On the theoretical aspects of inverse methods: reverse Monte Carlo simulation or potential determination?

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Abstract

We studied and evaluated the two simulation-assisted inverse methods: potential determination and the reverse Monte Carlo method. First, we proved that one step of the iterative scheme of Lyubartsev and Laaksonen corresponds to a perturbative potential determination of a dilute gas. Second, we performed reverse molecular dynamics simulations to study the dynamics of the system governed by the formal potential of χ^2, the acceptance-criterion function in the stochastic scheme. We found that the dynamics is unrealistic. These results indicate the need for caution when one attempts to calculate dynamical properties with reverse Monte Carlo-like methods.

1. Introduction

Determination of pair interactions based on the measured pair-distance statistics by diffraction methods is referred to as the 'inverse problem' of liquid state physics [1]. Since the cautious invention of reverse Monte Carlo (RMC) [2] and related methods, there are two simulation-assisted ways to solve the inverse problem. The approaches have the same, as a matter of fact, rather loose theoretical basis [1, 3–5]. As for the actual simulation work, however, they differ substantially. The RMC method provides three-dimensional arrangements of particle-centres in a Monte Carlo procedure, where the input is the experimental structural function. In the basic technique no interaction potential or dynamical information is used. Iterative potential-determination methods [6–16] usually start from an approximation of the pair interaction, and the potential is modified during subsequent classical mechanical simulations as long as the measured structural function is reproduced satisfactorily. We do not focus in this paper on direct methods, where the interaction potential is determined on the basis of applications of integral equation theories. In these approaches, no classical mechanical simulations are performed and the interaction potential is obtained solely by using the experimental data [17, 18].

In the following we discuss some aspects of the simulation-assisted methods based on recent numerical and theoretical works as a continuation of our previous studies [5, 19–22]. Emphasis will be on critical evaluation of a recent idea of dynamical reverse methods [23].

2. Some remarks on potential determination

There have been numerous attempts to develop a workable numerical technique to calculate interaction functions acting between particles of disordered systems [5–18, 22, 24]. As a result of theoretical reasoning, these methods are limited to determine only *effective* (typically radial-symmetric) pair potentials, i.e. pair interactions also containing many-body effects. Clearly, these potentials will be approximate in character. For some systems, where angle-dependent or many-body forces are important, they can be very inaccurate [25, 26]. However, in the case of properly approximated effective pair interactions, all further information on the system can be calculated, including dynamical information [1, 3–5].

The iterative simulation-assisted methods differ mostly in their input experimental functions (partial or total and real or inverse space functions) and in the way of modifying the potential after every iterative step of the simulation. One of the most recent of these methods was suggested by one of the authors [14, 15]. This method is the generalization of the ideas suggested by Lyubartsev and Laaksonen [10]. In the following we show that one iterative step of their derivation [10] corresponds to a perturbative potential determination of a dilute gas.

Let $g'(r)$ be the measured and tabulated pair correlation and $g(r)$ the calculated one of a simple, one-component fluid. (Lyubartsev and Laaksonen [10] provides a more general scheme but the essence is the same.) If we can express the potential energy as $\Phi(r^N) = \sum_i p_i g(r)$, then

$$\Delta \langle g(r) \rangle \equiv g'(r) - \langle g(r) \rangle = \sum_i \frac{\partial \langle g(r) \rangle}{\partial p_i} \Delta p_i + o(\Delta p^2), \tag{1}$$

where p_i is a parameter and the $\langle\ \rangle$ symbol marks the average of instantaneous $g(r)$ functions. Equation (1) is a linear approximation of the difference between the target and the calculated $g(r)$s. The aim is to diminish the difference by systematic iterative change of parameter values. The derivatives can be given as follows:

$$\frac{\partial \langle g(r) \rangle}{\partial p_j} = \frac{\partial}{\partial p_j} \left[\frac{\int d\mathbf{r}^N g(r) \exp\{-\beta \sum_i p_i g(r)\}}{\int d\mathbf{r}^N \exp\{-\beta \sum_i p_i g(r)\}} \right] = -\beta \left[\langle g(r)^2 \rangle - \langle g(r) \rangle^2 \right]. \tag{2}$$

