Fitting molecular dynamic potentials to inelastic neutron data

# Abstract

# Introduction

The MDMC method aims to compare molecular dynamics (MD) models against dynamic and static experimental data and finding MD models that fits such data best in a fast and efficient way. The best fit MD model can then be run separately to produce movies of how the atoms moves and to understand dynamical and static properties of materials. An important part of this process involves the fitting of MD potential energy parameters against S(Q, ω) data. MDMC stands for Molecular Dynamics Monte Carlo (Robert let me know if you can think of a better name).

Argon is a model material for which there is a high quality S(Q, ω) dataset available.

Reference to Gereben/Pusztai/McGreevy -> RMC and S(Q, ω).

Reference to Alan Soper work -> fit of potential shape to S(Q) data using MC.

# MDMC

## Method

The MDMC method follows the following steps

1. Specify starting values for the parameters that make up the potential energy (PE) function for the Molecular Dynamics (MD) part of the algorithm. Run initial MD simulation. Then calculate Sfit(Q, ω) from this initial run and the Figure of Merit (FOM) function that measures the discrepancy between Sfit(Q, ω) and the observed dynamical structure factor data: Sdata(Q, ω)
2. Store the initial FOM value and MD phasespace configuration
3. Select new values for the PE parameters by randomly modifying the previous PE parameters
4. Run MD, calculate Sfit(Q, ω) and FOM
5. Use the Metropolis criterion to accept or reject the new FOM and therefore the PE parameter set used to calculate this FOM; accept the new PE parameters with probability: , where the Monte Carlo (MC) 'temperature' parameter TMC controls the acceptance rate. Further, if this MC step (or MDMC cycle) is accepted overwrite the previously stored FOM value and phasespace configuration with the new FOM value and phasespace configuration.
6. Return to 3 until convergence has been achieved or maximum number of iterations reached.

In this work, the shape of an MD potential is adjusted against dynamical structure factor S(Q, ω) data. Such data can be collected at large scale neutron facilities. S(**Q**, ω) is related to the time-dependent pair distribution function G(**r**,t) through the Fourier transform

Eq. (Sqomega)

Ignoring Quantum effects then in the classical limit G(**r**,t) for a mono-particle sample is

Eq. (Grt)

Where <…> denotes the thermal average and this function gives information about how N particles move with respect to themselves and each other. The thermal average is calculated by averaging over statistical independent (or nearly independent) G(**r**,t) instances (typically 20 in this work). In this work G(**r**,t) instances were calculated from MD runs using the approach described in Ref. [Rapaport].

To compare with neutron data the summation in Eq. (grt) is split up into a self-part and distinct-part. The self-part is

Eq. (GSrt)

which describes the correlation of one particle with itself, i.e. single particle motion and the distinct-part is the difference Gd=G-Gs. The neutron partial differential cross section is proportional to , where Ss is the Fourier transform of Gs and σinc and σcoh are the incoherent and coherent cross sections respectively. For more details on this see, for instance, Gereben et al., 2007 and references therein. Note that for Argon the incoherent cross section can be neglected in which case the neutron cross section is simply proportional to S(**Q**, ω).

FOM is in this work calculated using the least squared expression:

The summation is over the observed data points.

## Calculation details

* MDMC may be run in 'semi' non-equilibrium
* MDMC may initially be run with a reduced box size

## Initial results

Results from the MDMC algorithm is demonstrated by fitting the Lennard-Jones (LJ) potential energy parameters against liquid Argon S(Q, ω) data, collected at T=120K and ρ=0.0176Å-3, see Figure (AgCompare)(a) (van Well et al., 1985). A simulation was executed where the and LJ parameters were varied and a box containing 864 atoms was used. The initial values were set to ε=1.5K/mol and σ=4.0Å and this system settles down to the finite temperature crystalline phase shown in Figure (AgCompare)(b), this was the initial starting point of the MDMC simulation. The MDMC is then continued, where the two LJ parameters are both modified by a value picked randomly within the interval [-0.1;0.1] before each MD run and this is repeated for a total of 400 cycles or MC steps. The values of the LJ parameter that produced the best fit to the Argon data were ε≈1.020K/mol and σ≈3.362Å and Figures (AgCompare)(c-d) show Sfit and Gd plots of this liquid. In Figures (AgCompare)(e-g) observed and calculated data are compared and it is seen that very good agreement is obtained for this MDMC simulation.

