Computer simulations of the restricted primitive model at very low temperature and density

Chantal Valeriani[1,2]**, Philip J Camp**[3]**, Jos W Zwanikken**[4,5]**,**
René van Roij[5] **and Marjolein Dijkstra**[2]

[1] SUPA, School of Physics and Astronomy, The University of Edinburgh, Mayfield Road,
Edinburgh EH9 3JZ, UK
[2] Soft Condensed Matter, Debye Institute for NanoMaterials Science, Utrecht University,
Princetonplein 5, 3584 CC Utrecht, The Netherlands
[3] School of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ,
UK
[4] Department of Material Science and Engineering, Northwestern University,
2220 Campus Drive, Evanston, IL 60208-3108, USA
[5] Institute for Theoretical Physics, Utrecht University, Leuvenlaan 4, 3584 CE Utrecht,
The Netherlands

E-mail: cvaleria@ph.ed.ac.uk

Abstract
The problem of successfully simulating ionic fluids at low temperature and low density states is
well known in the simulation literature: using conventional methods, the system is not able to
equilibrate rapidly due to the presence of strongly associated cation–anion pairs. In this paper
we present a numerical method for speeding up computer simulations of the restricted primitive
model (RPM) at low temperatures (around the critical temperature) and at very low densities
(down to $10^{-10}\sigma^{-3}$, where σ is the ion diameter). Experimentally, this regime corresponds to
typical concentrations of electrolytes in nonaqueous solvents. As far as we are aware, this is the
first time that the RPM has been equilibrated at such extremely low concentrations. More
generally, this method could be used to equilibrate other systems that form aggregates at low
concentrations.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Computer simulations have yielded invaluable insights into the
properties of ionic fluids. The nature of fluid–fluid ('vapour–
liquid') phase separation and the universality class of the
associated critical point have attracted particular attention. In
these studies, the restricted primitive model (RPM) has played
a central role [1–17]. The RPM is a simple representation of
molten salts and ionic solutions. It consists of an equimolar
binary mixture of positively and negatively charged hard
spheres with charges $\pm q$ and equal diameters σ, immersed
in a continuum with dielectric constant ϵ. In terms of
the model parameters, the reduced temperature is defined as
$T^* = k_\mathrm{B}TD\sigma/q^2$, where k_B is Boltzmann's constant, T is

the absolute temperature, $D = 4\pi\epsilon\epsilon_0$ and ϵ_0 is the vacuum
dielectric permittivity; the reduced density is defined as $\rho^* =
\rho\sigma^3$, where $\rho = N/V$ is the total number of ions per unit
volume. The most recent high-precision Monte Carlo (MC)
simulations locate the critical point at a critical temperature
$T_\mathrm{c}^* \simeq 0.05$ and a critical density $\rho_\mathrm{c}^* \simeq 0.08$ [18, 19]; the
critical point has been confirmed as belonging to the three-
dimensional Ising universality class [19]. Interestingly, the
critical temperature is close to room temperature conditions
for sub-nanometre monovalent ions in oily solvents with $\epsilon \simeq$
5–10. However, the ion concentrations in these nonaqueous
electrolyte solutions are often in the nM regime ($\rho^* \sim
10^{-10}$) [20–22] which motivates the parameter choice of the
present study.

It has been clear for a long time that physical clustering of the ions has an important effect in the vapour region [4, 23], as strongly suggested by the Bjerrum theory [24]. Analysing the features of this system in the low density–low temperature regime, Valleau [25] and Gillan [26] showed that the ionic fluid tends to form dimers, triplets and higher order clusters, and that clustering has a crucial effect on the equilibrium properties of the RPM. Weis and Caillol [27] and Bresme *et al* [28] characterized the cluster structures quantitatively at temperatures around T_c and at densities around $\rho_c/5$ and $\rho_c/3$, respectively. Later on, Camp and Patey identified different regimes of ion association well below ρ_c [29]: at low temperature the system apparently consists of only clusters; at intermediate temperature the system is predominantly associated, but with some free ions; and at high temperature the majority of ions are free. The RPM with *screened* Coulombic interactions can serve as a model for charged colloidal systems [30–32]. Caballero and co-workers studied such a model with an inverse screening length of $\kappa = 6\sigma^{-1}$, mimicking the effect of added electrolytes present in the medium: the critical point was located at $T_c^* \simeq 0.17$ and $\rho_c^* \simeq 0.22$, and the familiar clustering phenomenon (of the colloids) in the dilute phase was observed.

