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Establishing Uniform Acceptance in Force Biased Monte Carlo Simulations

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ABSTRACT: Uniform acceptance force biased Monte Carlo (UFMC) simulations have previously been shown to be a powerful tool to simulate atomic scale processes, enabling one to follow the dynamical path during the simulation. In this contribution, we present a simple proof to demonstrate that this uniform acceptance still complies with the condition of detailed balance, on the condition that the characteristic parameter $\lambda = 1/2$ and that the maximum allowed step size is chosen to be sufficiently small. Furthermore, the relation to Metropolis Monte Carlo (MMC) is also established, and it is shown that UFMC reduces to MMC by choosing the characteristic parameter $\lambda = 0$ [Rao, M. et al. *Mol. Phys.* **1979**, *37*, 1773]. Finally, a simple example compares the UFMC and MMC methods.

INTRODUCTION

The molecular dynamics simulation technique is a powerful tool used to investigate atomic scale processes happening on a time scale on the order of nano- to microseconds. Especially attractive is the fact that the full dynamical path of the system can be traced through space and time. MD simulations therefore are an excellent tool used to study processes such as particles impacting on surfaces, sputtering and etching, thin film growth, folding of proteins, chemical reactions, etc.[1,2]

However, many processes are taking place on time scales beyond the reach of pure MD simulations.[1] While various techniques have been developed through the years, these are typically most suitable for solid-state problems, such as adatom diffusion. These techniques are typically based on the concept of an "infrequent event system".[3] In such an infrequent event system, it is assumed that when the system is in a particular energy basin, it has no memory of how it got there. This essentially precludes the occurrence of correlated events (although in some cases these can be compensated for).

Nevertheless, it would be useful to have a method available that accelerates the observed processes but at the same time is not limited to an infrequent event system. One possible candidate is force biased Monte Carlo (fbMC).[4,5] fbMC is a little used method, which nevertheless shows great potential. Processes such as surface diffusion, phase transitions and carbon nanotube growth have successfully been modeled by fbMC or a hybrid MD/fbMC approach.[6−9] The method was originally conceived in the 1970s.[5] In this original version, fbMC made use of an acceptance criterion in order to satisfy detailed balance. However, fbMC can be turned into a uniform acceptance method ("uniform acceptance force biased Monte Carlo, UFMC"), i.e., in which each Monte Carlo step is accepted with unit probability,[6,10] while still complying with detailed balance, provided that the maximum allowed displacement is chosen to be sufficiently small. Here, we present, for the first time, the theoretical foundation for this uniform acceptance.

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The condition of detailed balance can be written as

$$W(\mathbf{r}'|\mathbf{r})\,P(\mathbf{r}) = W(\mathbf{r}|\mathbf{r}')\,P(\mathbf{r}') \tag{1}$$

Here, $W = W(\mathbf{r}'|\mathbf{r})$ and $W' = W(\mathbf{r}|\mathbf{r}')$ is the transition probability distribution for a particle to be displaced in configuration space from $\mathbf{r}$ to $\mathbf{r}'$ and from $\mathbf{r}'$ to $\mathbf{r}$, respectively, and $P(\mathbf{r})$ is the probability of the particle to be located at position $\mathbf{r}$. This is a correct expression for whichever distribution we choose. If we choose the Boltzmann distribution for $P(\mathbf{r}')$, the expression becomes

$$W(\mathbf{r}'|\mathbf{r})\,\exp[-\beta V(\mathbf{r})] = W(\mathbf{r}|\mathbf{r}')\,\exp[-\beta V(\mathbf{r}')] \tag{2}$$

In eq 2, $V(\mathbf{r})$ is the potential energy of the system when the particle is at point $\mathbf{r}$, and $\beta = 1/k_B T$. W can be specified as follows:

$$W(\mathbf{r}'|\mathbf{r}) = A(\mathbf{r}'|\mathbf{r})\,T_c(\mathbf{r}'|\mathbf{r}) \tag{3}$$

or

$$W = AT_c$$

Here, T_c is some specified conditional probability distribution to choose a new position $\mathbf{r}'$ from the old position $\mathbf{r}$, and A is the probability that this displacement is effectively accepted. T_c is then chosen such that T_c is normalized, and A must be chosen such that the condition of detailed balance is satisfied.

