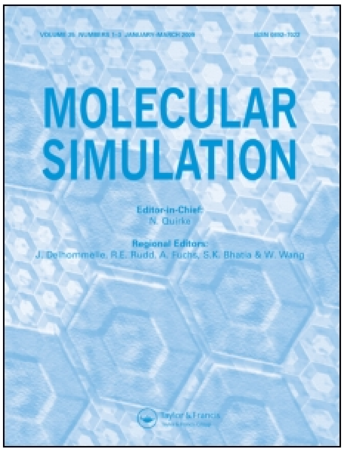

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Comment on Reverse Monte Carlo Simulation

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Note

COMMENT ON REVERSE MONTE CARLO SIMULATION

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In a recent paper McGreevy and Pusztai [1] have described an interesting simulation technique for determining the structure of disordered systems (liquids and glasses) that uses as input the experimentally measured radial distribution function $g_E(r_{12})$, or equivalently, the structure factor $a_E(k)$. The essence of their procedure is to generate, via Monte Carlo, a set of particle configurations that yield a $g(r_{12})$, where $r_{12} \equiv |r_2 - r_1|$ is the distance between particles, that is consistent with $g_E(r_{12})$. From these configurations further information about the structure can be extracted, including higher-order correlation functions such as the 3-body function $\rho^{(3)}(r_1, r_2, r_3)$ or bond-angle distributions. Although the idea of reverse Monte Carlo (RMC) is not new (see the references in [1]), McGreevy and co-workers have shown convincingly that it is computationally feasible and have produced results for a variety of liquids, including multicomponent systems. The RMC procedure is certainly appealing; it suggests that the data which is obtained from an X-ray or neutron diffraction experiment can be used to infer more structural information than that which is inherent in the *pairwise* function $g/(r_{12})$. Since, in certain quarters, this is regarded as heresay it is of some interest to ask what is the formal status of the RMC procedure.

Suppose that $g(r)$, or $a(k)$, were known exactly for a certain bulk liquid at a given density and temperature. Does this function determine *uniquely* the higher-order correlation functions? If it does then RMC might be expected to yield accurate structural information beyond that which is inherent in $g(r_{12})$. If it does not then one cannot be sure that RMC will make reliable estimates about anything other than the inputted pairwise correlations. The answer to the question is implicit in the statistical mechanics literature. If one knows, *a priori*, that the liquid is described by a Hamiltonian for which the interparticle forces correspond *solely* to a pairwise potential $\phi(r_{12})$ then $g(r_{12})$ determines $\phi(r_{12})$ to within a constant, i.e. the force $-d\phi/dr_{12}$ is uniquely determined. The proof of this result is due to Henderson [2] and is based on an adaptation of the well-known Hohenberg–Kohn–Mermin [3] theorem. It follows that, provided a solution exists for $\phi(r_{12})$, all the higher-order correlation functions are uniquely determined.

However, no real substance can be expected to be described by pairwise potentials alone; there are always 3 body, 4 body etc. forces, and then it is straightforward to show that Henderson's proof no longer applies - see also [4]. Not surprisingly what one finds instead is that $g(r_{12})$ together with $\rho^{(3)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3)$ will determine $\phi(r_{12})$ and the 3 body potential $\phi^{(3)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3)$ when there are only 2 and 3 body contributions to the potential function. $\rho^{(4)}$, $\rho^{(5)}$ and all higher-order correlation functions are then uniquely determined. More generally, all the correlation functions up to and including $\rho^{(n)}$ are required to determine ϕ, $\phi^{(3)}$, . . . $\phi^{(n)}$ if all of these potentials are present. Unfortunately, only the pairwise function $g_E(r_{12})$ can be obtained directly from a single diffraction experiment.

What is the relevance of this result for RMC? Two tests come to mind.

i) Take conventional simulation results for the radial distribution function of a given model fluid, say Lennard-Jones, and use these as the 'experimental' input $g_E(r_{12})$ in the RMC. From the configurations which are generated compute $\rho^{(3)}(r_1, r_2, r_3)$ and bond angle distributions. These results could then be compared with the same quantities obtained by conventional simulation using the given pairwise potential. Provided enough care has been taken in all simulations the theorem described above implies that the results should agree within statistical errors.

ii) Now suppose a friendly simulator can be persuaded to run his programs for a model which has an explicit 3-body potential $\phi^{(3)}$ in addition to the pairwise potential ϕ. This fellow would then pass on his data for $g(r_{12})$ to the RMC practitioner who would proceed to generate configurations and to calculate $\rho^{(3)}$ etc. In the meantime the first simulator, who has the potential function, would calculate the same quantities by conventional methods and would keep his results in a sealed envelope. The formal argument given above suggests that subsequent comparison would show that $\rho^{(3)}$ is not necessarily the same from both procedures, but it does not provide any indication of the magnitude or nature of any differences. Presumably the differences will depend on the form of $\phi^{(3)}$, i.e. on the relative importance of 3 and 2 body terms in the potential. Naturally, such exercises are (extremely!) tedious but they might prove to be quite valuable if one wants to understand RMC at a more fundamental level. In particular one might speculate that for monatomic liquids, i.e. the rare-gases and the majority of liquid metals, 3 body and higher-order potentials are relatively unimportant so that the RMC should provide rather accurate structural information beyond that inherent in $g_E(r_{12})$. Similarly in many molten salts one expects pairwise contributions to the potential function to be dominant and the higher-order contributions to play only a minor role in determining the details of the structure. One might imagine that for weak 3 body potentials an effective pairwise potential, $\phi^*(r_{12})$, should exist that will lead to the correct pairwise correlation function and thermodynamic properties. Indeed theories for such ϕ^* have been developed - see [5] and references therein. In this case the configurations generated in the RMC could be considered as those corresponding to $\phi^*(r_{12})$. However, the RMC higher-order correlation functions will still not be *identical* to those generated directly from the potential function.

The difficult cases are, of course, the interesting ones where the residuals of covalent bonding might manifest themselves in the liquid structure. For such systems, e.g. certain liquid semiconductors and molten salts, 3 body forces are probably very important. What the present formal argument implies is that whilst $g_E(r_{12})$ certainly depends upon any $\phi^{(3)}$ that might be present (in addition to ϕ) this dependence is not sufficient to determine uniquely any higher-order correlations. Although the degree of non-uniqueness cannot be measured for any real liquid it could be assessed for model liquids by means of the comparison of simulation results that is outlined above.

Finally we note that Ostheimer and Bertagnolli [6] have proposed an inverse Monte Carlo technique for calculating a pairwise potential from a given radial distribution function. Their procedure for generating configurations is equivalent to that in the RMC. The present work implies that, when $g_E(r_{12})$ corresponds to data for real liquids, any pairwise potential that is extracted can, at best, be identified with ϕ^*.

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