Second Order Exact Derivatives to Perform Optimization on Self-Consistent Integral Equations Problems

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ABSTRACT Great efforts have been made to search for enhanced semi-empirical forms of the bridge function $b$ appearing in disordered condensed matter problems which are solved using the integral equation method. Currently, parameterized forms of the bridge function are manually chosen to fit as closely as possible the thermodynamic self-consistent equations depending on $g$ and its derivatives. We discuss a second-order differentiation of the computer code that enables construction of parameterized bridge functions using optimal control techniques.

22.1 Introduction

In the method of distribution functions of the classical statistical physics, the microscopic properties of dense fluids [269] are described by the pair-correlation function $g$, which represents the local arrangement of atoms or molecules. The integral equation theory is one of the most powerful semi-analytic methods to obtain the pair-correlation function of a fluid. Even though its favorite field is the case of simple liquids, often taken as a benchmark, it can be applied to various complex situations including liquid metals, noble gases or polymer hard-chains.

The integral equation method solves the set of equations formed by the Ornstein-Zernike integral equation [407] and a closure relation involving $g$. Even if a formal exact expression for the closure exists [390], it includes a particular function $b$ involving the pair-correlation function $g$ itself. Therefore, considerable efforts have been made since the pioneering work of Rowlinson [444] to search for enhanced semi-empirical forms of the bridge function that satisfy thermodynamic self-consistency conditions.

The procedure of thermodynamic self-consistency involves an explicit numerical calculation of the density and temperature derivatives of the pair-correlation function [204]. Besides the classical finite difference method,
Vompe and Martynov [492] obtain these derivatives as solutions of differentiated integral equations. Both methods are approximate. Currently, parameterized forms of the bridge function have been manually tuned to fit as closely as possible a thermodynamic self-consistent condition. The inaccuracy of these derivatives is probably the main reason why optimal control methods were not in use in the liquid physics.

An alternate solution is to use algorithmic differentiation [238] to obtain exact derivatives of $g$ as discussed in [122]. The ability of automatic differentiation (AD) tools ADIFOR [78] and Odyssee [186] makes derivatives of $g$ available to the search for bridge functions using optimal control techniques. The aim of this chapter is to show that it is easy to construct codes that enable optimization for determining the parameterized function $b$, even though it requires second-order derivatives.

In this chapter, §22.2 briefly describes integral equation problems and objective consistency functions. Differentiation steps and numerical results are discussed in §22.3. Some research directions conclude the presentation.

### 22.2 Liquid State Theory

Let us consider a fluid of density $\rho$ and temperature $T$ whose molecules, separated by a distance $r$, interact via the Lennard-Jones pair potential

$$u(r) = 4\varepsilon \left\{ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right\},$$

(22.1)

where $\sigma$ is the position of the node, and $\varepsilon$ is the well-depth of the pair potential. The latter is generally used to model real fluids such as pure gases considered as homogeneous and isotropic [269]. Beside the simulation methods, such as molecular dynamics or Monte-Carlo methods, the integral equation theory has proven to be a powerful semi-analytic method to calculate the pair-correlation function $g$ from which it is possible to predict the structural and thermodynamic properties of fluids.

#### 22.2.1 Integral equation problem

Due to the homogeneity and isotropy of the fluid, all the correlation functions can be considered as spherically symmetric and expanded only on $r$, the modulus of vector $\vec{r}$. In this framework, Morita and Hiroike [390] derived a one-dimensional formal exact expression for the pair-correlation $g$ by means of the Ornstein-Zernike integral equation plus a closure relation:

$$\begin{align*}
\left\{ 
g(r) &= 1 + c(r) + \rho \int (g(r') - 1) c(\left| \vec{r} - \vec{r}' \right|) \, dr', \quad \forall r > 0 \\
g(r) &= \exp \left( -u(r)/k_B T + g(r) - 1 - c(r) + b(r) \right).
\end{align*}$$

(22.2)

In the former system, $c$ is the direct correlation function, and $k_B$ is Boltzmann's constant. The bridge function $b$ can be written as an infinite sum...