

GRAND ENSEMBLE MONTE CARLO

David Nicholson

For some years now we have made extensive use of grand ensemble (μ, V, T) simulations in the study of adsorbate phases.¹ This choice seems a natural one for such systems since experimental data are very often collected as isotherms of surface excess versus pressure as an independent variable. The very low pressures frequently employed in adsorption work, are of course readily calculated from μ . The use of this technique although by now fairly familiar, raises some questions which may be of interest to other practitioners.

The algorithm for carrying out GEMC work can be constructed in slightly different ways. Our initial method (when we also believed that we were the first to apply the technique to non-lattice systems) used a mixture of real and ghost particles with a fixed total number, in which creation or destruction steps could transfer particles from one category to the other. Subsequently we adopted the method proposed by Norman and Filinov which is more economical in the use of computer time. The decision for a creation/destruction attempt is determined by the conditions:

$$\exp(-\Delta E/kT) \geq RN \quad (\text{move})$$

$$\left[1 + \frac{N+1}{ZV} \exp(\Delta E/kT)\right]^{-1} \geq RN \quad (\text{create})$$

$$\left[1 + \frac{ZV}{N} \exp(\Delta E/kT)\right]^{-1} \geq RN \quad (\text{destroy})$$

where ΔE is the change in energy for the proposed step in the chain, Z is the activity, N the number of particles, V the volume of the box and RN a random number in the interval $(0,1)$. The activity can be expressed in terms of the chemical potential μ

$$\exp(\mu/kT)q_{\text{rot}}^3/\Lambda$$

The realisation of the Markoff chain is straightforward. Each step is an attempt to MOVE, CREATE and DESTROY molecules. Under the constraint imposed by detailed balancing equal numbers of creation and destruction steps should be attempted. This leaves the programmer free to choose the fraction of trials devoted to moves out of the total numbers as well as the maximum step length as is usual for canonical ensemble simulations.

One problem which particularly vexed early work is that of applying long range corrections. Although perhaps obvious with hindsight, it did not seem apparent initially that (a chosen variable) would require any correction of this kind. However such a correction is in fact essential because density fluctuates during a run, and when incorporated, accounts for the discrepancy between grand ensemble and the more tedious canonical ensemble calculations of the transition from the liquid to vapour phase in argon.^{1,3,4} Adsorbates are of course non-uniform so that long-range correction becomes somewhat more problematic for these, but suitable methods can be found, at least for non-polar species⁵.

To highlight the use of the GEMC method it is interesting to examine some MD simulations on 2D adsorbed Ar.⁶ These of course were carried out with fixed N and snapshots for

some runs clearly showed solid-like and gas-like (and less clearly liquid-like) areas of co-existence. One might ask what would become of such a system if GE creation/destruction trials were switched into the system ? Clearly there would be a tendency for the less dense regions to fill or the more dense to empty until a (statistically) uniform density was achieved. The fixed number chosen in this example must in fact correspond to a physically unstable state. But in that case what significance can be attached to the local structure in the dense and rarefied regions ? Is the system large enough to claim that these correspond to co-existing stable states, and if so how might one go about analysing properties such as distribution functions. Clearly one recourse for getting away from manifestly unstable states in MD or canonical MC is to choose a new value for N. But it is by no means always clear, especially in dealing with systems possessing density gradients, whether a given (N,V,T) or (N,V,E) corresponds to an unstable , stable or metastable state. Indeed we have found that metastable states can continue quite happily for several million configurations in a converged, or at least apparently converged, simulation run ⁷.

The last observation in fact also underlines another advantage of using GEMC in that, at the expense of calculating the pressure virial, it is possible to compare free energies for two such apparently converged simulations in order to determine which is the more stable. It may be of course that the free energy minimum can only be easily reached from an initial configuration which the simulator never even dreamt of, and which

is hidden behind ergodic barriers from all those which he/she has tried.