The main obstacle to successfully simulating ionic fluids in the low temperature regime, where coexistence occurs, is the strong association of ions at distances close to contact and the resulting extremely slow equilibration. Graham and Valleau [8] pointed out that, when studying the low temperature regime, conventional MC or molecular dynamics methods are not sufficient to equilibrate the system. Therefore, they first used a type of umbrella sampling named 'temperature scaling Monte Carlo' at several densities [33]. Next, Valleau proposed 'density scaling Monte Carlo', a novel algorithm based on umbrella sampling over broad ranges of densities [34], and applied it to the RPM near the critical point. Orkoulas and Panagiotopoulos computed the vapour–liquid phase diagram [11], and to accelerate convergence proposed ion pair and cluster moves capable of grouping and moving clustered ions. The primary motivation in this work was the computation of the vapour–liquid phase diagram, and hence reduced densities of no less than 10^{-4} were considered.

In recent work, Allahyarov *et al* [35] showed that, around the critical temperature, oppositely charged micro-ions tend to form 'Bjerrum pairs', in which oppositely charged particles are closer than the Bjerrum length $\lambda_B = q^2/k_B T D$. The authors of [35] found that at the lowest salt concentrations (around 10^{-9} mol l^{-1}, corresponding to a reduced density of around 10^{-10} for ions with $\sigma = 5$ Å), almost 90% of the ions resided in pairs. In a later publication [36], the same authors used a different definition of a cluster (with a cut-off of $\lambda = 3\sigma$), and narrowed their results down to a smaller concentration range: the new results became valid only for salt concentrations between 10^{-4} and 10^{-2} mol l^{-1} (or reduced densities between 10^{-5} and 10^{-3}). The main problem found by the authors was equilibrating the system at extremely low densities by means of standard simulation techniques.

The aim of our work is to present a novel MC technique that achieves rapid equilibration of the RPM at low

Table 1. Box edge L, Debye screening length λ_D, and Ewald real-space screening parameter α for all of the simulated densities and temperatures ranging from $T^* = 0.04$ to 0.07, and with $N = 256$. For each density, the smallest value of λ_D corresponds to the lowest temperature, and the largest λ_D to the highest temperature.

ρ^*	L/σ	λ_D/σ	$\alpha\sigma$
1.73×10^{-1}	11.39	0.135–0.179	0.49
8.68×10^{-2}	14.34	0.191–0.253	0.39
2.73×10^{-3}	45.45	1.080–1.428	0.12
1.10×10^{-3}	61.48	1.700–2.249	0.091
1.00×10^{-4}	136.13	5.642–7.460	0.041
6.70×10^{-6}	336.75	21.790–28.812	0.017
2.29×10^{-6}	481.62	37.283–49.296	0.012
1.05×10^{-6}	624.44	55.059–72.800	0.009 0
9.48×10^{-9}	2 999.78	579.457–766.167	0.001 9
9.03×10^{-11}	14 154.79	5937.193–7850.244	0.000 40

temperatures (around T_c) and very low reduced densities (from 10^{-3} down to 10^{-10}). This method might also be applied to the equilibration of other systems that form aggregates at low concentrations.