The condition of A satisfying detailed balance can be expressed by defining a quantity q as follows:

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$$q(\mathbf{r}'|\mathbf{r}) = \frac{T_c'\cdot P(\mathbf{r}')}{T_c\cdot P(\mathbf{r})} = \frac{T_c'}{T_c}\exp(-\beta\Delta V) \tag{4}$$

in which $\Delta V = V(\mathbf{r}') - V(\mathbf{r})$ is the energy difference between the system before the particle displacement ($\mathbf{r}$) and after the particle displacement ($\mathbf{r}'$). T_c' is the conditional probability distribution for the reverse displacement, i.e., from $\mathbf{r}'$ to $\mathbf{r}$. Using q, the condition to satisfy detailed balance then follows from eq 2 as

$$A = \mathrm{Min}[1, q] \tag{5}$$

This condition allows us to understand the uniform acceptance in UFMC. Let us first, however, apply this condition to Metropolis Monte Carlo.

1. Metropolis MC. In Metropolis MC,[11] T_c is chosen as follows:

$$T_c = \begin{cases} c & \mathbf{r}' \in D(\mathbf{r}) \\ 0 & \mathbf{r}' \notin D(\mathbf{r}) \end{cases} \tag{6}$$

Here, $D(\mathbf{r})$ is a chosen domain in the neighborhood of $\mathbf{r}$. Then, A becomes

$$A = \mathrm{Min}[1, \exp(-\beta\Delta V)] \tag{7}$$

This is simply the Metropolis MC acceptance criterion for the chosen displacement: if the displacement results in a decrease in energy, the displacement is always accepted. If the displacement results in an increase in energy, then the displacement is accepted with probability $\exp(-\beta\Delta V)$.

2. fbMC. In fbMC, T_c needs to be defined separately for each Cartesian coordinate, as it depends on the force in each direction. In the x direction, $T_{c,x}$ is chosen as follows:[4]

$$T_{c,x} = \begin{cases} K^{-1}\exp[\lambda\beta F_x(x' - x)] & x' \in D(x) \\ 0 & x' \notin D(x) \end{cases} \tag{8}$$

In this expression, K^{-1} is a normalization constant, F_x is the force in the x direction acting on a particle when located at position x, and λ is essentially an arbitrarily chosen parameter. The displacement $x' - x$ is represented as δ, and hence $\delta' = x - x' = -\delta$. Furthermore, if δ is kept sufficiently small, we can write for this particle $\Delta V_x = -F_x\delta$ and $\Delta V_x' = -\Delta V_x = -F_x'\delta' = F_x\delta$. In the interval δ, the force does not change appreciably if the δ is sufficiently small, such that $F_x = F_x'$. This corresponds to a first order Taylor expansion of the energy. Note in this respect, that in MD, the typical step size is on the order of 0.01 Å. In UFMC, on the other hand, a typical "conservative" step size is on the order of 5−10% of the nearest neighbors distance, say 0.10−0.15 Å.[6,8,9,12] Thus, the step size in UFMC is about 1 order of magnitude longer than in MD.

In fbMC, the acceptance criterion is determined by q (just as it is in Metropolis MC):

$$q(x'|x) = \frac{T_c'\cdot P(x')}{T_x\cdot P(x)} = \frac{T_c'}{T_c}\exp(-\beta\Delta V_x) \tag{9}$$

and hence by the ratio T_c'/T_c:

$$\frac{T_c'}{T_c} = \frac{K'^{-1}\exp(\lambda\beta F_x'\delta)}{K^{-1}\exp(\lambda\beta F_x\delta)} \tag{10a}$$

$$= \exp(-\lambda\beta F_x\delta - \lambda\beta F_x\delta)$$

$$= \exp(-2\lambda\beta F_x\delta) \tag{10b}$$

Note that in going from eq 10a to eq 10b we have assumed that $K = K'$, which is a direct consequence of the approximation $F_x = F_x'$. Although eq 10b is a quite convenient equation for the Monte Carlo version that we discuss further in this paper, one is not obliged to rely on this underlying approximation. If so desired, a correction could be applied to circumvent the approximation and make the Monte Carlo algorithm exact. We will show later in this work that this would result in rejecting the displacement in only a very small proportion of the cases. We have never found that using the approximation leads to noticeably distorted results.