It may be argued then that the reasons for applying the grand ensemble method to this type of investigation are very compelling. But are there disadvantages, apart from the trivial (!) one of extra programming? One difficulty is the choice of the parameters, maximum step length, and α_{CD} , the fraction of creation or destruction trials. Criteria for these seem to be somewhat arbitrary at the best, so that the extra freedom of choice is not altogether welcome, but in many cases the freedom is less real than might appear.

It is easy to show that if α^1 is the fraction of trials accepted and α_M^1 , α_{CD}^1 that of the move and creation/destruction trials respectively, then

$$\alpha^1 = (\alpha_M^1 - \alpha_{CD}^1) \alpha_{CD}^1 + \alpha_M^1$$

where α_{CD}^1 is the fraction of trials which are either creation or destruction out of the total. It is possible of course to regulate α_M^1 by changing the maximum step length, but α_{CD}^1 cannot be easily regulated in a similar way. It turns out that this quantity can be quite a small fraction (.001) when there is a sharp boundary between the dense and rarefied parts of the system (e.g. for a monolayer near to completion), but higher by perhaps an order of magnitude, for multilayer simulations. For practical purposes therefore the overall acceptance fraction is :

$$\alpha^1 \cong \alpha_M^1 (1 - \alpha_{CD}^1) \cong \alpha_M^1 \alpha_M^1$$

Obviously most of the creation or destruction occurs in the less dense regions, but because of the non-uniformity of the system, the variations in density gradient so caused will influence

possible moves in the more dense regions of the adsorbate.

How can the optimum values for α_M^1 and α^1 be decided ? Clearly systematic investigation would be very time consuming. Our own experience suggests that vastly increasing α_{CD} does not significantly affect thermodynamic quantities and intuitively it would seem that a low value for α_{CD} is preferable since there should be several passes for each creation/destruction in order that relaxation can occur. The extra time involved in attempting creation or destruction is also a disadvantage of the method. However this is not quite as demanding as might at first appear. In the first place the rejection of a creation attempt usually occurs because the new particle overlaps too much with its neighbors - a situation which can be trapped immediately at the beginning of the CREATE subroutine. Secondly both the CREATE and DESTROY subroutines involve far fewer programming steps than the MOVE subroutine. For these reasons the computing time per configuration is substantially lower than in a canonical ensemble simulation.

Another problem, the need to reorder the indices referring to a large number of molecules after a successful destruction step, can also be circumvented. This is done by updating a vector, LOC(I) whose elements are associated with those molecules which are currently in existence . The array elements (IS say) of these molecules are obtained by running through the index $I = 1, NMOL$ with $IS = LOC(I)$. Destroyed molecules are placed in the section of the LOC vector not accessed in the DO loops.

Most of our work with the grand ensemble technique has been

directed towards the investigation of the rare gas/graphite adsorption system, where we have found repeatedly that apparently converged runs can be obtained on either of the branches of a phase transition. It is particularly frustrating to see a run reach apparent stability over perhaps a million or so configurations and then suddenly begin to eject particles rapidly before achieving a new plateau, and it would indeed be valuable to have new or additional techniques which could speed up the stabilization process. Force bias applied to the external field part of the potential is a promising candidate. However the very existence of this type of phenomenon lends support to the conviction that a method of this type is essential if one is to be assured that simulation data for stable phases is being acquired.

References.

1. D. Nicholson and N.G. Parsonage. Computer Simulation and the Statistical Mechanics of Adsorption, A.P. 1982.
2. G.E.Norman and V.S.Filinov. High Temp Res.(USSR) 1,216 (1969)
3. L.A. Rowley, D. Nicholson and N.G. Parsonage, J.Comp. Phys.17, 409 (1975).
4. J.P.Hansen and L.Verlet. Phys. Rev. 184, 151 (1969).
5. L.A.Rowley, D.Nicholson and N.G.Parsonage, J.Comp. Phys. 26, 66 (1978).
6. F.Hanson and J.P.McTague, J.Chem. Phys. 72, 6363 (1980).
7. J.S.Whitehouse, D.Nicholson and N.G.Parsonage. Mol.Phys. 49, 829 (1983).