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Effective potentials from complex simulations: a potential-matching algorithm and remarks on coarse-grained potentials

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Abstract

The projection of complex interactions onto simple distance-dependent or angle-dependent classical mechanical functions is a long-standing theoretical challenge in the field of computational sciences concerning biomolecules, colloids, aggregates and simple systems as well. The construction of an effective potential may be based on theoretical assumptions, on the application of fitting procedures on experimental data and on the simplification of complex molecular simulations. Recently, a force-matching method was elaborated to project the data of Car–Parrinello *ab initio* molecular dynamics simulations onto two-particle classical interactions (Izvekov *et al* 2004 *J. Chem. Phys.* **120** 10896). We have developed a potential-matching algorithm as a practical analogue of this force-matching method. The algorithm requires a large number of configurations (particle positions) and a single value of the potential energy for each configuration. We show the details of the algorithm and the test calculations on simple systems. The test calculation on water showed an example in which a similar structure was obtained for qualitatively different pair interactions. The application of the algorithm on reverse Monte Carlo configurations was tried as well.

We detected inconsistencies in a part of our calculations. We found that the coarse graining of potentials cannot be performed perfectly both for the structural and the thermodynamic data. For example, if one applies an inverse method with an input of the pair-correlation function, it provides energetics data for the configurations uniquely. These energetics data can be different from the desired ones obtained by all atom simulations, as occurred in the testing of our potential-matching method.

1. Introduction

The projection of complex interactions onto simple distance-dependent or angle-dependent classical mechanical functions is a long-standing and actual theoretical challenge in the field of computational sciences, because the continuous development of computer simulations on condensed matter requires force fields on many new materials. There are a plenty of possible ways to determine the interactions. One may fit analytical or tabulated pair interactions in order to reproduce different experimental data. Some of the methods are connected to the so-called inverse theorem [1], where experimental structure factors or pair-correlation functions are intended to be reproduced with appropriately optimized potentials in simulations. One can determine potentials on a theoretical basis, or one can use quantum-chemical calculations to get an idea of the potential surface. There are two tendencies in the field of computer simulation on liquids and related materials. One direction is the demand for more and more accurate interactions, where rather complicated force fields are developed in many-body forms as well. There are methods in which the force and the potential are calculated on the fly by different quantum-mechanical methods in the system. A popular method is the Car–Parrinello simulation [2]. The increasing accuracy reduces the size of the system and the studied time domain, significantly limiting the possible results. In contrast, the other trend is to enlarge both the system size and the studied time domain. This usually means drastic simplification in the description of the interactions. In the all-atom simulations the interactions used can be extremely simple and they cannot describe fine details and interesting local effects in the systems. In biological and nanomaterial cases, a part of the system, e.g. the solvent, is treated as a background continuum or it is simple omitted. Furthermore, one has to use simple models for the interesting part of the system. A general method is to unify atoms, groups, or molecules into one interaction item.

The size and the time domain limit of the accurate simulations can be avoided, if one can derive correct and computationally cheap interaction functions. According to the current simulation algorithms, this means that the potential energy is written as a sum of pair-wise additive pair interactions, and it is preferable to use only distance-dependent functions in the simulation of anisotropic and homogeneous systems. The numerical details of the projection of multi-body forces onto pair-distance-dependent forces were elaborated first by Ercolessi and Adams [3]. In 2004, Izvekov *et al* [4] proposed a more robust method. It was called force matching. The main idea was to break the pair force into a short-range force described by cubic splines and into the Coulomb interaction. The coefficients of the cubic splines and the partial charges were optimized in a least-squares fit, where the ‘experimental’ forces were determined by Car–Parrinello simulations. The fitted input was a set of configurations with coordinates and actual *ab initio* forces for each atom. The method seems to be powerful, as was demonstrated in numerous applications [5–13]. The main part of our paper concerns the development of the potential analogue of Izvekhov’s force-matching algorithm. In our case, there are no force data in the input configurations. We used only the total potential energy of the given configuration. This means that our ‘experimental’ data can be obtained by Monte Carlo simulations, as well.