Generalizing to all coordinates j and all particles i,

$$\Delta V = \sum_{i,j}\delta_{i,j}F_{i,j} = \sum_{i,j}\Delta V_{i,j} \tag{11}$$

q then becomes:

$$\begin{aligned} q &= \exp(2\lambda\beta\Delta V - \beta\Delta V) \\ &= \exp(\beta\Delta V(\lambda - 1) + \lambda\beta\Delta V) \end{aligned} \tag{12}$$

From this expression, three different cases can be discerned.

Case a: $\lambda = 0$. Using $\lambda = 0$, eq 11 becomes

$$q = \exp(-\beta\Delta V) \tag{13}$$

Using

$$A = \mathrm{Min}[1, q]$$

the acceptance criterion then becomes

$$A = \mathrm{Min}[1, \exp(-\beta\Delta V)] \tag{14}$$

which is identical to the Metropolis MC scheme.

Case b: $\lambda = 1/2$. Using $\lambda = 1/2$, the expression for q becomes

$$q = \exp\left(-\frac{1}{2}\beta\Delta V + \frac{1}{2}\beta\Delta V\right) = 1 \tag{15}$$

and therefore $A = 1$, i.e., each displacement is accepted. This constitutes the uniform acceptance in force biased Monte Carlo, while still satisfying detailed balance.

Case c: $\lambda = 1$. Using $\lambda = 1$, the expression for q becomes

$$q = \exp(\beta\Delta V(1 - 1) + \beta\Delta V) = \exp(\beta\Delta V) \tag{16}$$

Therefore, in this case, displacements that lead to a decrease in energy are accepted with a probability $\exp(\beta\Delta V)$, while displacements leading to an increase in energy are always accepted.

DISCUSSION

In principle, an arbitrary value for λ can be chosen while still satisfying detailed balance. However, as shown above, only the value $\lambda = 1/2$ leads to an acceptance probability = 1 while still satisfying detailed balance. Using a value of $\lambda = 0$ leads to the Metropolis MC scheme, including the typical acceptance criterion.

From the above expressions, we can determine the actual displacement in the case of uniform acceptance force biased Monte Carlo. Following the notation of Timonova et al.,[6] the actual displacement δ can be rewritten as a normalized displacement ξ as follows:

$$\xi = \frac{\delta}{\Delta/2} \tag{17}$$

Here, Δ constitutes the domain to which the displacement is confined, and therefore $\Delta/2$ is the maximum displacement length. This domain can be selected by the user but should be sufficiently small to ensure that the force does not change appreciably when executing the displacement. Hence, ξ is confined to the interval $[-1,1]$. Since the total probability density function $p(\xi)$ must be normalized, i.e,

$$\int_{-1}^{1} p(\xi)\, \mathrm{d}\xi = 1 \tag{18}$$

and in each Cartesian coordinate, T_c is given by

$$T_c = K^{-1} \exp(\lambda\beta F\delta) \tag{19}$$

the probability density function is given by

$$p(\xi) = \frac{|\gamma|}{e^{|\gamma|} - e^{-|\gamma|}} \exp(\gamma\xi) \tag{20}$$

in which γ is given by

$$\gamma = \lambda \frac{F\Delta/2}{k_B T} = \frac{F\Delta/2}{2k_B T} \tag{21}$$

The actual normalized displacement in each Cartesian coordinate is then sampled as follows:

$$\xi = \frac{1}{\gamma} \ln[\eta(e^{|\gamma|} - e^{-|\gamma|}) + e^{-|\gamma|}] \tag{22}$$

