

**New Perspectives on Integral Equation and Density
Functional Techniques in view of Applications to
Complex Molecular Systems**

Proposed dates and place

Autumn 2011 or early 2012, LPTCM, UPMC, T13-12

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1.1 Proposal

1.2 Introduction and motivation

Integral Equations (IE) and Density Functional Theory (DFT) from Liquid State theory are a tantalising tool to study equilibrium properties of simple and complex liquids. Yet, despite numerous important progresses, they are still trailing behind computer simulations when it comes to practical applications ranging from simple solution theory to more complex biological systems. One example that comes to mind is the case of water, for which *none* of the existing IE or DFT are able to reproduce the structure the liquid in par with computer simulations of any model. The reason for this is well known for IE: they are missing an important set of diagrams known as bridge diagrams, and such diagrams play an important role in describing the exact properties of any system, even for the canonical hard spheres model. IE have been tested on various complex liquids, ranging from simple polar molecules to water, and the quality of the results quickly deteriorates when explicit highly directional interactions are present, such as hydrogen bonding interactions, for example. This rules out the study of many realistic systems by IE techniques. None of the existing approximations for the missing bridge function are able to close this gap with computer simulations.

However, recent work has shown that computer simulations can be put in difficulty with many realistic systems, starting from simple aqueous mixtures, such as water-alcohol mixtures. The reason is the presence of strong micro-heterogeneity which is due to the micro-segregation of the oily (-e.g.- carbon or methyl groups) and polar parts present in the various constituents. This micro-heterogeneity relaxes at the scale of the nanosecond and nanometer scale, while the molecular motions relaxes at the picosecond scale. This makes the evaluation of equilibrium properties often unrealistically expensive in terms of computer resources. This situation calls for serious theoretical alternatives that would be in par with these “exact” but expensive simulations. This problem becomes even more serious when biological systems are to be considered, as for example the description of the complex aqueous environment of proteins, that involves water, ions, and many active molecules.

The aim of the workshop is to investigate possibilities to push the application of IE and DFT towards complex molecular systems, for example molecular liquid mixtures or aqueous solutions in complex environments. Recent advances on this topic will be discussed and new strategies are welcome to improve the existing ones. The discussion meeting will be limited first to mainly the French community which has a long history and broad competence in this field, in order to evaluate which common strength can be gathered for this challenging problem. A few key European colleagues who are already tackling complex molecular systems will be invited too. The possibility of proposing an international CFCAM workshop in this matter in 2012 will be discussed.

1.3 State of the art

In IE theory, bridge functions are known for many simple *model* liquids, such as hard spheres or Lennard-Jones systems by direct inversion of the simulation correlation functions. None of the theoretical guesses are in par with the accuracy of such direct

approaches. The most reliable theoretical approach to the evaluation of the bridge function remains the term-by-term evaluation of the diagrams in the series density expansion. An important caveat of this approach was the lack of information on the convergence of the series. It has been shown recently that the exact evaluation of the bridge function for hard rods in one dimension could not be obtained from a diverging series expansion. This throws strong doubts that such approach could be used in three dimensional situations, especially realistic ones. In fact, it is about time we all simply accept that the bridge function cannot be evaluated by analytical methods. This opens routes towards possibilities of coupling integral equations with simulations, with the aim of producing reliable bridge functions that would serve as template to investigate systems not accessible by simulations alone. Direct inversion of the correlation functions obtained from the simulation results is a challenge in itself. One needs very accurate simulations and the distance range over which correlations are calculated is important. Finite size simulations bring long range corrections that have been documented in the early 70s by Lebowitz and Percus, but have not been implemented in practical cases. Direct inversion of the Molecular Ornstein-Zernike equation, or that of the equivalent site-site analogues pose each different challenges. One point that this workshop should examine in detail is the various ways to couple simulations with various strategies involving integral equation or DFT techniques, in order to infer accurate bridge functions. The workshop is equally aimed at examining the possibility of obtaining accurate free-energy functionals. We wish to investigate routes such as 3D-density functionals based on fundamental measure theory for the repulsive interactions, while using effective attraction beyond.

1.4 Objectives

All invited participants have contributed to the development of integral equations and density functional theory. We expect high-level output on the feasibility of the project and the various strategies that can be deployed. It is important to underline that this is not a project about coming up with an engineering methodology. Rather, it is a change of paradigm about integral equation or density functional theory, where the recognition of the absence of bridge function or realistic excess free-energy functional is considered as pivotal, and the need to infer such functions from computer simulations should not be uniquely confined to realistic systems, even though this is the first motivation of the project. The route towards such goal will and should explore possibilities of obtaining the bridge function for crucial models that have paved the way to the development of the integral equation theory, such as the RPM or DHS models for example. This workshop is a first call to revitalise the field of integral equation theory that is fundamental to the statistical theory of liquids both from theoretical and applications, especially in the current context of a worldwide need for detailed microscopic investigations of liquid and biological matter.

We are aiming at slightly above 10 participants for 3 half-days including scientific talks and the planning of a future CFCAM meeting.

1.5 Participant List

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2. Financial Support

2 invités étrangers (Stefan Kast + Andrew Masters) + 4 provinciaux + une dizaine de contributeurs potentiels en IdF.

Transport (avion, train): 1500 Euros

6 nuits d'hôtel dans un l'hôtel convenable du quartier latin: 750 Euros

Pauses café + un déjeuner commun au restaurant + indemnités de séjour pour étrangers/provinciaux: 750 Euros

Total: 3000 Euros