Let $f'(r)$ and $f(r)$ be the pair potentials with the correct and the approximate parameter values, respectively. Using the previous two equations we obtain

$$g'(r) - \langle g(r) \rangle = -\beta \left[\langle g^2(r) \rangle - \langle g(r) \rangle^2 \right] \rho 4\pi r^2 \, dr (f'(r) - f(r)), \tag{3}$$

where $\rho = N/V$ is the number density. Invoking our previous result about the fluctuation of the pair-correlation function [27]

$$\left[\langle g^2(r) \rangle - \langle g(r) \rangle^2 \right] = \frac{\langle g(r) \rangle}{\rho 4\pi r^2 \, dr}. \tag{4}$$
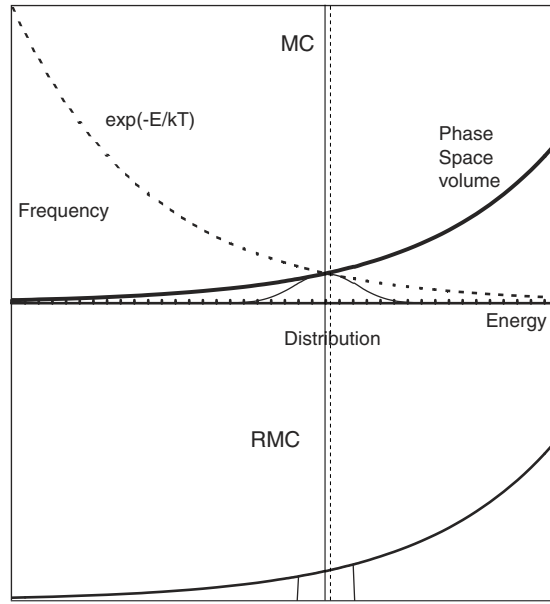
Comparing (3) and (4) we get

$$1 - \frac{g'(t)}{\langle g(t) \rangle} = \beta (f'(r) - f(r)). \tag{5}$$

Equation (5) is an expanded version of

$$\frac{g'(t)}{\langle g(r) \rangle} = \exp[-\beta (f'(r) - f(r))] \tag{6}$$

which describes the connection between the correlation functions and pair interactions of two dilute gases.

Figure 1. Schematic comparison of the phase-space sampling of the Metropolis Monte Carlo and the reverse Monte Carlo methods. The solid vertical line denotes the average energy of the Metropolis Monte Carlo sampling and the dashed line denotes the same one for the reverse Monte Carlo sampling.

Instead of the experimental partial $g(r)$ used by Lyubartsev and Laaksonen the method of Tóth uses exclusively the structure factor. Instead of equation (3) he suggests [14]

$$\frac{\partial \langle S \rangle}{\partial p_i} = \frac{\partial}{\partial p_i} \left[\frac{\int d\mathbf{r}^N S(\mathbf{r}) \exp(-\beta \Phi(\mathbf{r}^N))}{\int d\mathbf{r}^N \exp(-\beta \Phi(\mathbf{r}^N))} \right] = -\beta \left[\left\langle S \frac{\partial \Phi}{\partial p_i} \right\rangle - \langle S \rangle \left\langle \frac{\partial \Phi}{\partial p_i} \right\rangle \right]. \tag{7}$$

This approach works well for simple systems [14, 15].

In addition to this, we mention only one more development in this area. This method is the most popular nowadays, and is the work of Soper [12] which was elaborated on the basis of the method of Schommers [6, 8]. In addition to the iterative process of modifying the interaction potential, the simulation data and the experimental data are mixed together in the separation of partial functions. As for other studies the reader should turn to the literature [6–16].

3. The χ^2 potential of the RMC method

The reverse Monte Carlo method was introduced 15 years ago [2]. Due to the simplicity of the code, RMC became popular quickly and numerous applications of the method can be found in the literature [28, 29]. Recently, we studied the RMC method from the aspects of statistical mechanics and simulation methodology in general [5, 22]. We will not reiterate the main results of this study, but rather we present a qualitative figure which compares the normal or Metropolis Monte Carlo (MMC) method to RMC.

The upper half of figure 1 depicts the essence of the MMC method. The volume of phase space increases quickly in terms of its energy because it is bounded from below. (Configuration with the lowest energy can be determined for each model given the interaction potential and the density.) However, exponential decrease of the Boltzmann-factor does not allow high energy configurations. It is the temperature which for a given density and set of interaction

functions determines the expectation value of the energy where these two opposing effects get in equilibrium. The distribution of energy follows a Gauss-curve around its expectation value.