We tested our potential-matching algorithm on different systems. We focused on the other task mentioned above: on the development of effective one-component potentials for a selected species of a multi-component system, where the net effect of the other species is incorporated in the effective one-component potential. This field of statistical mechanics seems to have become important in the last few years. A general description of the methods can be found for example in [14, 15], where these potentials are called coarse-grained ones. We were interested in the connection of coarse-grained potentials and the inverse theorem of liquids, because the simulation-assisted methods for the solution of the inverse problem were used several times

to obtain effective interactions. We mention here the applications [16–25] of the Lyubartsev–Laaksonen [26] method.

2. Details of the potential-matching algorithm

The input data for the force-matching algorithm are the coordinates of the atoms and the forces acting on the atoms for several configurations. The use of forces limits the complex simulations to molecular dynamics ones, because the forces cannot be obtained in Monte Carlo simulations. The main aim of our potential matching was to develop an algorithm that can be applied on Monte Carlo simulation data as well. Our input data are the coordinates of the atoms and the total potential energy of the simulation system. For example, in the case of a two-component system, one can calculate the potential energy, $E^{(k)}$, of the k th configuration as the corresponding sum of the partial pair-correlation functions ($g_{\alpha\beta}^{(k)}(r_i)$) and $v_{\alpha\beta}(r_i)$, the tabulated partial pair potential.

$$\begin{aligned}
 E^{(k)} = E_{11}^{(k)} + E_{22}^{(k)} + E_{12}^{(k)} = & \frac{1}{2} \sum_i^{N_r} V \frac{4\pi\rho_1^2}{3} (r_i^3 - r_{i-1}^3) g_{11}^{(k)}(r_i) v_{11}(r_i) \\
 & + \frac{1}{2} \sum_i^{N_r} V \frac{4\pi\rho_2^2}{3} (r_i^3 - r_{i-1}^3) g_{22}^{(k)}(r_i) v_{22}(r_i) \\
 & + \sum_i^{N_r} V \frac{4\pi\rho_1\rho_2}{3} (r_i^3 - r_{i-1}^3) g_{12}^{(k)}(r_i) v_{12}(r_i),
 \end{aligned} \tag{1}$$

where ρ_α is the number density, N_r is the number of the bins in the pair-correlation and potential functions and V is the volume of the system. The number of actual equations is equal to the number of configurations (N_k). If one calculates more configurations than the number of the unknown tabulated potential values with non-zero $g_{\alpha\beta}^{(k)}(r_i)$ in the configurations ($N_{\text{columns}} \leq 3N_r$), the $v_{\alpha\beta}(r_i)$ s can be obtained by a multidimensional least-squares fit of

$$A\mathbf{v} = \mathbf{e}, \tag{2}$$

where an element of the $N_k \times N_{\text{columns}}$ coefficient matrix A includes $g_{\alpha\beta}^{(k)}(r_i)$ and its multipliers in equation (1), \mathbf{v} is the vector of the three tabulated potential functions written one by one (unknowns), and \mathbf{e} contains the $E^{(k)}$ potential energies.

The rows of the coefficient matrix are rather similar to each other, especially in the case of large systems. Therefore, the traditional multidimensional least-squares methods cannot be used. Sophisticated methods, e.g. the iterative routine named DLSBRR included in the IMSL Computational technology toolkit package¹, provided acceptable results in all of our calculations.

3. Results and discussions

3.1. One-component Lennard-Jones system

We performed some test calculations, in which the input data (coordinates of the atoms and the potential energy of the system) were obtained in classical mechanical simulations. Our first system was a one-component Lennard-Jones system around the triple point of the liquid, and the Lennard-Jones parameters were the standard argon ones ($\sigma = 3.405 \text{ \AA}$, $\varepsilon = 165.4 \text{ J}$, $T = 86.3 \text{ K}$ and $\rho = 0.022103 \text{ \AA}^{-3}$). The number of particles in the simulation cell was 216.