In eq 22, η is a random number in the interval $[0,1]$. If η is uniformly distributed, then this choice of ξ leads to eq 19. Therefore, the probability density function contains a factor 2 in the denominator, which is unexpected with respect to the normal Boltzmann distribution:

$$p(\xi) \propto \exp(\gamma\xi) = \exp\left(\frac{F\delta}{2k_B T}\right) = \exp\left(\frac{-\Delta V}{2k_B T}\right) \tag{23}$$

This effectively means that every displacement is effectively sampled from a Boltzmann distribution, albeit containing a factor 2 in the denominator. As demonstrated above, this factor 2 is a direct result of the uniform acceptance criterion of force biased Monte Carlo using $\lambda = 1/2$.

Now, we continue by showing that this UFMC scheme generates the same result as the Metropolis MC scheme.

APPLICATION TO 1D DIFFUSION

As a very simple test case of the method,[6] we consider the diffusion of a single particle in a 1D sinusoidal potential

$$U(x) = \frac{Q}{2}\left(1 - \cos\left(\frac{2\pi x}{L}\right)\right) \tag{24}$$

In this expression, Q is the imposed activation barrier of the potential, L is the period, and x indicates the position of the particle. In a first simulation, the particle is displaced by the UFMC method. In a second simulation, the particle is displaced according to the Metropolis algorithm (including the acceptance criterion), in order to demonstrate that both lead to the same result for the apparent activation energy. The simulation is run for various maximum displacement lengths $\Delta/2$, in the range 0.025−0.2 Å. The period L is set to 1.0 Å. For each specific displacement length, each run consists of $N = 10^7$ steps and is repeated 20 times, in order to obtain statistically reasonable results. The apparent activation energy Q_a can then be derived from the Arrhenius equation by performing a series of simulations at different temperatures:

$$\ln\left(\frac{n}{N}\right) = -\frac{Q_a}{kT} + \ln\left(\frac{\nu_0 t}{N}\right) \tag{25}$$

where n is the number of jumps over the barrier detected, T is the temperature, ν_0 is the Arrhenius pre-exponential factor, and t is the elapsed time. Note that both ν_0 and t have no direct meaning in UFMC (nor in fbMC or MMC), but the product $\nu_0 t$ springs into existence when the Arrhenius equation is used to determine the apparent activation barrier and represents the number of attempts in the time considered.

In Figure 1, a plot is shown for the (absence of) variation of the apparent activation barrier as a function of $\Delta/2$, for an imposed barrier height $Q = 0.25$ eV. Each point in the plot is the average value of the 20 independent runs. The error bars are the corresponding standard deviations determined from these 20 independent runs per point.

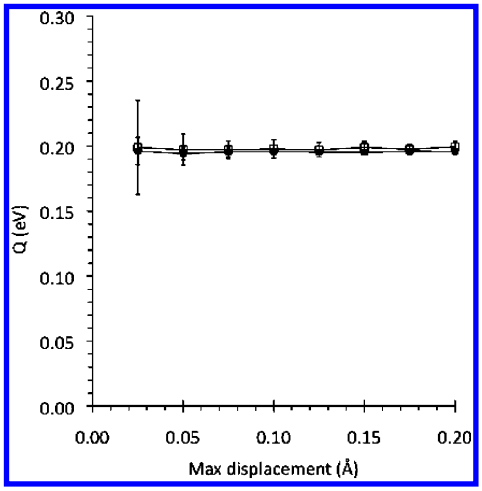

Figure 1. Apparent activation energy Q_a as a function of the maximum allowed displacement for both the UFMC algorithm (closed symbols) and the Metropolis MC algorithm (open symbols).

From this figure, it is obvious that the in the UFMC scheme, in which each displacement is accepted, the particle feels the same energy barrier as in the Metropolis MC procedure, in which the traditional acceptance criterion is applied. This result therefore corresponds to the analytical result given above.

A second result that is obvious from the figure is that the apparent activation energy Q_a is seen to be independent of the value of $\Delta/2$. Note, however, that this seems to be dependent on the method of counting the number of barrier crossings (see below).

