
Robert E Beardmore
**A Numerical Bifurcation Analysis of the Ornstein-Zernike
equation**

Department of Mathematics
Imperial College London
South Kensington Campus
London SW7 2AZ
UK
`r.beardmore@ic.ac.uk`
A Peplow
F Bresme

The isotropic Ornstein-Zernike (OZ) equation

$$h(r) = c(r) + \rho \int_{\mathbb{R}^3} h(\|\mathbf{x} - \mathbf{y}\|) c(\|\mathbf{y}\|) d\mathbf{y}, \quad (1)$$

that is the subject of this paper was presented almost a century ago to model the molecular structure of a fluid at varying densities. In order to form a well-posed mathematical system of equations from (1) that can be solved, at least in principle, we assume the existence of a closure relationship. This is an algebraic equation that augments (1) with a pointwise constraint that is deemed to hold throughout the fluid and it forces a relationship between the total and direct correlation functions (h and c respectively).

Some closures have a mathematically appealing structure in the sense that the total correlation function is posed as a perturbation of the *Mayer f -function* given by

$$f(r) = -1 + e^{-\beta u(r)}.$$

This perturbation depends on the potential u , temperature (essentially $1/\beta$) and the indirect correlation function through a nonlinear function that we denote G , as follows: $h = f(r) + e^{-\beta u(r)} G(h - c)$, ($G(0) = 0$), *so that* $(1 -)$ *are solved together with* β and ρ as bifurcation parameters. There are many closures in use and if we write $\exp_1(z) = -1 + e^z$ then the hyper-netted chain (HNC) closure $G(\gamma) = \exp_1(\gamma)$ *has the form of () and is popular in the physics and chemistry literature.*

The purpose of the talk is show that *any reasonable* discretisation method applied to (1-) suffers from an inherent defect if the HNC closure is used that can be summarised as follows: phase transitions lead to fold bifurcations. The existence of a phase transition is characterised by the existence of a bifurcation at infinity with respect to h in an L^1 norm at a certain density, such that boundedness of h is maintained in a certain L^p norm. This behaviour is difficult to

mimic computationally by projecting onto a space of fixed and finite dimension and, as a result, projections of (1-) can be shown to undergo at least one fold bifurcation if such a bifurcation at infinity is present. However, other popular closure relations do not necessarily suffer from the same defect.