Theses

of the Ph.D. dissertation

Classical Simulation Aided Studies on the Structure of Liquids

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Introduction

The enormous growth in affordable computational capacity (according to Moore's law) eased the spreading of computer simulations, which created a new branch of science called computer experiments. Models, which are represented by mathematical functions, replace real materials and computers provide the space of experiments.

Computer simulations are used in virtually all aspects of science (physics, chemistry, biology, materials science, etc.) and its use is expected to grow substantially in applied science (pharmaceutical industry, chemical technology) as well. Computer simulations are useful in substituting experiments, where the studied system allows for a simple description, which still gives correct results on the examined properties. Another use of computer simulations is the study of system response to extreme conditions (pressure, temperature, etc.), where experimental setup is not available. Computer simulations are similar to both theories and experiments, however at the same time also complement both: theories can be tested by comparing theoretical results with computer simulations, while a model can be evaluated by comparing experimental results and computer simulations.

Aim of the Study

This dissertation concentrates on the structure of disordered systems with the help of classical simulations; the articles, on which this work is based, are not tightly related. The three main topics are the following.

The inverse theorem of liquids states that there is a one to one correspondence between the structure of the liquid and the interaction among the particles. The theorem is theoretically important for the pairs of the constituents, where the structural function can be the pair correlation function (or its experimental equivalent the structure factor) and the interactions are classical mechanical pair potentials. The practical solution of the inverse theorem in one direction is resolved: one can get the structure by molecular simulations for known interactions. In the other direction, there are no widely accepted methods up to now. In the first study of my thesis, we examined the power of the artificial neural networks as non-linear approximative methods for the solution of the inverse theorem in this structure to potential direction.

In the second part of the thesis we focused on a computational challenge, namely the simulation of asymmetric binary hard sphere systems as those systems are of great scientific interest and there was no comprehensive study especially regarding pair-correlation functions with large size ratios to be found in the literature. It is a cumbersome task according to the number of particles increasing cubic with the asymmetric ratio. We developed an optimised molecular dynamics code for 1:5 and 1:10 ratios considering the architecture of nowadays-available personal computers. Our performed simulations provided a good base to test different theories and approximations on binary hard sphere systems.

The simulation of systems with short range potentials can be solved with linear scaling algorithms while the presence of long range interactions increase the scaling up to n squared or even higher. There are plenty of efficient solutions for different, mostly Coulomb systems. Some of the solutions involve a rather complicated program code or their applicability is limited to e.g. special system sizes. In the third part of my thesis, I would like to show our efforts on a simple parameterisation of the Coulomb force, which can be easily embedded in codes written for short-range interactions.

Methods

To investigate the applicability of neural networks for the solution of the inverse theorem of statistical mechanics we used a scheme of the traditional supervised trained, monolayer neural network. The input data were molecular dynamics simulation generated structure-factor pair-potential pairs, three types of pair potentials were used: Lennard-Jones, Morse and Buckingham potentials. We used altogether 2000 pairs for the training of the network and we tested the performance on further 200 function pairs. For the optimised solution, we checked many factors e.g. the number of hidden neurons, modifications of the merit functions, etc.

In the case of the binary hard sphere simulations, we started with Monte Carlo technique, but for feasible results, we had to turn to molecular dynamics. We developed an algorithm that uses the link-cell method and the traditional calculation of next collision times, but according to the size asymmetry of the constituent particles, it was differentially interpreted for the particle types. The asymmetric ratio was 1:5 and 1:10 and the partial packing fractions of the spheres ranged from 0 to 0.5 in 0.1 increments as feasible. We obtained a reasonable set of partial pair correlation

functions for these systems, in contrary to the majority of earlier studies also for the large-large partials. Our data provided a good basis for the test of the applicability of the one component hard sphere approximation and for comparison to theoretical methods, namely the Percus-Yevick and Rational Function Approximation methods.