However, while the particle surmounts the same barriers in both methods, it diffuses much faster in UFMC than in MMC. To see this, consider the frequency factor as determined from eq 25. In Figure 2, this frequency factor is plotted for both algorithms. It can be seen from the figure that in UFMC, the particle has a much higher attempt frequency to move over the barrier, which can be interpreted as having a much higher frequency of vibration in the energy basin. Since the barriers are identical in both algorithms (and hence are the curvatures and the opposing forces), this implies that the particle is moving much "faster" in UFMC than in MMC. Note, however, that the

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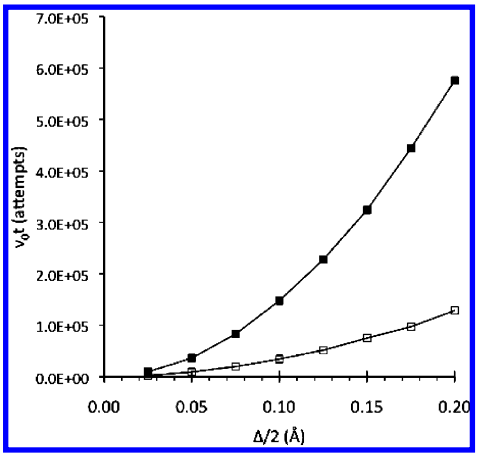

Figure 2. Calculated number of attempts in N MC steps, determined from the MMC simulations (open symbols) and the UFMC simulations (closed symbols).

velocities are not considered in either of both methods. This enhanced frequency factor is why UFMC is such a powerful tool to accelerate the simulation.

Note that the result regarding the apparent activation energy obtained using the UFMC algorithm differs from the result obtained by Timonova et al.[6] Indeed, in ref 6, a dependence of Q_a on the maximum displacement length was found, while we here do not find such dependence. This seems to be due to a different counting method: while in ref 6 a moving average of the consecutive particle positions was used to determine the number of jumps, we here determine the number of minimum-to-minimum transitions based on the actual instantaneous position of the particle.

As mentioned above, a correction could be applied to circumvent the approximation that $K = K'$ and make the Monte Carlo algorithm exact. Thus, we have quantified q without the approximation and calculated the corresponding rejection probability. This is shown in Figure 3.

In this figure, the atomic displacement rejection probability is shown as a function of the temperature for a maximum allowed displacement of 0.05 Å, 0.075 Å, and 0.1 Å, for the same

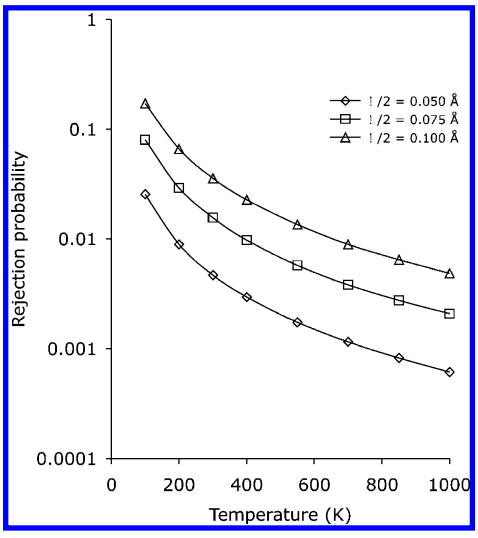

Figure 3. Rejection probability for atomic displacements as a function of temperature for various maximum displacement lengths Δ/2.

sinusoidal potential as discussed above. It can be seen from the graph that in principle, an arbitrarily small rejection rate can be obtained by decreasing the maximum allowed displacement. As mentioned above, recall that in MD, the typical step size is on the order of 0.5% of the equilibrium bond length, whereas Figure 3 indicates that at temperatures at or above room temperature, a "conservative" step size is on the order of 5−10% of the equilibrium bond length, such that the step size in UFMC is about 1 order of magnitude longer than in MD.