2. Simulations

The interaction potential for the RPM is

$$
U(r_{ij}) = \begin{cases} \infty & r_{ij} < \sigma \\ q_i q_j / D r & r_{ij} \geqslant \sigma, \end{cases} \tag{1}
$$

where $q_i = \pm q$. The system comprises $N/2$ cations and $N/2$ anions in a cubic box of length L, with periodic boundary conditions (PBCs) applied. We use MC simulations of $N = 256$ ions in the NVT ensemble. The choice of such a relatively small number of particles is justified by the fact that, as the densities under study are so low, the simulation box is always large enough to exclude any significant finite-size effects due to the PBCs; with $N = 256$ ions and $\rho^* \propto 10^{-10}$, the simulation box length is around $10^4\sigma$. We checked for finite-size effects by running simulations at $\rho^* = 10^{-4}$ with either 256 or 1000 particles, and making sure that the computed energy per particle was the same within statistical uncertainties. Moreover, the box lengths are large compared to the range of Debye-like screening, equal to the Debye length $\lambda_D/\sigma = \sqrt{T^*/4\pi\rho^*}$. Table 1 shows the values of L and λ_D at the densities and temperatures considered in our work; the density range is $10^{-10} \leqslant \rho^* \leqslant 10^{-3}$ and the temperature range is $0.04 \leqslant T^* \leqslant 0.07$. In this paper we will concentrate on simulations at the lowest density and temperature; the full range of state points will be considered in a forthcoming publication.

The long-range interactions were handled using the Ewald sum with tin-foil boundary conditions [37–40]. For each density we carefully tuned the Ewald parameters α, r_c and k_{max}, being the width of the Gaussian distribution characterizing the screening term in real space, the real-space cut-off and the reciprocal-space cut-off, respectively. α was chosen using the empirical rule $\alpha L = 5.6$ [41], r_c was set to $L/2$, and k_{max} such that the relative error in the reciprocal-space sum was of the

order of 10^{-5} [38]. The values of α are indicated in table 1; k_{max} was always set to $10 \times (2\pi/L)$. To test our code, we computed the energy per ion pair u_p in a liquid at $T^* = 0.042$ and $\rho^* = 0.17$; we obtained $\langle \beta u_p \rangle = -1.26 \pm 0.01$, which is in perfect agreement with that computed for the same state point by Romero-Enrique *et al* [42]. We have also computed the energy per particles at $\rho = 0.175$ and $T = 0.05$, and compared with the results in table 7 of [27] our result is $\langle U/Nk_BT \rangle = -12.38 \pm 0.01$ in perfect agreement with their results of $U/Nk_BT = -12.38$. Moreover, we computed the energy per particle at lower densities where the system is in a vapour phase, at $\rho^* = 0.002$ and $T^* = 0.05$ [27], and found $\langle U/Nk_BT \rangle = -10.20 \pm 0.05$, in good agreement with that computed for the same state point by Caillol and Weis [27] ($U/Nk_BT = -10.15$).

It is well known that the RPM forms clusters in the subcritical vapour phase. In order to identify the clusters, we use Gillan's definition, according to which two particles belong to the same cluster if they are separated by a distance shorter than a given cut-off λ [26]. In this way, we detect the total number of isolated ions, the total number of associated ions, and the total number of clusters of a given size. In what follows, and unless stated otherwise, we will study the cluster formation when $\lambda = 2\sigma$.

3. Techniques to equilibrate the RPM at low temperatures and densities

In order to study the RPM at low temperatures and densities, ad hoc simulation methods have been employed to overcome the problem of slow convergence towards equilibrium. The main obstacle to simulate the RPM in the low temperature region is the strong binding effect of oppositely charged ions at short distances, as the thermal energy available to drive two oppositely charged particles away from each other is much less than the attractive Coulomb energy, i.e. $T^* \ll 1$. Therefore, in order to reach equilibrium, the system would have to be simulated for a prohibitively long time. In our simulations, this equilibration problem is going to be even more pronounced, since we aim to study very dilute systems where isolated ions are so far apart from each other that they spend most of the time freely diffusing in the empty space. Once they finally find an oppositely charged ion, they strongly bind to it forming a neutral dimer (or a higher cluster) that rarely breaks. As a consequence, the computational time needed to equilibrate the system can be astronomically long. To improve the equilibration time in our NVT MC scheme, we have adopted two established MC moves and implemented a new one:

- small and large particle displacements;
- small and large cluster displacements;
- formation and breakage of clusters.