In the third investigation of the thesis, we started with a theoretical problem: how one should partition the energy of a periodic system. We showed with numerical calculations, using the ergodic equivalence of Monte Carlo and molecular dynamics simulations, that the most commonly used definition is the unique correct one. We decomposed the Coulomb interactions of the periodic systems into an intra-cell and two inter-cell parts. We randomly generated several sets number of points, each system consisted 10,000 distances with interactions and forces calculated by the Ewald and the trivial sum methods. The inter-cell interactions were parameterised by simple polynomials and rational functions. We compared the performance of this parameterisations and earlier methods in detail.

Results

1. Neural Networks have been successfully applied to solve the inverse problem of statistical mechanics: a neural network trained on a training set consisting of 2000 simulation generated pair potential – structure factor pairs provided an encouraging reproduction of the pair potentials, especially in the case of Lennard-Jones and Morse potentials.
2. A whole set of pair correlation functions of binary hard-sphere mixtures at 1:5 and 1:10 size ratios for a wide and systematic range of packing fractions have been obtained.
    a) For the limit of the approximation of two-component hard-sphere structure with one-component hard-sphere one: we found that this approximation cannot be applied, if the packing fraction of the large spheres is greater than about 0.2.
    b) We studied the performance of the Percus-Yevick and the Rational Function Approximation theoretical methods in the creation of pair correlation functions. These two methods were chosen only from a practical viewpoint. The performances of these theoretical methods were convincing in the small-small and small-large cases. On contrary, the large-large pair correlation functions can be used only as a very crude approximation at medium and large densities. The two

methods behave rather similarly, but the Percus-Yevick method seemed to be worse than the Rational Function Approximation method.

c) In the comparison of the 1:5 and 1:10 data, we concluded that both the approximation of the one-component hard-sphere model and the theoretical models are less successful as we approach the colloid limit.

d) Finally, we reported a set of contact values of $g(r)$-s for the binary hard-sphere systems studied by molecular dynamic simulations.

3. A simple method to calculate Coulomb interactions in three-dimensional periodic systems has been devised.

a) As a prerequisite for the calculations, we checked how the energy of one cell in a periodic system should be calculated as there were some contradicting definitions to be found in literature. The devised equation has been proven correct with the help of Monte Carlo and molecular dynamics simulations.

b) We have shown that the crucial part of the Coulomb interaction, which is the extra term besides the contribution within the minimal image convention, can be easily parameterised with simple functions. We used polynomials of up to the 7^{th} degree and rational functions with a sum of 5, 6 and 7 of the degrees in the numerators and denominators.

Publications

Publications related to the thesis

Tóth, G., Király, N., Vrabecz, A. *Pair potentials from diffraction data on liquids: A neural network solution,* Journal of Chemical Physics 123 (17), pp. 1-8, 2005

Vrabecz, A., Toth, G., *Simulation of binary hard-sphere systems with 1:5 and 1:10 size ratios,* Molecular Physics, 104 (12), pp. 1843–1853, 2006

The publication of the study in Chapter 4 (*Parameterization of Coulomb Interaction in Three-Dimensional Periodic Systems*) is in preparation

29th International Conference on Solution Chemistry, Portorož, 2005, Simulation of Binary Hard-Sphere Systems at the Colloidal Limit (poster)

ELTE Statisztikus Fizikai Napok, 2005, Aszimmetrikus merevgömbi folyadékok szimulációja (presentation)

Other publications

G.G. Lang, A. Vrabecz, G. Horanyi, *Radiotracer and analytical evidences proving the reduction of ClO4- ions at the cobalt/electrolyte solution interface*, Electrochemistry Communications 5 (7), pp. 609-612, 2003

Tóth, G., Körmendi, K., Vrabecz, A., Bóta, A., *Evaluation of small-angle x-ray scattering data of a Raney-type Ni catalyst with computer simulation,* Journal of Chemical Physics 121 (21), pp. 10634-10640, 2004

Láng, G., Inzelt, G., Vrabecz, A., Horányi, G., *Electrochemical aspects of some specific features connected with the behavior of iron group metals in aqueous perchloric acid/perchlorate media,* Journal of Electroanalytical Chemistry 582 (1-2), pp. 249-257, 2005

Kende, A., Vrabecz, A., Angyal, V., Rikker, T., Eke, Zs., Torkos, K., *Liner as the key of injection optimization in pesticide analysis,* Chromatographia 63 (3-4), pp. 181-187, 2006