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<p>Note: The following files were submitted by the author for peer review, but cannot be converted to PDF. You must view these files (e.g. movies) online.</p> <p>selective_pivot.tex</p>	



Selective-pivot sampling of radial distribution functions in asymmetric liquid mixtures

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We present a new method for selectively sampling radial distribution functions and effective interaction potentials in asymmetric liquid mixtures by a Monte Carlo simulation. We demonstrate its efficiency for hard-sphere mixtures, and for model systems with more general interactions, and compare our simulations with several analytical approximations. For interaction potentials containing a hard-sphere contribution, the algorithm yields the contact value of the radial distribution function.

Keywords: Asymmetric liquid mixture; Monte Carlo simulation; Pair-correlation function; Potential of the mean force

1 Introduction

Liquid mixtures have been studied in the past decades with objectives ranging from understanding basic theoretical questions to answering questions of technological relevance. The simplest model of liquid mixtures, binary hard spheres, has been an important test bed for experimental, analytical and numerical techniques.

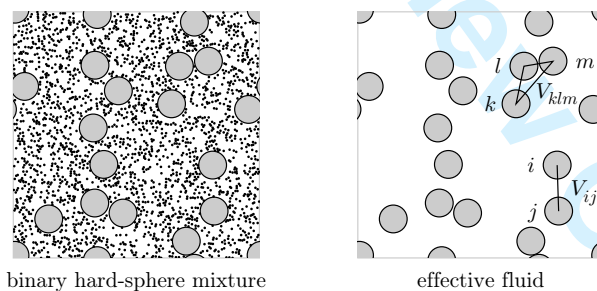


Figure 1. Asymmetric hard-sphere mixture (left), and its effective fluid of solutes (pair interaction V_{ij} and triplet interaction V_{klm} shown, right).

In asymmetric binary mixtures consisting of few large particles (solutes) and many small particles (solvent) (see Fig. 1), one may in principle integrate out all the degrees of freedom of the solvent, and arrive at an equivalent effective fluid of only the large particles, with complicated effective interactions involving pairs, triplets, and, more generally, n -tuples of solutes [1]. Usually, all contributions beyond the pair interaction are neglected (see for example [2]), but their contribution cannot be

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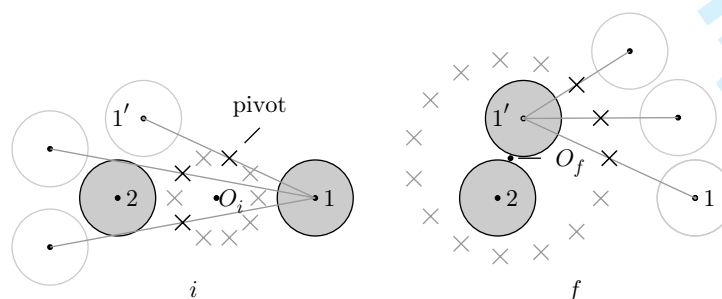
1 excluded a priori [3–5]. Moreover, integral-equations or density functional theories
 2 [6], among others, allow to study the mixtures directly. However, many theories
 3 may fail in extended regions of parameter space when the size asymmetry increases
 4 (for problems with the integral-equation theories, see [7]). On the other hand, for
 5 hard-sphere interactions, the pressure can be expressed entirely through the contact
 6 values of the pair-distribution functions. It is therefore important to have reliable
 7 simulation data when one tries to settle empirical equations of state based on ansatz
 8 for the contact values (see for example [8]).

9 Numerical simulation is thus a crucial tool to validate the above methods.
 10 However it also meets difficulties for asymmetric mixtures. On the one hand,
 11 the displacement of each solute is highly constrained by the surrounding solvent
 12 (see [9]). This strongly slows down both the local Monte Carlo algorithms and the
 13 molecular dynamics method. The standard Monte Carlo Pivot-cluster Monte Carlo
 14 algorithms [10] have partially overcome this problem for hard-sphere models [11]
 15 and for interacting mixtures [12, 13], as long as the overall density of the system
 16 is not too high [14]. On the other hand, the difference in size of solutes and of solvent
 17 particles generates a sampling problem for observables such as the pair-distribution
 18 functions, which vary strongly on the very small scale of the solvent. To describe
 19 these observables, one needs many data (generally contained in a histogram with a
 20 fine grid). On close approach of two solutes in asymmetric mixtures, the pair cor-
 21 relation functions rise steeply. Therefore, the contact value of the pair-correlation
 22 function cannot be obtained precisely by extrapolation as is usually done [15].