The case of the RMC is depicted on the lower half. It does not have Boltzmann-factor determined by energy differences and temperature. The latter is replaced by an adjustable parameter controlling the tightness of the fit. The sampling is hindered both from the low and the high energy parts. Since the number of configurations with higher energies is much larger than that of configurations with lower energies, the distribution of the volume of the collected phase-space is asymmetric and not Gaussian. The average energy of the collected phase-space points is higher than that one of the MMC method [5, 20, 22]. For a given case the average energy of the RMC is denoted with a dashed line. If one would like to increase the symmetry of the low and high energy phase space volumes, which in turn ensures the correct energy, the distribution becomes much narrower than the corresponding MMC Gaussian. (To avoid confusion we mention that these calculations were carried out for the model of liquid argon where properties of MMC and RMC calculations were directly comparable [5, 20, 22].) A previous attempt to improve the shape of this distribution by using the two-particle entropy brought only limited success [22, 30].

In the present paper we use a different approach to characterize the RMC. This study was motivated by recent arguments about the theoretical superiority of RMC to iterative potential determination [23]. The possibility of the dynamic version of the method also drew some attention [30].

The interesting point in this argument [23] is that the RMC is superior to potential determination because the potentials are effective pair potentials, while the RMC simulation does not assume any potential, therefore, with additional information, it is capable of modelling systems not describable by pair-wise additive effective potentials. However, formally χ^2 can be considered as the *potential* of the method. Clearly, it is a strange potential because, contrary to the usual potential energy of simulations, it cannot be separated into additive terms each depending only on one pair distance. If structure factors are used as experimental functions, the non-additive terms are caused by the power of square applied in the calculation of χ^2. The potential can be extended by involving further information from measurements. The extra terms can serve as additional criteria of acceptance of random particle moves. There is, however, no reason to believe why such extra information cannot be incorporated into iterative potential-determination schemes or into any other classical mechanical simulations.

The application of additional information so far came from trivial chemical evidence like hard-sphere repulsion, number of neighbours, etc [28, 29]. In the case of the RMC it is very hard to verify the statistical mechanical correctness of these constraints. For example, if one fixes the average number of first neighbours, there is no guarantee that the fluctuation or distribution of the first neighbour-shell will be a reasonable representation of that of the real system. Ad hoc additional simulation criteria of that kind, in most of the cases, possess a certain amount of arbitrariness difficult to assess theoretically.

An additional danger of extending χ^2 might come from the improper construction of the combined potential [23, 28, 29, 32]. The extra term must be complementary and consistent with the original one. By complementary we mean the need for *extra* structural information, which cannot interfere destructively with the original one, i.e. it must also be consistent. The addition of dynamical information is not an easy task, because these quantities cannot be calculated on a single configuration, but over many configurations of a real-time period.

4. Dynamics of the χ^2 potential

Construction of a dynamical trajectory on the basis of random Monte Carlo steps cannot be done because the error is larger than that caused by the lack of the correct timescale. The main

reason is the collective feature of the moves. For example, a Monte Carlo move tends to put a particle in a local minimum of the potential energy, while in real dynamics this minimum often vanishes before the particle can reach it. Therefore, dynamics can only be investigated with dynamical methods.

In a previous paper we suggested a molecular dynamics version for RMC [31]. The algorithm is straightforward if one handles χ^2 as a real potential. The derived forces provide a collective dynamics. Every imaginable constraint or extra structural information on the RMC can be included in this reverse molecular dynamics (RMD) code.

Since χ^2 is an unusual potential function, dynamics of the system will also be unusual. However, we have a certain amount of flexibility in terms of scaling, incorporating constraints and thermostatting in order to be as close to the realistic dynamics as possible. We applied the following procedure to test how close we can get to this.

A traditional molecular dynamics simulation was performed containing 1728 Lennard-Jones particles in a cubic cell. The parameters were set to mimic a system of liquid argon: $\sigma = 3.405$ Å and $\varepsilon = 120/k$, where k is the Boltzmann-constant. The temperature of the system was $T = 86.3$ K, the number density was 0.022 Å^{-3} and an isokinetic thermostat [33] was applied in the canonical ensemble with an integration time step of 10^{-15} s. The static structure factor, the velocity autocorrelation function (VACF) and the spectral density of the latter were calculated in the simulation.

Thereafter we started RMD simulations with identical conditions, and the structure factor of the traditional molecular dynamics simulation was used as 'experimental' data. The x direction of total force of the χ^2 potential acting on a particle was calculated according to [24]

$$F_{xj} = -c \sum_i^{nq} \frac{1}{q_i} \left(S^{\mathrm{sim}}(q_i) - S^{\mathrm{exp}}(q_i) \right) \sum_{\substack{k \\ k \neq j}}^n \frac{x_{jk}}{r_{jk}} \left(\frac{q_i \cos(q_i r_{jk})}{r_{jk}} - \frac{\sin(q_i r_{jk})}{r_{jk}^2} \right),$$ (8)

where nq is the number of the inverse space points, q_i, n is the number of particles, r_{jk} is the distance of particle j and k, and x_{jk} is the same for the x direction. The similar equations are used for y and z directions.

