Response to "Comment on 'A new algorithm for reverse Monte Carlo simulations'" [J. Chem. Phys. 111, 5620 (1999)]

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Response to ''Comment on 'A new algorithm for reverse Monte Carlo simulations''' [J. Chem. Phys. 111, 5620 (1999)]

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As already pointed out by Tóth *et al.*,[1] ''there is no *proof* for the correctness of *any* RMC algorithm.'' Moreover, it was stated before that ''methods that produce structures which are equally consistent with the data are equally valid.''[2] Thus, given an input radial distribution function, rdf, or structure factor, $S(q)$, the method should provide a set of configurations that, on average, have the same structural properties as the system corresponding to the input function. If the input information is an rdf, then a minimum requirement is that the generated set of configurations reproduce the input rdf. An algorithm that fails in this respect will of course not be able to reproduce thermodynamic averages like the internal energy, chemical potential, etc. The algorithm we proposed in Ref. 3 does, in contrast to several other algorithms, meet these requirements. It reproduces the input rdf and relevant thermodynamic properties with good accuracy both for monoatomic and polyatomic liquids.[3–5] Under these circumstances the only relevant criticism against our algorithm would be to show by numerical comparison that it fails in some respect. We invite the authors of the preceding Comment to undertake such a study instead of presenting an excessively confusing verbal criticism.

The focus of Ref. 3 was to perform rigorous tests of the RMC algorithms and codes developed in this Laboratory. Since it was a strictly theoretical work, we avoided swelling the text with well-known experimental details. In such tests, there is no reason to prefer a minimization in terms of $S(q)$.[6]

The similarities between our algorithm and the early work of Kaplow *et al.*[7] were pointed out in Ref. 3. However, the key difference between the algorithms is the manner in which new and old configurations are treated. In our algorithm, both configurations could be interpreted as trial moves (i.e., the particle can move to a new position or move to the old one). This together with the definition of the χ^2 parameter as a discrete summation, help the system to avoid being trapped, a problem that earlier algorithms have suffered from.[8] Figure 1 shows that trapping does not occur with the present algorithm.

Another indicator for sampling properties is the so-called ''translational order parameter,'' $O(t)$,[9] which measures if the system is in a liquid or crystalline state,

$$O(t)=\frac{1}{3}\sum_{i=1}^{N}\{\cos Kx_i(t)+\cos Ky_i(t)+\cos Kz_i(t)\}, \quad (1)$$

where t is assumed to be the RMC step, N is the number of particles in the system, L is the box side, K is defined as $4\pi N^{1/3}/L$, and $x_i(t)$, $y_i(t)$, and $z_i(t)$ are particle i coordinates at a particular t. If the system is in the liquid state, we should find oscillations around zero with an amplitude of $\sim N^{1/2}$.[9] In fact, a plot of $O(t)$ as a function of the number of RMC cycles shows this [e.g., for the LJ system of Fig. 1 the mean value of $O(t)$ is -2.6 and the amplitude of oscillations are about 20].

In order to illustrate the features of the present scheme we have repeated some of the simulations of Tóth and Baranyai.[6] Table I shows a comparison of metropolis Monte Carlo (MMC) and our RMC results. Note that the standard deviations in our MMC simulations as well as others in the literature[10] are an order of magnitude smaller than those reported by them.[6] This discrepancy could be due to a trivial mistake in their simulation, but it could also explain some of the confusion in their Comment.

The r-dependent standard deviation of rdf,[6] $\sigma_g(r)$, is displayed in Fig. 2 for the same LJ system. We did not find the deviations reported in Ref. 6 (e.g., see Fig. 4 in Ref. 6).

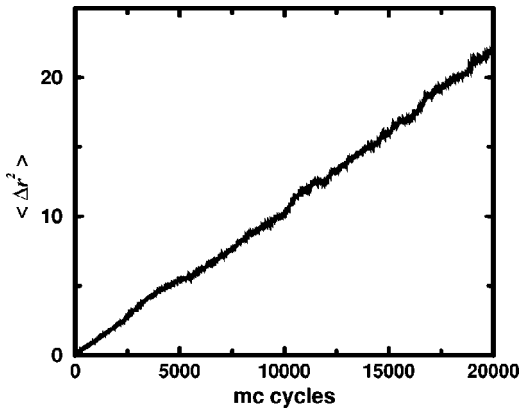

FIG. 1. Mean squared displacement, $\langle \Delta r^2 \rangle$, as a function of the number of RMC cycles in units of Å^2. Data for a LJ system with $\rho^*=0.7$ and $T^*=1.20$. See Ref. 3 for details.

