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A Numerical Bifurcation Analysis of the Ornstein-Zernike equation with Hypernetted Chain Closure

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The isotropic Ornstein-Zernike (OZ) equation

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

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: h = f(r) + e$^{-\beta u(r)}G(h-c)$, $\quad (G(0) = 0), sothat(1-)aresolvedtogetherwith\beta$ 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(γ) = $\exp_1(\gamma) hastheformof()andispopularinthephysicsandchemistryliterature.$

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.