# Reconstruction of Pair Interaction Potentials from Radial Distribution Functions

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## Abstract

A method to reconstruct the pair interaction potential from radial distribution functions within the Monte Carlo simulation scheme is described and some applications are briefly discussed.

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## 1 Introduction

We have recently suggested a new method for reconstruction of atom-atom pair interaction potentials from radial distribution functions (RDF) using Monte Carlo simulations [**?**]. It can be proven that for any set of RDFs, there exists a unique set of pairwise effective potentials, reproducing the original RDFs [**?**]. Moreover, it can be proven, that the corresponding (pairwise) Hamiltonian provides maximum computational entropy among all other (non-pairwise) Hamiltonians, consistent with a given set of RDFs [**?**]. Below we will give a brief description of the algorithm to reconstruct the pair potential and discuss some of its applications.

## 2 Computational Algorithm

In the present communication we implement our method to one-component systems. A generalization to a multicomponent system is straightforward.

Consider following Hamiltonian with pair interactions:

$$H = \sum_{i,j} V(r_{ij}), \tag{1}$$

where $V(r)$ is a pair potential and $r_{ij}$ is the distance between $i$ and $j$ particles. Let us use a grid approximation to the potential, approximating a continuous function $V(r)$ by its values on a grid:

$\tilde{V}(r) = V(r_\alpha) \equiv V_\alpha \quad$ for $\quad r_\alpha - 1/(2M) < r < r_\alpha + 1/(2M); \quad r_\alpha = \alpha r_{cut}/M; \quad \alpha = 1, ..., M; \quad r_{cut}$ is some cutoff distance.

Then the Hamiltonian (eq. **??**) can be written as:

$$H = \sum_\alpha V_\alpha S_\alpha \tag{2}$$

where $S_\alpha$ is the number of pairs between the particles with the distances found inside $\alpha$-slice. Evidently, $S_\alpha$ is an estimator of the radial distribution function: $\langle S_\alpha \rangle = 4\pi r^2 \rho(r) N^2/(2V)$. The average values of $S_\alpha$ are some function of the potential $V_\alpha$, and one can write the expansion:

$$\Delta\langle S_\alpha \rangle = \sum_\gamma \frac{\partial \langle S_\alpha \rangle}{\partial V_\gamma} \Delta V_\gamma + O(\Delta V^2) \tag{3}$$

where the derivatives $\partial\langle S_\alpha\rangle/\partial V_\gamma$ are expressed using exact statistical mechanics relationships [**?**]:

$$\frac{\partial \langle S_\alpha \rangle}{\partial V_\gamma} = -\left(\langle S_\alpha S_\gamma \rangle - \langle S_\alpha \rangle \langle S_\gamma \rangle\right)/(kT) \tag{4}$$

The equations (**??**) and (**??**) allow us to find the interaction potential $V_\alpha$ from radial distribution functions $\langle S_\alpha \rangle$ iteratively. Let $V_\alpha^{(0)}$ be a trial potential. For example, it can be the potential of mean force (PMF): $V_\alpha^{(0)} = -kT ln\rho(r_\alpha)$. By carrying out standard Monte Carlo simulations, one can evaluate the averages $\langle S_\alpha \rangle$ and their deviations from the reference values $S_\alpha^*$, defined from the given RDF: $\Delta\langle S_\alpha\rangle^{(0)} = \langle S_\alpha\rangle^{(0)} - S_\alpha^*$. Then, by solving the system of linear equations (eq. **??**) with the coefficients, defined by eq.(**??**), and omitting terms $O(\Delta V^2)$, we obtain corrections to the potential $\Delta V_\alpha^{(0)}$. Then the procedure is repeated with the new potential $V_\alpha^{(1)} = V_\alpha^{(0)} + \Delta V_\alpha^{(0)}$, until a convergence is reached. The whole procedure resembles a solution of a multidimensional non-linear equation using the Newton-Raphson method.

If the initial approximation of the potential is poor, some regularization of the iteration procedure is needed. In this case, we multiply the required change of the RDF by a factor between 0 and 1. By doing so, the term $O(\Delta V^2)$ in eq. (**??**) can be made small enough to guarantee a convergence of the whole procedure, although the number of iterations will increase in this case.

The described above algorithm is implemented in the computer program called *InvMC* which makes one iteration of the reverse procedure. The program code for mono-atomic multicomponent systems is available from the authors by request.

## 3 Discussion

To find possible applications to the suggested algorithm is easy. One can calculate effective pair interaction potentials from experimental RDFs, obtained from neutron scattering experiments. In practical terms this task may encounter some problems because of possible uncertainty of the experimental RDFs. Although the solution of the reverse task is unique [**?**], nothing is said about the precision, and in some cases the small changes in RDFs may correspond to large changes in the interaction potentials. This problem turned out to be rather severe for molecular liquids, of which we have tested water.

The evaluation of the precision can be made within the given scheme by calculating the eigenvalues of matrix (eq. **??**). An undesirable case for the reverse task is when some of the eigenvalues are close to zero. In these cases the corresponding eigenvectors show changes in the potentials, affecting the RDFs only very little.

The analysis of the eigenvalues of matrix (eq.**??**) for the SPC water model has shown, that they may be as low as $10^{-4}$ in the reduced units. This means that some certain changes in RDF of order 0.01 may correspond to changes in the potential of order of $100kT$ for water-like models. A more detailed analysis of the precision problem, as well as some result to reconstruct potential for water from experimental RDFs will be given in our forthcoming paper.

Another application of the inverse procedure, originally suggested in [**?**], is reconstruction of effective potentials from RDFs, obtained in accurate all atom simulations. For example, one can calculate ion-ion distribution functions from MD simulations of ions in water and then use the inverse procedure to reconstruct effective solvent-mediated ion-ion potentials. In contrary to the case of experimental RDFs, we have a much more reliable control over the precision of the simulated RDFs. Moreover, higher-order correlations, from the accurate molecular dynamics simulations and from simulations with effective potentials can be compared [**?**]. The effective potentials, obtained in this way, can be used to simulate electrolyte solution on much large scale, since the water molecules are not explicitly taken into account. Thus, in ref.[**?**] the effective ion-ion potentials were applied to calculate osmotic and activity coefficients of NaCl solution, reproducing perfectly the experimental curves without adjustable parameters like hydrated ion radius.

The calculations of effective potentials using the inverse MC procedure from the accurate simulation data resembles the renormalization group Monte-Carlo method [**?**] in a way that we reduce the description of the system by removing, for us, uninteresting degrees of freedom and calculate the effective, or renormalized Hamiltonian for the interesting degrees of freedom. Other examples of this approach are calculation of effective potentials between ions and biomacromolecules from the corresponding all-atomic MD simulations, or calculations of effective atom-atom potentials from the *ab-initio* (e.g. Car-Parrinello) molecular dynamics. Investigations along these lines are in progress in our laboratory.

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