RMCt: Development of models for atomic-scale dynamics
A summary of O Gereben et al (2007) *J. Phys.: Condens. Matter* **19** *335223*

Rasmus Tang Christiansen
University of Copenhagen
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INTRODUCTION

The goal in condensed matter science is to determine the properties of materials and their underlying atomic-scale structure and dynamics responsible for these properties. Atomic-scale modelling can be cumbersome, especially when it comes to non-crystalline or disordered structures, since such models often have many parameters and the materials are difficult to probe with conventional methods.

The summarized article [1] describes the time-dependent Reverse Monte Carlo (RMCt) method, a non-parametric method for modelling the dynamics of materials from inelastic neutron scattering experiments. The method is an evolution of the traditional Reverse Monte Carlo (RMC) method, originally developed by McGreevy and Pusztai [2].

OVERVIEW OF RMC

Before I begin my summary it is necessary to be familiar with the basics of RMC.

At it's core RMC is a conceptually simple method. It is a variation of the standard Metropolis-Hastings Monte Carlo algorithm and it is a non-parametric method for structural modelling of materials from experimental data (e.g. neutron or x-ray diffraction) [3].

The only requirement is some experimental data which depends on the atomic structure (e.g. the radial distribution function [4]) and a theoretical method for calculating the measured quantity given a model for the structure.

To initialize the RMC fitting, one creates an ensemble of N atoms with periodic boundary conditions within a volume V. The ensemble can be of any shape, but the size should be such that the density ρ (which is determined from V and N) matches ρ of the material in question. The ensemble is called the *configuration*. Afterwards the basic steps of RMC are as follows [3]:

1. Pick a random atom in the configuration and move it a random distance in a random direction

2. Calculate all distances between atoms, which yields a distance distribution

3. From the distance distribution, calculate the measured quantity and from that the χ^2 test statistic, given the current configuration and the experimental data

4. Accept the random movement of the atom if the χ^2 decreases. If it increases, accept the random movement with a probability proportional to the inverse increment of the χ^2

5. Repeat steps 1 through 4 until the χ^2 is minimized

Et voilá! The final configuration is now the structural model with the best fit to the experimental data.

One should note that one can fit to several different experimental data sets simultaneously during step 3. This means that for n_{exp} independent data sets the χ^2 becomes a sum of different contributions:

$$\chi_{tot}^2 = \sum_{i=1}^{n_{exp}} \chi_i^2 = \sum_{i=1}^{n_{exp}} \sum_{j=1}^{n_{data,i}} \frac{(A_{i,j}^{RMCt} - A_{i,j}^E)^2}{\sigma_{i,j}^2} \qquad (0.1)$$

where the i sum runs over all data sets and the j sum runs over all data points in each data set. $A_{i,j}^E$ is the j'th measured quantity in experiment i and $A_{i,j}^{RMCt}$ is the corresponding quantity calculated form the RMC. $\sigma_{i,j}$ is the uncertainty on the j'th measured quantity in experiment i and is often taken to be constant within experiments (thus $\sigma_{i,j} = \sigma_i$)

RMCt

Now for the actual summary.

The goal for RMCt is to extend RMC to also model atomic-scale dynamics (in addition to modelling structural properties). Such a model allows us to calculate dynamic structure factors which then can be compared to dynamical data (e.g. from inelastic neutron scattering).

In RMCt the model consists not only of a single configuration like in RMC, but of a series of configurations divided by a user-determined time difference (Δt). The steps are essentially the same as presented for RMC, except you pick a random configuration from the time series in step 1 before you pick a random atom.

This modification of step 1 also requires a slight modification of step 2 since a simple distance distribution is no longer sufficient. In addition to all distances between atoms within each configuration, one also needs to calculate all distances between atoms in all different configurations. This means that a time dimension is added to the distance distribution, which now depends on both space and time.
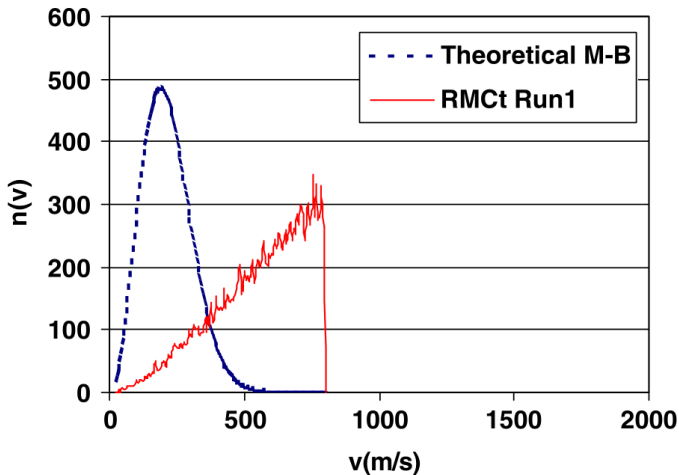
FIG. 1: Theoretical MB (blue) and RMCt (red) average velocity distribution for liquid Ar at 86.3 K. Figure taken from [1].