3.1. Small and large particle displacements

The first move we select is the standard single-particle displacement, where the x, y and z coordinates of a randomly selected particle are each displaced by a small amount

δ chosen randomly from the interval $\{-\delta_{max}, \delta_{max}\}$. The move is accepted with the standard Metropolis probability $\min(1, e^{-\beta[u(n)-u(o)]})$, where $u(o)$ and $u(n)$ are the energies of the particle before and after the trial move, respectively, and $\beta = 1/k_BT$. According to normal practice, δ_{max} can be adjusted to give some desired acceptance rate for the move over the course of the simulation. In principle, such moves should allow each particle to diffuse as a free ion, and join or leave a cluster. However, when the density is very low (and the simulation box is very large), short single-particle displacements are not sufficient to sample the phase space properly. Thus, we also randomly attempt displacements where $\delta_{max} = L/2$. These occasional large displacements are intended to accelerate cluster formation (if thermodynamically favourable) and to allow the system to explore more significant regions of phase space within the simulation timescale.

3.2. Small and large cluster displacements

Single-particle MC moves are not enough to equilibrate highly clustered systems, and so we also implement a cluster move similar to that proposed by Orkoulas and Panagiotopoulos [11]: we first identify all of the clusters in the system, then choose a cluster at random and select displacements from either a small or a large interval, as in the single-particle moves. Cluster moves that result in the merging of two or more clusters have to be treated extremely carefully in order to respect detailed balance; the reverse move has to be attempted with equal probability to the forward move. Here we take a simple solution, and simply reject all cluster moves that lead to the merging of clusters [11, 27]. In this way, the instantaneous cluster distribution is left intact, and detailed balance cannot be violated. With this simple approach, the cluster move is accepted with the normal Metropolis probability $\min(1, e^{-\beta[U(n)-U(o)]})$, where $U(o)$ and $U(n)$ are the energies of the system before and after the trial move, respectively. Of course, this move does not lead to the formation or breakage of clusters; a specific move to effect these transformations is detailed next.

3.3. Novel move for the formation and breakage of clusters

The last attempt we make to improve the equilibration of the system is to introduce a novel move that offers the opportunity of forming and breaking clusters. This 'cluster formation/breakage' (CFB) MC move is designed to respect detailed balance, and is implemented as follows:

(i) we choose a particle at random (particle 1), without knowing *a priori* whether it belongs to a cluster;
(ii) we identify all of its neighbours within a cut-off distance Δ, which can be tuned to give optimal performance, as described below;
(iii) we choose a neighbour at random (particle 2), irrespective of its charge, and store its separation from particle 1, $r_{12}(o)$;
(iv) we then move particle 2 to a new separation from particle 1, $r_{12}(n)$, chosen randomly and uniformly from the interval $\sigma \leqslant r_{12}(n) \leqslant \Delta$, and with a random orientation of the corresponding separation vector;
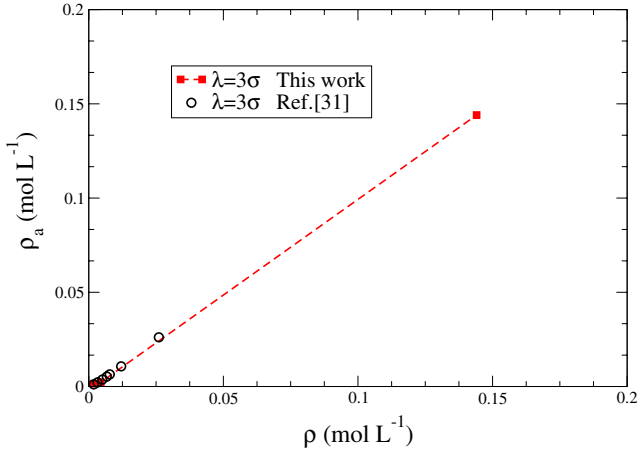
Figure 1. Concentration of associated ions ρ_a against the total ion concentration ρ. The open circles are results from [36] and the red squares are our results. The cut-offs chosen to identify the clusters are indicated in the legend.