¹ Compaq Visual Fortran 6.

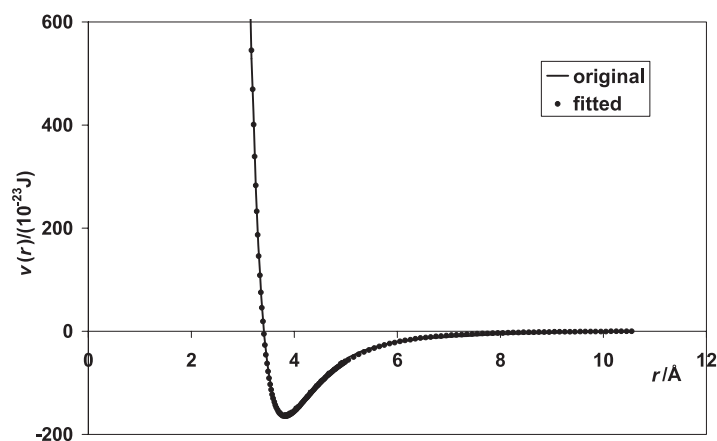


Figure 1. Pair potentials of the one-component Lennard-Jones test system.

The configurations were obtained in a canonical Monte Carlo simulation and they were sampled at every 1064 moves after the system reached equilibrium. The Δr grid of the pair-correlation function was 0.02 up to 4 Å, and it was 0.1 Å beyond it. The number of determined bins in the potential matching was around 150. A repulsive part was added to the potential-matched pair potential by simple linear extrapolation at the small distances where the pair-correlation functions was zero. We got reasonable smooth potentials, if the number of unknown potential bins was at least ten times less than the number of configurations obtained by the canonical Monte Carlo method ($N_k \geq 10 \times N_{\text{columns}}$). The original pair potential and the one obtained by the potential-matching procedure are shown in figure 1. One can see that the reproduction of the pair interaction was perfect.

3.2. Classical water simulation

Our next test system contained 200 flexible water molecules at ambient conditions. The Bopp–Jancsó–Heinzinger model [27] was used in molecular dynamics simulations. The question here was twofold. The modelling of water solely with pair interactions is questionable, because it is a rather complex system. Usually, auxiliary potential terms beyond the site–site pair interactions are used in its modelling. The other question was whether our potential-matching algorithm is able to separate the site–site interactions. To study this we used the potential-matching algorithms to obtain fits on separate parts of the potential energy. We decomposed the interaction energy of the flexible water system to intra-molecular and inter-molecular parts. The inter-molecular part was divided into a Coulomb and a dispersion part. The separate types of the fits qualitatively provided the pair-distance-dependent interactions of the original model. Thereafter, we applied our algorithm on the total potential energy of the system. The partial pair-correlation functions of the original simulation with the Bopp–Jancsó–Heinzinger model and with the interactions derived by our potential-matching algorithm on the total energies are shown in figure 2. There are small differences at the intra-molecular parts and at the first inter-molecular H–H peak. The difference between the O–H intra-molecular peaks cannot be seen in figure 2. It was similar to the difference between the intra-molecular H–H peaks shown in figure 2. Perhaps the differences are caused by the simplifications of the tabulated molecular dynamics code, where simple tabulation of both the potential and the force was used without any interpolation method. Surprisingly, if one compares the inter-molecular interactions of