23 We introduce in this paper a new selective-pivot sampling algorithm, which allows
 24 us to compute the ratio of the radial distribution functions $g(R)/g(R')$ for two
 25 arbitrary inter-particle distances R and R' . For hard-sphere mixtures, we compute
 26 the pair-correlation function of the solutes and especially its contact value. We also
 27 determine the potential of the mean force. We finally discuss the extension of the
 28 method to systems with arbitrary pair interactions.
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33 2 Selective-pivot sampling

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 35 As mentioned in the introduction, the pivot cluster algorithm allows us to ther-
 36 malize systems with very different length scales, but does not address the sampling
 37 problem which arises from the strong variations of structural quantities on the very
 38 small scale of the solvent. This is the main problem we address in this work. In our
 39 new method, we allow the distance between a pair of tagged particles to take on
 40 only two possible values. While keeping the benefits of the cluster algorithm, this
 41 variant allows us to perform precision calculations of radial distribution functions,
 42 and even of their value at contact.
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 57 Figure 2. Selective-pivot move $1 \rightarrow 1'$ (configuration *i*, left) and return move $1' \rightarrow 1$ (*f*, right). In *i*, the
 58 distance $R_{12} = R_i$, and $R_{1'2} = R_f$. All pivots resulting in a new distance R_f lie on a sphere S_i with
 59 center O_i and radius $R_f/2$ (crosses).
 60

For simplicity, we first discuss selective-pivot sampling for an isolated pair of three-dimensional hard spheres. To sample the ratio of the pair correlation function for two arbitrarily distances, R_i and R_f , we consider a configuration i , with a distance R_i between the two particles, and all moves of one particle ($1 \rightarrow 1'$) such that the new distance is R_f (see Fig. 2). Any such move can be interpreted as a reflection around a pivot located on a sphere S_i with radius $R_f/2$ and center O_i , half-way between the two particles. We choose the pivot randomly on the sphere S_i (using Gaussian random numbers, see [9]). The a priori probabilities for proposing the move $i \rightarrow f$ and the return move $f \rightarrow i$ are, respectively,

$$\mathcal{A}(i \rightarrow f) = \frac{1}{S_i} \propto \frac{1}{R_f^2}, \quad \mathcal{A}(f \rightarrow i) = \frac{1}{S_f} \propto \frac{1}{R_i^2}.$$

The detailed-balance condition connects the stationary probabilities $\pi(i)$ and $\pi(f)$ with the a priori probabilities:

$$\pi(i)\mathcal{A}(i \rightarrow f) = \pi(f)\mathcal{A}(f \rightarrow i).$$

It follows that the probabilities of the two configurations are biased by a geometric factor with respect to the constant hard-sphere probabilities,

$$\frac{\pi(i)}{\pi(f)} = \frac{S_f}{S_i} = \frac{R_f^2}{R_i^2}. \quad (1)$$

For spherically symmetric systems, the pair correlation function depends solely on the distance between particles and reduces to the radial distribution function $g(R)$, which is linked with the probability $\pi(R)$ to observe a particle in an infinitesimal spherical shell of radius R , the other one being at its center, by

$$\pi(R) \propto R^2 g(R) dR.$$

The biasing factor in eq. (1) cancels the geometric factor ($\propto d\Omega$) of the radial distribution function, and the ratio of the probabilities $\pi(i)$ and $\pi(f)$ equals the ratio of the radial distribution functions:

$$\frac{\pi(i)}{\pi(f)} = \frac{g_i}{g_f}. \quad (2)$$

The above algorithm and the relation of eq. (2) between the probabilities of observing the distances R_i and R_f remain valid for two or more solute particles in a box with periodic boundary conditions, in the presence of other components (solvent). It suffices to permanently tag two solutes. One Monte Carlo move involves a single pivot, but may transform many particles (see [9]), including both tagged ones, so that the distance between them may not change.

3 Applications

To validate the selective-pivot sampling algorithm, and to explore possible applications, we compute the distribution function of the solutes for asymmetric binary mixtures, and compare it with simulation data obtained with standard cluster simulation methods, as well as with analytic approximations. In this system, we also compute the contact value of the distribution function. This can be done directly,

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without extrapolation. Furthermore, we use the selective-pivot sampling algorithm to compute the potential of the mean force, that is, the distribution function for two solutes in a large bath of solvent, approaching the regime of infinite dilution.

3.1 Radial distribution function of solutes

We consider an asymmetric binary mixture of spheres with diameters D_s (small particles—solvent) and D_l (large particles—solute), and size ratio $R = D_l/D_s = 10$, at packing fractions $\eta_s = 0.126$ and $\eta_l = 0.121$, where the cluster algorithm performs well. The packing fraction of the solvent, η_s , is linked to the number of solvents N_s in the simulation box of volume V by $\eta_s = \frac{\pi}{6}(N_s/V)D_s^3$, and the packing fraction of the solutes is simply $\eta_l = \frac{\pi}{6}(N_l/V)D_l^3$. The Pivot-cluster algorithm performs better when the overall packing fraction is moderate ($\eta \approx 0.25$ for hard sphere mixtures [11]). But one may hope to obtain data for more dense fluids, when the solvent packing fraction is not too high. As example, for $R = 10$, $\eta_l = 0.33$ and $\eta_s = 0.016$ the Pivot-cluster algorithm is still efficient even if it slows down because of the size of clusters. The selective-pivot sampling shows obviously the same limitation.