Figure 2. Reduced density of associated ions versus Monte Carlo cycle for the MC0, MC1 and MC2 protocols and the same initial configuration at $T^* = 0.04$ and $\rho^* = 9.03 \times 10^{-11}$. The legend indicates the cut-off Δ chosen for CFB.

(v) we accept the move with a probability $\min(1, [r_{12}(n)/r_{12}(o)]^2 \, e^{-\beta[U(n)-U(o)]})$, where $U(o)$ and $U(n)$ are the energies of the system before and after the trial move, respectively.

This CFB move respects detailed balance, and does not add any bias towards the formation or breakage of a cluster, since clusters can form and break, and isolated ions can simply be displaced (see the appendix).

In the current work, the target acceptance rate for the single-particle and cluster moves is approximately 40%, while the acceptance rate for the CFB moves varies between a few per cent (at high density) and 40% (at very low density).

4. Results

We start by comparing our simulation results (using single-particle, cluster and CFB moves) with those obtained by Allahyarov *et al* [36] under the conditions $T = 300$ K, $\epsilon = 8$, $q = e$, and $\sigma = 10$ Å, corresponding to a reduced temperature $T^* \simeq 0.14$. The molar concentrations of salt lie in the range 10^{-4}–10^{-2} mol l^{-1}. Allahyarov *et al* counted 'the number of oppositely charged pairs which are closer than 3σ', whereas we consider associated ions belonging to clusters with two or more ions (with the same cut-off). Figure 1 shows the total concentration of associated ions ρ_a as a function of the total ion concentration ρ. Data from figure 1 of [36] are included after multiplying the salt concentration and associated ion pair concentration by 2; in keeping with these data, we quote the concentrations in units of mol l^{-1}, assuming a particle diameter $\sigma = 10$ Å. All we want to emphasize here is that we get good agreement with the established results for concentrations in the range 10^{-4}–10^{-2} mol l^{-1}.

After having confirmed that the algorithm is working in the density regime that has already been studied, we move to the central aim of this paper, i.e. equilibrating the RPM at extremely low density. The lower the temperature and the density, the longer it takes to equilibrate the system. Thus, a
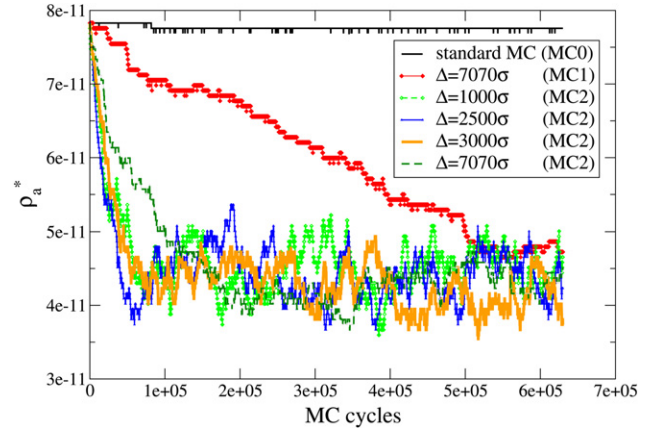
good test for the algorithm is to equilibrate the system at the lowest density and lowest temperature of interest, i.e. $T^* = 0.04$ and $\rho^* = 9.03 \times 10^{-11}$. From preliminary tests, it appears that at the same temperature and higher densities of around $\rho^* = 10^{-6}$ the system equilibrates in a reasonably short time.