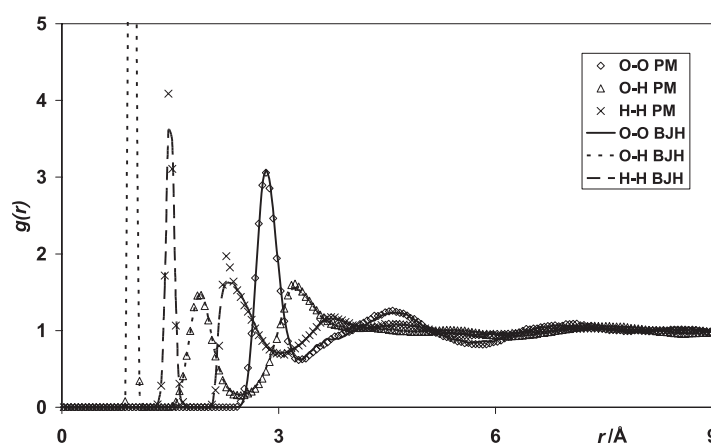


Figure 2. Comparison of the pair-correlation functions of ambient water with the Bopp–Jancsó–Heinzinger flexible water model and the simulation with the potentials obtained by the potential-matching algorithm.

the applied water model and the potential-matched functions, there are huge differences. One can see in figure 3 that the original model consisted of a large Coulomb part and another part that was responsible for the dispersion and repulsive effects. In contrast, our potentials behave differently and they are far away from the sum of the two original interactions. We were able to reproduce the structure of the system with this qualitatively different potential. The main reason could be that there is a minimal value in the partial pair-correlation functions at given distances in each configuration. This means that a minimal number of particle pairs is present at a given distance range in each configuration. There is no information in our method on how to distribute the potential contribution of these pairs among the partials. In a model this corresponds to the physical basis, e.g. the Coulomb interaction. In our case, this background energy is simply distributed according to the least-squares condition. Anyway, this example of relatively the same structural results for two qualitatively different inter-particle interactions is a good example of having to be more rigorous in the practical use of the inverse theorem of liquids. Furthermore, there is an arbitrary constant term in the total potential function according to the inverse theorem. In the case of multi-component systems, the constant is distributed among the partials in an indefinite way.

We derived the intra-molecular interactions too; they can be seen in figure 4. Here we could not compare to the original potential, because the original intra-molecular part contains three-particle terms as well. Checking the structural results in figure 2, we may say that our method works correctly for the projection of the intra-molecular three-body interaction onto a two-body one as well.

3.3. Reverse Monte Carlo configurations

The determination of interaction potentials from experimentally determined structural functions is a long-standing question in statistical mechanics. The task is called the inverse problem and one can find several methods and theoretical studies about it [26, 28–34]. Most of the methods use iterative simulations with different potential modification recipes to create interactions reproducing the experimental structure factors or pair-correlation functions. The reverse Monte Carlo method [35] is a frequently used data processing technique, in which the input is the structure factor and the output is a set of configurations being consistent to the experimental