We performed several set of simulations with different c constants of equation (8), with different hard core diameters as auxiliary constraints and at different temperatures. In addition to the structural functions (the pair-correlation function and the structure factor) we calculated the velocity autocorrelation functions, their spectral densities, and the average force exerted by a particle at a distance r from the particle in question.

The variation of the force scaling constant, c, changed the dynamics drastically. As we concluded in the paper about the RMD method [31], large c values were necessary to achieve good reproduction of experimental $S(q)$ functions. The corresponding $g(r)$s are shown in figure 2. The RMD simulations with small c (1000–5000, if the force were in the units of 10^{11} N mol^{-1}) show the VACF of a simple liquid, but with longer decay than the VACF of the traditional molecular dynamics simulation (figure 3). If $c = 7500$, the minimum and the decay of the traditional MD and the RMD VACFs are similar, but oscillations appear in the RMD curve. Further increasing of c enhances the oscillations and also the minimum and the decay of the curve is shifted. This behaviour can be easily seen in the spectral densities of VACFs of figure 4. The maxima of the spectra shift to smaller frequencies and high frequency peak(s) appears with increasing c.

The average force, $F(r)$, shows crude oscillations at small c values. Surprisingly, the absolute value of the average force of the $c = 1000$ simulations produces the same magnitude as for $c = 20\,000$. In the case of a traditional force field, we should get a ratio of $1/20 = 1000/20\,000$. We think the reason for this is that at high c χ^2 is small and the system is
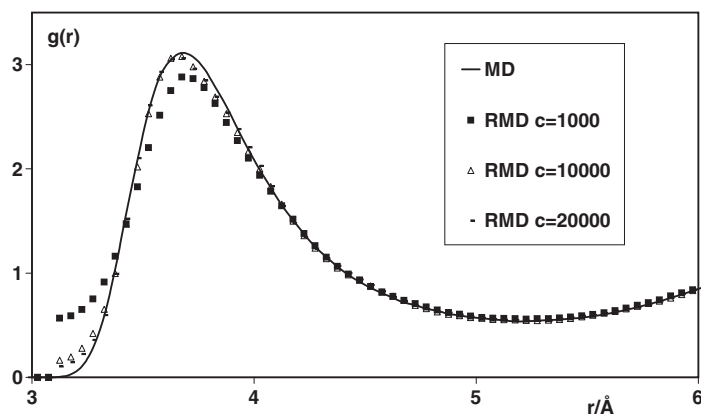
Figure 2. Comparison of the first peak of the pair-correlation function of the MD results and the RMD simulations with different c constants. Note that not the pair-correlation function, but the structure factor was the target experimental data in all RMD simulations.
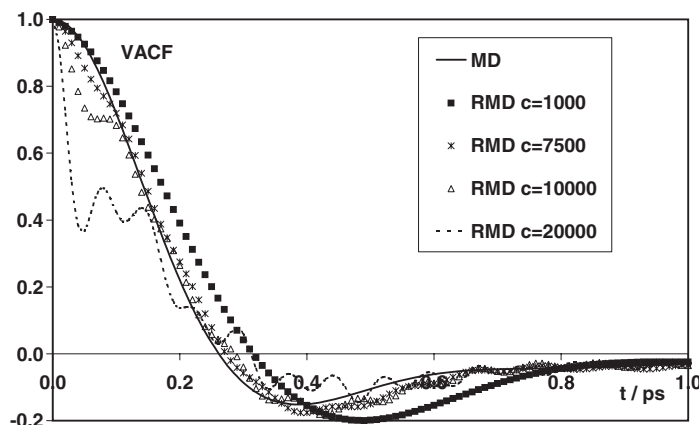
Figure 3. Comparison of the normalized velocity autocorrelation function of the MD results and the RMD simulations with different c constants.

in a local minimum, where most of the neighbouring configurations have also similarly small χ^2s. An additional feature of figure 5 is that minima and maxima of the $F(r)$ functions for different cs are shifted relative to one another. Thus, while the use of large c is necessary for good reproduction of the static structure (see the explanation of figure 1 earlier in this paper), in terms of dynamics application, large cs creates artificial and false behaviour.