For clarity, we define three different MC cycles: Monte Carlo cycle 0 (MC0) consists of N moves, 90% of which are small displacements of single particles, 3% are large displacements of single particles, 3% are small displacements of randomly chosen clusters, and 4% are large displacements of randomly chosen clusters; Monte Carlo cycle 1 (MC1) consists of N moves, 90% of which are small displacements of single particles, 3% are large displacements of single particles, 3% are small displacements of randomly chosen clusters, 2% are large displacements of randomly chosen clusters, and 2% are CFB moves; Monte Carlo cycle 2 (MC2) consists of N moves, 70% of which are small displacements of single particles, 10% are large displacements of single particles, 5% are small displacements of randomly chosen clusters, 5% are large displacements of randomly chosen clusters, and 10% are CFB moves. In all cases, we define a cluster according to $\lambda = 2\sigma$; in MC1 we choose $\Delta = L/2$, whereas in MC2 we consider different values of Δ.

In figure 2 we show the reduced density of associated ions, ρ_a^*, versus MC cycle for simulations run according to the MC0, MC1 and MC2 protocols, and starting from the same initial configuration. MC0 shows almost no structural evolution on the simulation timescale, and hence is entirely inadequate for simulations at low temperature and density. This is caused by the incredibly long distances an ion must cover in order to find another ion (difficult cluster formation), and at the same time by the low probability of thermally activated dissociation of ion pairs at very low temperature (difficult cluster breakage). It is evident that all of the MC2 runs and the MC1 run equilibrate to the same structure, within our simulated timescale. Moreover, the equilibration times are quite different: MC2 (with 10% CFB moves) equilibrates faster than MC1 (with 2% CFB moves).
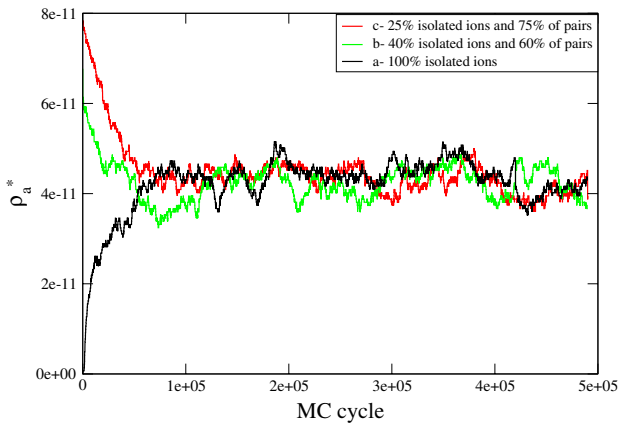
Figure 3. Reduced density of associated ions versus Monte Carlo cycle in simulations started from configurations (a), (b) and (c) (see text), at $T^* = 0.04$ and $\rho^* = 9.03 \times 10^{-11}$.

Next, we select the MC2 Monte Carlo scheme and equilibrate the system using different values of Δ, to show that the final equilibrium state does not depend on the choice of Δ but that its equilibration rate does. To this end, we use different values of Δ, ranging from 1000σ up to half of the box length $L/2$ (7070σ), and plot the reduced density of associated ions versus MC cycle. Figure 2 shows that all of the chosen values of Δ lead to the same equilibrium density of associated ions. Strikingly, the equilibration rate decreases with increasing Δ. Choosing a small value for Δ allows for a faster equilibration; however, Δ cannot be too small compared to the mean separation of clusters, as it will lead again to inefficient sampling, not allowing clusters to merge or break. Therefore, the optimal value of Δ should decrease with increasing density.

We now demonstrate that the convergence of the algorithm does not depend on the initial configuration chosen, and that the system is quasi-ergodic on the simulation timescale. To this end, we set $\Delta = 1000\sigma$ and compute the density of associated ions in simulations starting from three completely different initial configurations: (a) a configuration containing only isolated ions; (b) a configuration containing 40% isolated ions and 60% ions in pairs; and (c) a configuration containing 25% isolated ions and 75% ions in pairs. Figure 3 shows that convergence is achieved irrespective of the initial configuration. It is also encouraging that the algorithm allows for significant fluctuations in the number of associated ions, which indicates that there is a dynamic equilibrium involving the formation and breakage of clusters.