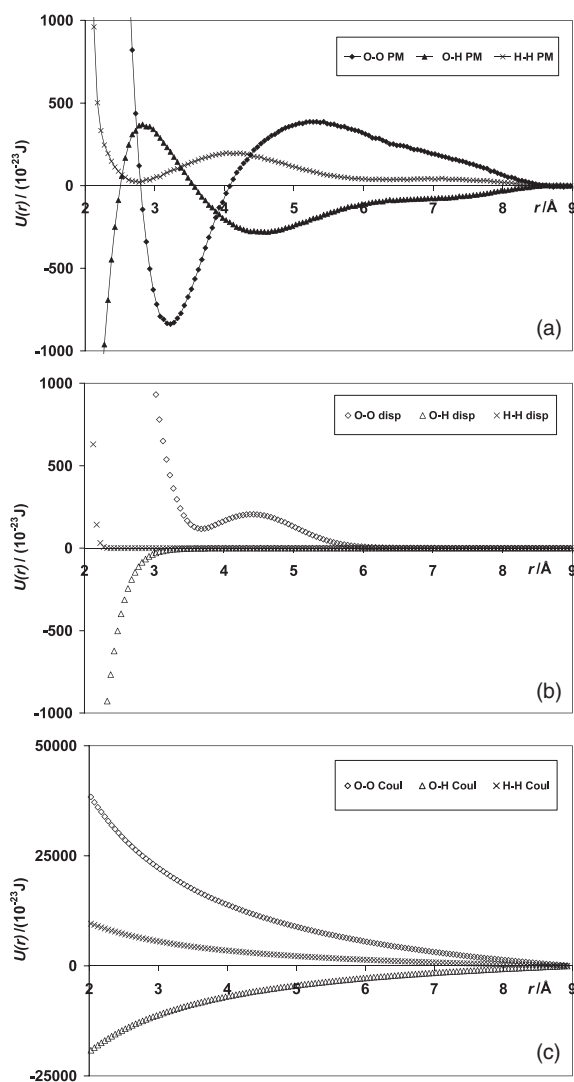


Figure 3. Comparison of the inter-molecular pair potentials of the Bopp–Jancsó–Heinzinger (BJH) model and the tabulated functions obtained by the potential-matching algorithm. (a) Functions obtained by potential matching, (b) dispersion part of the BJH model and (c) Coulomb part of the BJH model (note the different energy scale here).

data. Unfortunately, the method does not determine the interactions; it stops half way through the task. Our potential-matching method starts directly there, where the reverse Monte Carlo approach stops, and our output is the desired pair potential. We tried to combine the two methods. One set of data is missing for the reverse Monte Carlo configurations: the potential energy of the configurations. We tried several methods to supply these data.

We used the structure factor of the one-component Lennard-Jones system simulated with canonical Monte Carlo method as ‘experimental’ data (for details see section 3.1). We performed a reverse Monte Carlo simulation on these data and we got a set of configurations corresponding to this ‘experimental’ structure factor. The acceptance ratio was 0.1 with

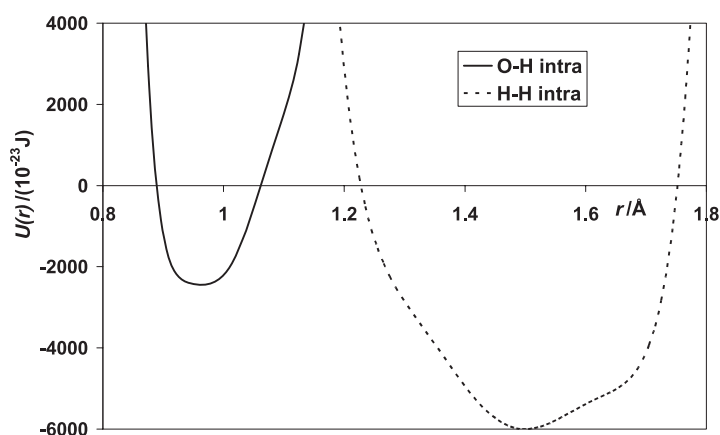


Figure 4. Intra-molecular pair potentials of water obtained by the potential-matching algorithm.

$\sigma_{\text{RMC}} = 0.001$ and maximal particle displacement of 0.3 \AA . The average χ^2 of one data point was about 0.16 in the calculation (the χ^2 definition of [35] was divided by the number of experimental data points). The relatively high value of χ^2 was because of the small system size (216 particles). At first, we added random energetics data for each configuration, where the data corresponded to a sample with the same mean and variance obtained in the canonical Monte Carlo simulation ($\langle U \rangle = 1.5236 \times 10^6 \text{ J}$, $\sigma_U = 5.6 \times 10^3 \text{ J}$). We applied our potential-matching algorithm on these extended configurations, but we did not get reasonable potential functions. The interactions obtained by the least-squares fits depended strongly on the actual assignment of the energies to the configurations, and the shape of the functions did not resemble the usual interaction potentials. If we applied these potential functions in canonical Monte Carlo simulations, the results were not reasonable liquid structures. Thereafter, we investigated the correlation of the potential energy of the configurations and some quantities which can be calculated without the knowledge of the potential on a given configuration. For example, we calculated the χ^2 -potential energy and the two-particle configuration entropy-potential energy correlations [36, 37]. We assigned energies to the configurations using the observed statistical correlations, but if we applied our potential-matching algorithm, we did not get acceptable pair potentials. Finally, we tried to establish a self-consistent method, in which we used the strong correlation of the potential energy and the configuration temperature of the configurations [37], but we were not able to obtain satisfactory results. If we summarize our unsuccessful trials, we get the same conclusion as before [33, 36–38]. We were not able to find a simple recipe to overcome the biased phase-space sampling of the reverse Monte Carlo method.

