Theoretical models for fluid thermodynamics based on the quasi-Gaussian entropy theory
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Chapter 1

General introduction

The theoretical modeling of fluid thermodynamics is one of the most challenging fields in physical chemistry. In fact the fluid behavior, except at very low density conditions, is still extremely difficult to be modeled from a statistical mechanical point of view, as for any realistic model Hamiltonian the configurational part of the partition function cannot be evaluated, i.e., the corresponding high dimensional integral is far too complex to be solved. Hence once a molecular Hamiltonian has been modeled, often severe approximations are necessary in order to obtain a model for the thermodynamics.

The usual approximations, based on integral equations or on perturbation theory,²⁻⁵ make use of different kinds of expansions in the particle correlation functions or energy fluctuations for a given molecular Hamiltonian model. Much has been done on this from the 50s on and in the literature many different versions of these two basic approaches can be found. However, these methods still cannot be used in general for polar fluids, and even in the case of the simpler apolar fluids, where the Lennard-Jones potential seems to be a good model, they do not always provide an accurate thermodynamic description. In Chapters 3, 4 and 5 a more extended discussion on these approaches is given, addressing specific aspects of models based on cumulant expansions, usual in perturbation theory.

Direct molecular simulations of fluids are also severely limited by the difficulties connected to the still insufficient computer power to simulate large enough
systems reaching a sufficient sampling of phase space. In addition, the modeling of molecular Hamiltonians for real fluids is difficult and often can be achieved only with the use of approximations in the molecular description.

Recently a new theoretical approach, the quasi-Gaussian entropy (QGE) theory, has been proposed. In this theory the basic statistical mechanical relations are rewritten in terms of the distribution of the fluctuations of a macroscopic property instead of the partition function. In fact, for each statistical mechanical ensemble it is possible to define a proper reference state such that the free energy difference between the actual condition and the reference one can be expressed exactly in terms of the moment generating function, defined by the distribution of a specific macroscopic fluctuation. Instead of modeling as usual a molecular Hamiltonian, in the QGE theory we model the distribution and hence the moment generating function, in order to describe the thermodynamics of the system. In this way we obtain for each model distribution a corresponding model system at the level of thermodynamic behavior.

In modeling the fluctuation distributions we can use basic physical principles to restrict the possible set of distributions. In fact, considering that a (macroscopic) thermodynamic system can be always decomposed into a large set of identical virtually independent subsystems, defined as “elementary systems” in the QGE theory, we realize that the distribution for the fluctuations of a macroscopic property is the convolution of a large set of independent “elementary” distributions. Hence applying the central limit theorem we obtain that every distribution of a macroscopic property must be “quasi-Gaussian”, and thus can be modeled as a unimodal distribution. Note that the concept of elementary systems is purely a consequence of the thermodynamic principle of linear scalability of extensive properties and size independence of the intensive ones. The elementary system hence defines the “universal” minimum size required to obtain the thermodynamic behavior.

To obtain (unimodal) distributions of increasing complexity in a systematic way, we use the generalized Pearson system\(^6\)\(^\text{-}\)\(^11\) for unimodal curves as described in the following chapters of this thesis.

Moreover, each type of model distribution provides a closure relation for a general thermodynamic equation, resulting in an ordinary differential equation, the thermodynamic master equation (TME). According to the combination of the ensemble and distribution chosen, the TME solution provides the temperature or density dependence of the thermodynamic properties. Each model distribution, combined with the input information at a single thermodynamic state point, defines a corresponding “statistical state” of the system, and hence for a given model distribution the corresponding exact thermodynamics is obtained.

It should be clear that modeling the moment generating function (which is directly connected to the entropy of the system) in terms of quasi-Gaussian distributions tremendously simplifies the statistical mechanical description, substituting a high dimensional integral, the partition function, with a one dimensional
integral, the moment generating function. Many different types of molecular Hamiltonians could in principle result in the same type of distribution and thus the Hamiltonian fixes the distribution and not vice versa. It should also be noted that a good model distribution for a real fluid is likely to have a mathematical complexity which is still relatively low, although the corresponding model Hamiltonian can be rather complicated. Only in the critical point region and at phase transitions extra complications can arise and it will be shown that a proper choice of the ensemble and type of fluctuation used is essential to keep a relatively simple model distribution.

In a previous thesis the basic principles of the QGE theory were described and for different statistical mechanical ensembles the basic statistical states for the temperature dependence were derived and applied. In this thesis we describe in a systematic way the thermodynamic models for the temperature dependence based on these statistical states (chapters 2-3) and extend them using a simple perturbation approach (chapter 6). In chapter 4 we derive new thermodynamic models for the density dependence based on statistical states for the volume or particle number fluctuations and in chapter 5 it is shown how this theory can be used in combination with molecular simulation data. In these last three chapters also a direct comparison is given of the statistical states obtained from the QGE theory with cumulant expansion models of comparable complexity, usual in perturbation theory. In chapter 6 a complete equation of state for Lennard-Jones fluids is derived, using a simple interpolation of the statistical states for the temperature dependence obtained from the theory at different isochores. In the following chapter a systematic application of the theory to water data is also given. Finally in chapter 8 the results are summarized and discussed and two new developments of the theory are presented.