5. Conclusions

In this paper we have presented a numerical method for speeding up computer simulations of the restricted primitive model at low temperatures (around T_c) and very low reduced densities (down to 10^{-10}). Our method involves the combination of conventional single-particle and cluster moves with a novel 'cluster formation/breakage' move, designed specifically to equilibrate the system in a reasonable time, even

at such extreme thermodynamic conditions. The suggested Monte Carlo scheme is straightforward to implement: after having set the value of the maximum neighbour distance Δ the method is inherently efficient, in that the system quickly converges to its equilibrium state. This method might also be applied to the equilibration of other systems that form aggregates at low concentrations. We should mention that we are aware of other techniques that might prove useful to equilibrate very low concentration systems, such as the 'geometric cluster algorithm' by Liu and Luijten [43], demonstrated to speed up simulations of complex fluids near criticality and/or with differently sized components, and a novel cluster move by Almarza [44, 45]. As far as we are aware, our results extend to far lower concentrations than in any previous studies on the vapour phase of the restricted primitive model. The algorithm presented here allows for a comprehensive study of the vapour phase around the critical temperature and at reduced densities down to 10^{-10}: such low densities seem to be relevant for experiments on low concentration solutions of ions in low-dielectric organic solvents. A detailed report of our investigations is in preparation.

Appendix. Acceptance move of the cluster formation/breakage move

Below we derive the acceptance rule for the CFB move, and show that it satisfies the detailed balance condition. Detailed balance requires that

$$p(o)\pi(o \rightarrow n) = p(n)\pi(n \rightarrow o) \qquad \text{(A.1)}$$

where $p(o)$ is the probability that the system is initially in the old configuration o, $\pi(o \rightarrow n)$ is the transition probability from the old to the new configuration n, $p(n)$ is the probability the system is initially in the new configuration, and $\pi(n \rightarrow o)$ is the transition probability from the new to the old configuration. Each transition probability in equation (A.1) can be expressed as the product of two terms:

$$\pi(o \rightarrow n) = \alpha(o \rightarrow n) \times \text{acc}(o \rightarrow n). \qquad \text{(A.2)}$$

$\alpha(o \rightarrow n)$ is the probability of generating a new configuration n starting from o, and $\text{acc}(o \rightarrow n)$ is the probability of accepting the move. A similar equation holds for $\pi(n \rightarrow o)$. In our simulations, the old configuration is defined by choosing two particles (1 and 2) at random, and computing their relative distance $r_{12}(o)$, and the total energy of the system $U(o)$; the new configuration is generated by displacing particle 2

with respect to particle 1, and computing their new relative distance $r_{12}(n)$, and the new total energy of the system $U(n)$. $r_{12}(n)$ is generated uniformly on the interval $\{\sigma, \Delta\}$, and hence $\alpha(o \rightarrow n) = \alpha(n \rightarrow o)$. The Boltzmann probability goes like $p \propto r_{12}^2 e^{-\beta U}$. Combining equations (A.1) and (A.2) gives

$$\frac{\mathrm{acc}(o \rightarrow n)}{\mathrm{acc}(n \rightarrow o)} = \frac{\alpha(n \rightarrow o)}{\alpha(o \rightarrow n)} \frac{p(n)}{p(o)} = \left[\frac{r_{12}(n)}{r_{12}(o)} \right]^2 e^{-\beta[U(n) - U(o)]}. \tag{A.3}$$

To conclude, we implement a Metropolis sampling scheme using an acceptance probability for a move from o to n of

$$\mathrm{acc}(o \rightarrow n) = \min\left(1, \left[\frac{r_{12}(n)}{r_{12}(o)} \right]^2 e^{-\beta[U(n) - U(o)]} \right). \tag{A.4}$$

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