3.4. Effective one-component potential for two-component systems

We performed Monte Carlo simulations on two-component Lennard-Jones systems to mimic a solvent-solute or a solvent-colloid situation. A total of 400 solvent particles were used with the same Lennard-Jones parameters as were used in the one-component calculation. Additionally, 40 particles were added as solutes. These ‘colloid’ particles were larger, with a ratio of $\sigma_c/\sigma_s = 2$. The temperature of the system was 86.3 K, ρ_s was 0.01228 \AA^{-3} and ρ_c was $0.001228 \text{ \AA}^{-3}$. We performed four simulations with different ε_{cs} and ε_{cc} parameters. The parameters are detailed in table 1. The aim of our simulation was to mimic the determination of an effective potential, where we would like to describe the subsystem of large particles by an

Table 1. Simulation details and results of the two-component Lennard-Jones test systems in the study of the derivation of one-component effective potentials.

| System no. | Partial LJ ϵ parameters | | Partition of potential energy (%) | | | Correlation coefficients of the potential energies (see text) | | |
|------------|----------------------------------|-------------------------------|-----------------------------------|----------|----------|---------------------------------------------------------------|-----------|-------|
| | $\epsilon_{cc}/\epsilon_{ss}$ | $\epsilon_{cs}/\epsilon_{ss}$ | E_{cc} | E_{ss} | E_{cs} | PM-binary | IT-binary | PM-IT |
| 1 | 1 | 1 | 3 | 63 | 34 | 0.30 | 0.13 | 0.45 |
| 2 | 5 | 2.24 | 10 | 35 | 55 | 0.48 | 0.30 | 0.73 |
| 3 | 10 | 3.16 | 18 | 24 | 58 | 0.94 | 0.91 | 0.97 |
| 4 | 10 | 1 | 44 | 45 | 11 | 1.00 | 1.00 | 1.00 |

effective interaction among only large particles. This means we used a set of linear equations in which the total energy was \mathbf{e} , but the matrix A consisted of only the large–large pair-correlation function contribution in equation (1).

$$E^{(k)} = E_{cc}^{(k)} + E_{ss}^{(k)} + E_{cs}^{(k)} = E_{\text{eff}(cc)}^{(k)} = \frac{1}{2} \sum_i^{N_r} V \frac{4\pi\rho_c^2}{3} (r_i^3 - r_{i-1}^3) g_{cc}^{(k)}(r_i) v_{\text{eff}(cc)}(r_i). \quad (3)$$

The solution of the over-determined set of linear equations provided effective interactions for the large–large particles in the case of the four systems. Thereafter, we performed one-component Monte Carlo simulations with the new tabulated effective interactions. The resulting pair-correlation functions differed from the original large–large partial pair-correlation functions. We compared the deviations, and we found drastic differences in the case of systems 1 and 2, but there were small differences for the other two cases as well. The deviation can be explained easily, if one checks the approximation of equation (3) and the data about the energy partition in table 1. We supposed in equation (3) that the overall energy changes (including the solvent–solvent and solvent–colloid parts as well) can be described by functions depending only on the pair-distance statistics of the large–large particles. Our calculations showed that this assumption cannot be used, if the dominant part of the overall energy is not the large–large particle interaction in the original systems. One can see in figures 5, 6 and table 1 that an increasing ratio of the large–large potential term means convergence of the structural data between the two-component and the effective one-component simulations. The structure was qualitatively the same, if half of the potential energy belonged to the large–large partial in the two-component system. In the limit where 100% of the potential energy belongs to the large–large interaction, our potential-matching algorithm reduces itself to the one-component case tested and shown previously.