TABLE I. Summary of LJ runs performed with different N for the system described in Ref. 6. All RMC runs were carried out with a bin size of 0.17 Å, except for a, where the bin size was 0.05 Å. See Ref. 3 for simulation details. * Ref. 6 quoted $-8.6\pm1.1NkT$.

N	$-U_{\mathrm{MMC}}(NkT)$	$-U_{\mathrm{RMC}}(NkT)$
108	8.780(3)	8.6447(2)
256	8.745(3)	8.6751(1)
1728	8.747(5)*	8.6783(2)
	...	8.7230(2)[a]

On the contrary, there is a perfect agreement between MMC and our RMC data.

To the best of our knowledge, before our work, almost all previous RMC calculations have been performed with a common algorithm and variations of the same code,[2] where it has been common practice to adopt hard-core constraints. Despite the presence of these constraints, deviations can still be found in the RMC literature and thermodynamic properties are not always accurately reproduced.[1,6] This is in sharp contrast to the tests performed with our algorithm where the same properties usually are well reproduced.

It should be stressed that there is no need for the initial configuration to be free of overlapping distances. On the opposite, the presence of overlaps in the equilibration run will create a driving force to avoid further overlaps. Regarding the size of the system, there is nothing to prevent our algorithm to work with large systems. However, it is of course always a computational advantage to limit the simulation to a small system when it produces results within the statistical error of a larger system.

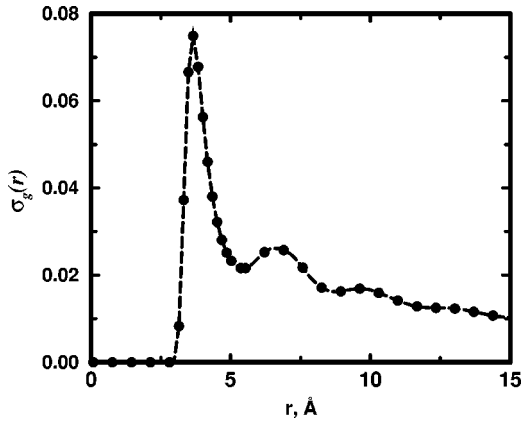

FIG. 2. The r-dependent standard deviation of rdf, $\sigma_g(r)$ for the LJ system described in Ref. 6. Both MMC (●) and our RMC scheme (− − −) data are shown. Simulations were performed with $N=1728$ particles, rdf bin size of 0.17 Å and potential cutoff at half of the simulation box.

In order to study three-body correlations, one may in principle choose functions as the bond angle correlation, $b(\theta)$, or nearest neighbor distributions.[11] However, these functions have a disadvantage in common being insensitive to details of the underlying triplet correlation function $g^{(3)}$. This was clearly shown in our previous work,[3] where we were able to accurately reproduce $b(\theta)$ from the rdf and the well-known Kirkwood superposition approximation. Since the RMC approach is based on an optimization of the rdf the agreement between $b(\theta)$ obtained by MMC and RMC is for many cases appearing in the literature trivial. Eventually, analyses based on the three-body entropy[12] could reveal structural information. Yet, as described in Ref. 12, the calculation of this function could be quite involved and suffers from slow convergence with the size of the system.

Instead of choosing properties that only implicitly depend of $g^{(3)}$, we suggested an examination of $g^{(3)}$ itself, or the closely related $\delta^{(3)}$ which gives the deviation from the superposition approximation. For the system studied,[3] only configurations where three particles are close to each other give δ-values deviating from unity. A critical and clear test of the RMC method is consequently to analyze $\delta^{(3)}$ for such cases, which is exactly the procedure undertaken in Ref. 3 (Note that $g^{(3)}$ was calculated in both our MMC and RMC simulations and then compared).

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