The progress of this MDMC simulation as a function of MC step is shown in Figure (fomCombined), where the crosses and circles plot the FOM value, on a log scale, for the accepted and rejected MC steps respectively. Within the first 20 MC steps the FOM value drops very sharply transforming the system from a crystalline to a liquid state and the system thereafter settles in this liquid state. After the first 200 MC steps the TMC parameter was reduced from TMC=1 to TMC=0.25. This reduced the percentage of acceptance steps from about 32% to 18% but no significant change in the liquid state is observed.

The crosses in Figure (sigma-epsilon) show the values of σ and ε for the all the accepted MC steps starting from the 15th accepted MC step, and the horizontal and vertical dashed line the published values for ε=1.0243K/mol and σ=3.36Å for this liquid (van Well et al., 1985). Figure (diffusion Ag) shows the values of the diffusion constant for the accepted MC steps. After about 20 MC steps the system settle in the liquid phase with a calculated diffusion constant fluctuating around a value close to the published diffusion constant value for this system: D=0.68 10-8 m2s-1 (van Well et al., 1985).

# Discussions

Could as well use S(Q) or a combination of S(Q) and S(Q,omega) data.

Could use constraints or restraints such as the diffusion constant.

# Conclusions

# Acknowledgements

Many thanks goes to Keith Refson for advising on how to get started with writing the molecular dynamics module.

# References

D. C. Rapaport, “The Art of Molecular Dynamics Simulation”, 2nd ed., Cambridge University Press 2004.

A. A. van Well, P. Verkerk, L. A. de Graaf, J.-B. Suck and J. R. D. Copley, Phys. Rev. A31, 3391 (1985)

O. Gereben, L. Pusztai and R. L. McGreevy, J. Phys.: Condens. Matter 19, 335223 (2007)

# Captions

Figure (AgCompare): (a) Shows the T=120K, ρ=0.0176Å-3 Argon S(Q, ω) data from Ref. [vanWell] multiplied by . This multiplication is performed to ‘un-symmetrise’ the symmetrised S(Q, ω) data in Ref. [vanWell], see Eq. [5] in that work. (b) shows the distinct part of the pair-distribution function at the start MDMC simulation described in the text. (c-d) show plots of Sfit and Gd for the best best fit obtained from the MDMC simulation described in the text and (e) the difference between S(Q, ω) in (a) and (c). The solid line in (f) shows and the dashed line . Units used for the figure axes are: t [10-13 s]; [1013 s-1]; r [10^-10 m]; Q [1010 m-1].

Figure (fomCombined): Shows the FOM value, on a log scale, for accepted (crosses) and rejected (circles) MC steps. During the first 200 MC steps TMC=1. The MDMC simulation is then continued, after the first 200 MC steps, using as a starting point the LJ parameters with the lowest FOM value during the first 200 MC steps and with TMC reduced by a factor of four.

Figure (EpsilonSigma): Plots the values, as crosses, of the LJ parameters for the accepted MC steps after settling in the liquid state. The '+' at right hand corner shows the values of the LJ parameters at the start of the MDMC simulation. Also, to compare with the published LJ values for this system, the horizontal and vertical dashed line show the published LJ values: ε=1.0243K/mol and σ=3.36Å respectively (van Well et al., 1985).

Figure (diffuse): Shows the value of the calculated diffusion constant in units of [10-8 m2s-1] for all accepted MC steps. The horizontal solid line plots the published value for the diffusion constant: D=0.68 10-8 m2s-1 (van Well et al., 1985).

Figure (AgCompare)

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Figure (epsilonSigma)

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Figure (fomCombined)

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Figure (diffuse)

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