We looked into the theoretical grounds for the unsuccessful results in our potential-matching algorithm for the case of coarse-grained potentials. Our main question was whether there is any effective (coarse-grained) potential that can describe simultaneously the structure of the chosen particles and the energetics for a given system. We could not prove the existence or the non-existence of such a potential theoretically, but we found a theoretical and numerical explanation, given below. It seems to suggest the lack of such a potential.

The inverse theorem of liquids was proved several times and it states the existence of a unique and mutual relationship between the pair-distance statistics and the pair interactions of a system at a given state point. The theorem is valid for any system that is in equilibrium and can be described by pair-wise additive classical mechanical potential functions. It can be extended to higher-order structural and potential functions. In the case of multi-component systems, the relation is valid for the entirety of the system [33]. There are several methods of solving the inverse problem, which means determination of the interaction on the basis of known structural

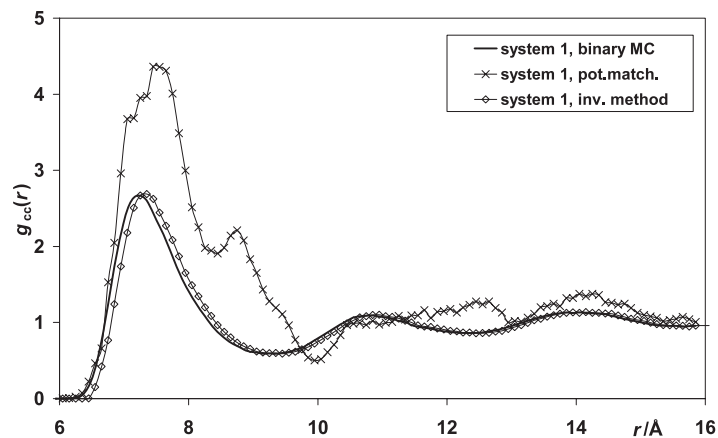


Figure 5. Large-large particle pair-correlation functions from the two-component simulation and the one-component ones with effective potentials determined with the potential matching and inverse algorithms for system 1.

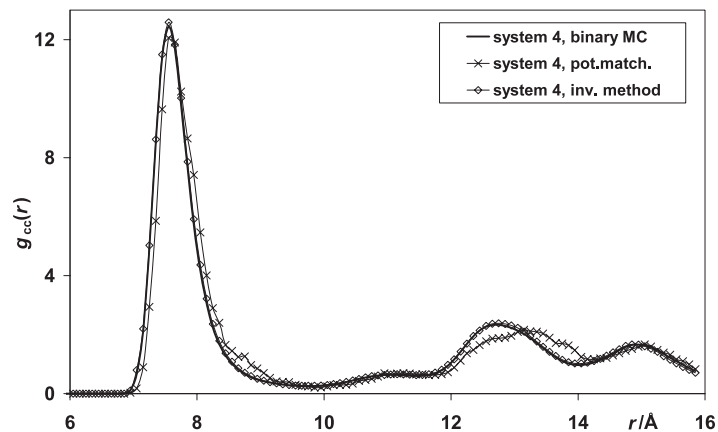


Figure 6. Large-large particle pair-correlation functions from the two-component simulation and the one-component ones with effective potentials determined with the potential matching and inverse algorithms for system 4.

functions, e.g. $g(r)$. Practically, if one knows a $g(r)$, the density and the temperature, they uniquely determine all features of the system. This means that not only can the pair potential be obtained, but also other quantities, such as the potential energy, should be available. In the case of coarse graining, one searches for an effective potential of a one-component system that reproduces correctly some interesting data. In the case of our work, it was the potential energy, while in the case of coarse graining by inverse-techniques [16–25], it is the pair-correlation function. Our negative results showed that the reproduction of the potential of a two-component system with an effective potential of a one-component system did not mean the reproduction of the pair-correlation function of the chosen particles. We were interested in the opposite case as well. Namely, does the reproduction of a partial pair-correlation function of a two-component system with a one-component system effective potential mean the reproduction of the energies?