However, this raises a statistical issue. Imagine e.g. a time series with M=51 configurations each separated by the time Δt (resulting in $t_{tot} = 50\Delta t$). Such a time series will give 50 data points (in the space- and time-dependent distance distribution) for a time scale of $\tau = \Delta t$ but only a single data point for the time scale $\tau = 50\Delta t$, resulting in poor statistics at large time scales.

To mitigate this, The author implemented calculations windows in the RMCt algorithm. That is, for any atom in each configuration, the algorithm only calculates the distances to atoms in configurations up a time $t_W = W\Delta t$ ahead in time ($0 < W \leq M$, $W \in \mathbb{N}$).

This means that only dynamics up to the time scale of $t_W \leq t_{tot}$ is probed by the RMCt, but one gets a sufficient amount of statistics for each data point.

AN EXAMPLE

In [1] the use of RMCt is exemplified on quasi-experimental data obtained from a Molecular Dynamics (MD) simulation of liquid Ar at 86.3 K. The initial conditions (IC) for the RMCt is obtained from a similar MD simulation at 120 K.

The quasi-experimental data has an average velocity distribution (VD) similar to the theoretical Maxwell-Boltzmann (MB) distribution, which allows the MB distribution to act as an experimental data set to which we fit the atomic-scale dynamics. However, from Figure 1 ([1]) it quickly becomes clear that the RMCt fit has not converged as the algorithm does not produce a VD that matches the MB distribution. This is an artefact of the RMCt method; the 'experimental data' simply does not contain enough information about the short-range-short-time dynamics to fit the VD.

To address this issue the author applies constraints to the RMCt fit. This limits parameter space and results in faster converging. The constraint is implemented by biasing the contribution to the χ^2 from the VD fit. The bias is added as:

$$\chi^2_{VD} = \frac{1}{\sigma^2_{VD}} \sum_j (V_j^C - V_j^{MB})^2 w_j(v) \qquad (0.2)$$

where σ_{VD} is the weighting factor of the constraint, $w_j(v)$ is the velocity-dependent bias and V_j^C and V_j^{MB} is the calculated and theoretical velocity distribution, respectively. The weighting factor is defined as:

$$w_j(v) = \begin{cases} \exp\left(\frac{v_j}{\sigma^{exp}}\right) & \text{if } \sigma^{exp} > 0 \\ 1 & \text{if } \sigma^{exp} \leq 0 \end{cases}$$

The author also applied other constraints to the example with which I will not go into detail.

CONCLUSION AND OUTLOOK

The author have developed a RMCt method to model atomic dynamics of material based on experimental data.

From Figures 7 through 9 in [1] we see that the author succeeded in fitting th RMCt model to the dynamical pair correlation $g(r,t)$ function as well as both static $S(Q)$ and dynamical $S(Q,\omega)$ structure factor and has thereby developed a tool for non-parametric modelling of atomic-scale dynamics. Converging issues were addressed by applying constraints via biasing the underlying calculations of the χ^2.

However, due to lack of the information in the experimental data, a parameter governing the constraint of the velocity distribution had to be added to the model. Furthermore, a concession to low statistics had to be made which limited the amount of configurations used by the simulation. This concession was also a parameter set by the user of the method.

In general, this encapsulates the general problem of RMCt (and RMC) quite well. An intrinsic property of RMCt is that it samples a space of all models consistent with some limited amount of data, which leads to a lack of uniqueness [4]. Indepedent *a priori* knowledge of the system can help limit this problem.

Despite it's issues, RMCt (and RMC) remains an invaluable method for atomic-scale modelling in condensed matter sciences.

[1] O Gereben et al, 2007, *J. Phys.: Condens. Matter 19 335223*

[2] R L McGreevy and L Pusztai, 1988, *Mol. Simul. 1 359*

[3] R L McGreevy, 2001, *J. Phys.: Condens. Matter 13 R877*

[4] P Biswas et al, 2004, *Phys. Rev. B 69, 195207*