorption, colloidal science and phase transitions in fluids. Typical DFT equations are highly non-linear, stiff and contain several convolution terms. We propose a novel, efficient pseudo-spectral collocation scheme for computing the non-local terms in real space with the help of a specialized Gauss quadrature. Due to the exponential accuracy of the quadrature and a convenient choice of collocation points near interfaces, we can use grids with a significantly lower number of nodes than most other reported methods. We demonstrate the capabilities of our numerical methodology by studying equilibrium and dynamic two-dimensional test cases with single- and multispecies hard-sphere and hard-disc particles modelled with fundamental measure theory, with and without van der Waals attractive forces, in bounded and unbounded physical domains. We show that our results satisfy statistical mechanical sum rules.

Keywords: Density functional theory, pseudospectral methods
2010 MSC:

1. Introduction

Nanoscale effects associated with fluid interfaces play an important role in a wide range of natural phenomena and technological applications. These include the design of water-repellent surfaces, inkjet printing, oil recovery, as well as a growing number of applications in the rapidly developing field of micro- and nanofluidics [48, 7, 21]. In the modern literature on soft-matter systems, particle-based approaches such as molecular dynamics (MD) or Monte-Carlo (MC) computations are popular tools which allow to obtain particle trajectories and phase-space configurations of statistical mechanical systems. However, the high numerical cost of direct simulations renders them intractable for large system sizes or long observation times.

In this context, classical density functional theory (DFT) has emerged in the past decades as a useful tool for investigations of nanoscale phenomena in soft-matter systems. DFT was first used to study fluid interfaces in the late 70's [15, 17], and since then has been applied to cover a wide range of fields [71], from the modeling of atomic [59], molecular [10] and polyatomic [12, 76] systems to electrolyte solutions [31], and even water interfaces [34]. Within DFT, a fluid is described in terms of its one-body density alone. This is achieved by approximating the free energy of the system as a functional of the density and obtaining the density profile from a minimisation procedure, e.g. by employing the variational principle [17]. This is significantly less computationally demanding compared to MD/MC, whilst retaining nanoscale properties of the fluid [71].

The typically employed DFTs for atomic fluids, such as a Lennard–Jones (LJ) fluid, are based on the perturbation theory expansion of the free energy density in powers of the attractive intermolecular potential, with the reference free

*Corresponding author

Email address: s.kalliadasis@imperial.ac.uk (Serafim Kalliadasis)

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