We applied the iterative scheme of Schommers [28] to find the effective large–large particle potential for the systems in table 1. The method is iterative, with a simulation and a potential modification in each step. The scheme was extended with numerical details: the iterative modification of the potential was controlled by a weight factor and the potential was smoothed in each iteration by the Golay–Savitzky method. We got reasonable fits to the pair-correlation functions after a few tens of iterations in each case. The fitted $g(r)$ s are shown in figures 5 and 6. The difference between the two methods is obvious in these graphs. The next step in our investigation was to compare the potential energies belonging to given configurations. We chose 10 000 configurations obtained by the two-component Monte Carlo simulations. We calculated the potential energies by using the all-atom (binary Lennard-Jones) potentials, the potential determined by our potential-matching (PM) method and the potential obtained by the simulation-assisted solution of the inverse theorem (IT). We calculated the correlation coefficients between the three sets. As can be seen in table 1, there is a very limited correlation between these data for the systems 1 and 2. There is an acceptable correlation for system 3 and a significant correlation for system 4. The coarse-grained potentials obtained by the potential-matching algorithm seemed to perform better than the inverse-theorem-based ones, but they reproduced the energies to be reasonably weaker than was expected. We calculated the correlation between the PM and the IT energies as well. We found higher correlation here than the correlation between the coarse-grained potentials and the original binary system. We think the description of systems 1 and 2 is not possible by pair-wise potentials. To summarize our data, the large–large subsystem of systems 3 and 4 can be described correctly by coarse-grained effective potentials, but we could not find effective potentials for systems 1 and 2 that describe both the structure and the energetics correctly.

What is the theoretical background for the weak performance of both methods on systems 1 and 2? There are two related details in the proofs of the inverse theorem. The theorem is valid for the sum of the interactions and structural data. In the reality, if there is a change in a partial function (e.g. $g_{cc}(r)$), there is also a change in the other partials (e.g. $g_{ss}(r)$ and $g_{cs}(r)$). The change is neglected in the derivation of the coarse-graining processes. This neglected effect is more pronounced if the weight of the chosen particle-pair statistics is smaller, as in the case of systems 1 and 2. The proofs of the inverse theorem use a convex behaviour of the corresponding energy and the structural change of the system. This convex behaviour is not straightforward in multi-component cases, if only one structural change is taken into account and the others are neglected. Furthermore, the slope of this convex behaviour can also be rather small in this case, which may cause the weak performance of our potential-matching algorithm.

4. Conclusions

We have presented a new potential-matching algorithm and some related results obtained during the test calculations. The input data for our method are configurations containing particle positions and the total potential energies of the configurations. The output is a set of tabulated pair potentials. The input data can be obtained by complex, e.g. Car–Parrinello, simulations and the method can be termed as a projection technique of the multi-body interactions onto pair interactions. The main difference between the force-matching method of Izvekhov *et al* and ours is that the input data for our method are simpler and they can be obtained by Monte Carlo simulations as well. We tested our method on a one-component Lennard-Jones system and it provided the correct output.

In the case of the reproduction of a classical mechanical water system simulation, we obtained the correct structure, but we have to emphasize that the potentials obtained were not the same as the original ones used in the production of the input data. This result seems to

be a good example of the possibility of simulating the same structure with two qualitatively different potential sets. This does not mean that the inverse theorem is not valid. It simply shows the insensitivity of the structure to the pair interactions, especially in multi-component cases, in which the total potential energy is distributed differently for the partials in the two distinct models.

Our tests and some supplementary calculations showed numerically that there is an inconsistency between the determination of effective one-component interactions of multi-component systems and the inverse theorem. We think that it is usually not possible to derive an effective one-component (or coarse-grained) pair interaction that reproduces correctly both the structure and the energetics data of the original multi-component system. This means that one should be very careful in the use of coarse-grained interactions. Detailed checking of the interactions and the results is necessary in all cases. We have provided some theoretical explanations for the causes of the inconsistency, and we have shown what kind of conditions should be fulfilled in the systems to get reasonably effective one-component pair interactions.

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