We could not find clear trends in these functions if the hard core diameter of the particles was varied. It was rather accidental; the best reproduction of the dynamical functions of hard core diameter seldom coincided with the best reproduction of the pair-correlation function.

The slowing down or acceleration of the particle motions by varying the temperature of the system (switching the temperature to lower or higher values than that of the reference MD) caused similar effects as the increase or decrease of c, the force multiplier.

5. Conclusion

The aim of the present study was to investigate and discuss some recent trends in the application of RMC. We are convinced that RMC is very useful and can be used until better methods are
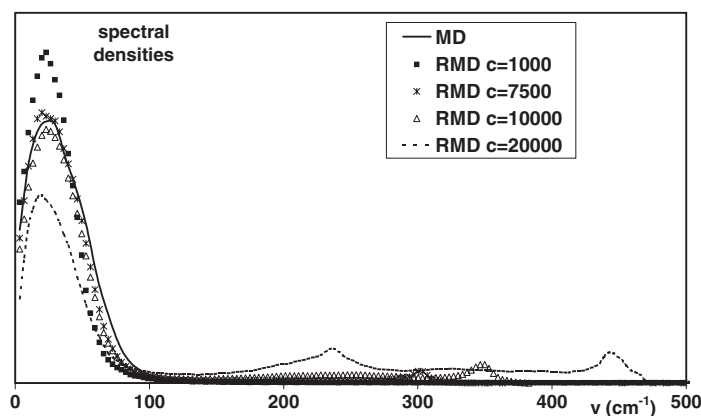
Figure 4. Comparison of the spectral densities of the velocity autocorrelation function of the MD results and the RMD simulations with different c constants. The spectral densities are in arbitrary units.
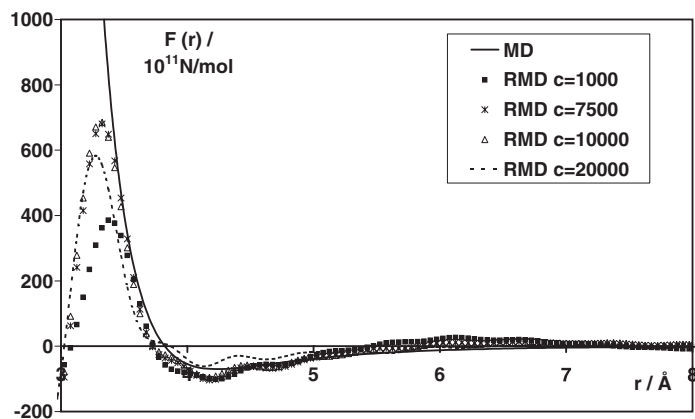
Figure 5. Comparison of the average pair forces of the MD and the RMD simulations with different c constants.

available. On the other hand, as has been pointed out several times [5, 20–22], the RMC is a *minimization procedure* and must not be confused with classical mechanical simulations. Clearly, the χ^2 criterion can be considered as a potential. However, this potential is strange and unable to produce correct dynamics and structural properties simultaneously. Extension of the χ^2 criterion might get the RMC method closer to a 'reverse' Metropolis Monte Carlo simulation but the same is valid for simulation-assisted potential determination as well. We believe that the RMC cannot be contrasted with the methods of simulation-assisted iterative potential determinations as a superior approach because of the lack of an approximated therefore inaccurate potential. This idea is based on the assumption that the RMC is unique in the flexibility of incorporating constraints and in the variety of fitted experimental data. There are some encouraging trials of potential determination methods where one can use at least as many constraints and experimental data as the RMC. For example, the form of the interaction potentials is already a constraint in the method of Soper [11, 12], or there is a method where theoretically all quantities can be incorporated that can be calculated from a single configuration [14, 15].

Our results provide no encouragement to use the RMC to calculate or even visualize some kind of motion. The dynamics based on the χ^2 potential is rather different from the real dynamics. In this respect the collective motion of particles of RMD is no help, because the problem lies in the form of the χ^2 potential.

The inverse theorem connects the structure factor to the effective pair potential. Unfortunately, the theorem does not say how to derive the effective pair potential from the measured structural functions and what the effect of the error of the experiments is. We think when the simulation-assisted iterative (and direct) potential determination methods are able to treat the errors and incompleteness of the measurements, and they are robust on the variety of experimental data and also on the computation, they will be able to provide the correct dynamics and can be more useful than the RMC-like methods.

Acknowledgments

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