Finally, note that it would be worthwhile to study if the time scale enhancement by UFMC as presented here could be further improved by coupling the method to other methods such as Goldman's energy-scaled displacement method.[13] Goldman himself already mentions this possibility. In Goldman's method, the maximum displacement is made dependent on the energy of the atom. In ref 13, Goldman's method is compared with force-biased Monte Carlo and was found to be slightly superior, but the Monte Carlo version used the value $\lambda = 1$ and not the (more efficient) value $\lambda = 1/2$ applied here. In addition, Goldman's work is predominantly concerned with equilibrium properties, while we have used our UFMC method particularly to study the realistic time evolution of systems, such as recrystallization[6] and nanotube growth.[8,9] It is therefore not straightforward to conclude that the two methods would operate constructively if jointly applied to the same problem. Nevertheless, a combination study may be useful.

CONCLUSIONS

A simple proof is presented to demonstrate that the uniform acceptance force biased Monte Carlo (UFMC) method using $\lambda = 1/2$ correctly samples from the Boltzmann distributions, complying with detailed balance, and is in this sense equivalent to the traditional Metropolis Monte Carlo (MMC) method with the Boltzmann acceptance criterion. Contrary to MMC, however, each displacement in UFMC is accepted. The method relies on atomic displacements small enough to allow the force to be considered constant over the considered displacement, such that unphysical displacements are avoided. The simple one-dimensional diffusion of a particle in a sinusoidal potential is presented in order to compare both methods in practice.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Oxford University Press: New York, 2003.

(2) Frenkel, D.; Smit, B. *Understanding Molecular Simulation*; Academic Press: San Diego, CA, 2002.

(3) Voter, A. F.; Montalenti, F.; Germann, T. C. Extending the time scale in atomistic Simulation of materials. *Annu. Rev. Mater. Res.* **2002**, *32*, 321−346.

(4) Rao, M.; Pangali, C.; Berne, B. J. Force bias monte-carlo simulation of water - methodology, optimization and comparison with molecular-dynamics. *Mol. Phys.* **1979**, *37*, 1773−1798.

(5) Pangali, C.; Rao, M.; Berne, B. J. Novel monte-carlo scheme for simulating water and aqueous-solutions. *Chem. Phys. Lett.* **1978**, *55*, 413−417.
(6) Timonova, M.; Groenewegen, J.; Thijsse, B. J. Modeling diffusion and phase transitions by a uniform-acceptance force-bias Monte Carlo method. *Phys. Rev. B* **2010**, *81*, 144107.
(7) Neyts, E. C.; Bogaerts, A. Numerical Study of the Size-Dependent Melting Mechanisms of Nickel Nanoclusters. *J. Phys. Chem. C* **2009**, *113*, 2771−2776.
(8) Neyts, E. C.; Shibuta, Y.; van Duin, A. C. T.; Bogaerts, A. Catalyzed Growth of Carbon Nanotube with Definable Chirality by Hybrid Molecular Dynamics-Force Biased Monte Carlo Simulations. *ACS Nano* **2010**, *4*, 6665−6672.
(9) Neyts, E. C.; van Duin, A. C. T.; Bogaerts, A. Changing Chirality during Single-Walled Carbon Nanotube Growth: A Reactive Molecular Dynamics/Monte Carlo Study. *J. Am. Chem. Soc.* **2011**, *133*, 17225−17231.
(10) Dereli, G. *Mol. Simul.* **1992**, *8*, 351−360.
(11) Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. Equation of State Calculations by Fast Computing Machines. *J. Chem. Phys.* **1953**, *21*, 1087−1092.
(12) Mees, M. J.; Pourtois, G.; Neyts, E. C.; Stesmans, A. A Uniform-Acceptance Force-Bias Monte Carlo Method with Time Scale to Study Solid-State Diffusion. *Phys. Rev. B* **2012**, *85*, 134301.
(13) Goldman, S. A simple new way to help speed up Monte Carlo convergence rates: Energy-scaled displacement Monte Carlo. *J. Chem. Phys.* **1983**, *79*, 3938−3947.