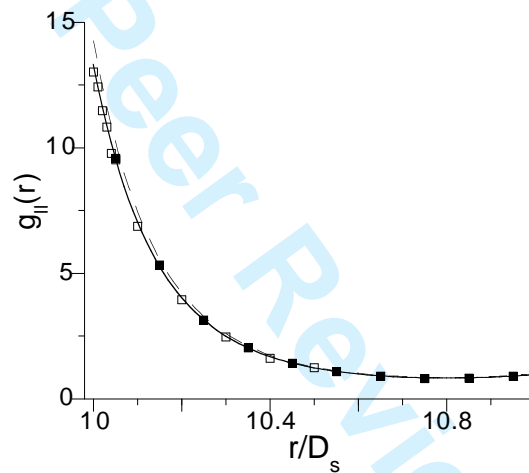


Figure 3. Radial distribution function of the solutes for hard spheres with $R = 10$, $\eta_s = 0.126$ and $\eta_l = 0.121$. Symbols: Cluster algorithm (filled squares: standard sampling method; empty squares: selective-pivot sampling); full line: density functional theory; dashed line: RHNC-MSA [7]. Simulation details are given in Table 1.

In Fig. 3, we compare the radial distribution function of the large spheres $g_{11}(r)$ obtained from selective-pivot sampling and from a standard cluster algorithm and we find very good agreement between the two methods. As a common use of simulation data, we also compare the pair-correlation function with density functional theory, which agrees very well [16,17], and with the Ornstein-Zernike integral equation with the RHNC-MSA closure, which overshoots for small separation [7].

	l	s	l	s	l	s	l	s
η	0.12	0.08	0.14	0.08	0.1	0.1	0.126	0.121
N	79	52800	92	52800	66	66000	80	82939

Table 1. Number of large (l) and small (s) particles in a cubic box of $L = 70D_s$ used to study hard sphere mixture with size ratio $R = 10$. For $R = 20$, we took $L = 140D_s$.

Our method has this advantage that it provides the contact value $g_{11}(r = D_l)$ of the radial distribution function. For Monte Carlo simulations, it was previously

obtained only by extrapolation because the probability of observing two solutes exactly at contact is zero. For moderate size ratios the extrapolation remains possible (see for example [18] for $R = 10/3$ or [19] for $R = 5$). By molecular dynamics, $g_{11}(r = D_1)$ may be obtained by counting collisions. As example Lue and Woodcock [20] computed contact values for $R = 10$ (see also [21] for additional data at the same size ratio) but for systems with few solvent particles (total number of particles $N = 10000$). Nevertheless, as mentioned above, the different length scales in the system make those standard methods fail when size ratio and/or packing fractions increase. To illustrate the accuracy of the selective pivot algorithm, we present data in Table 2. The precision is considerably higher than what was obtained with standard molecular dynamics performed under similar conditions. For example, at size ratio $R = 10$ ($\eta_l = 0.1, \eta_s = 0.1$), we obtain for the contact value 7.1 ± 0.1 , where previous calculations obtained a rough estimate with a $4.45 \pm 25\%$ [22].

η_l, η_s	0.12, 0.08	0.14, 0.08	0.1, 0.1	0.126, 0.121
$R = 10$	5.712 ± 0.05	6.351 ± 0.05	7.1 ± 0.1	13.03 ± 0.26
$R = 20$	21.56 ± 0.5	24.97 ± 0.5	34.10 ± 1.13	91 ± 30 (a)

Table 2. Contact value of the radial distribution function for hard-sphere mixtures with $R = 10$ and $R = 20$. (a) is inside the fluid–solid coexistence domain. Simulation details are given in Table 1.

3.2 Potential of the mean force

As another application of selective-pivot sampling, we consider the potential of the mean force obtained from the solute pair-correlation function in the limit of infinite dilution of the solute particles:

$$\lim_{\eta \rightarrow 0} g_{11}(r, \eta^b) = \exp[-\beta U(r)], \quad (3)$$

where $U(r) = u_{11}(r) + \Phi_{\text{eff}}(r)$ is the total pair interaction between the solutes, $u_{11}(r)$ the direct interaction, $\Phi_{\text{eff}}(r)$ the solvent-mediated potential of the mean force and η_b the bulk solvent fraction. It should be noted that the computational effort for calculating the potential of the mean force is much smaller than for simulating the binary mixture because only the small particles need to be displaced. However, most simulation methods gives the effective force between the two solutes and thus direct comparison with analytical result is more difficult.

In the selective-pivot sampling algorithm, one simply puts the two tagged solutes into a bath of solvent and determines the potential differences for several pairs R_i, R_f . The size of the bath plays almost no role in this simulation because the two large particles are kept at two fixed distances, and cannot escape to infinite separation. The simulation can thus take place in a large box, approaching the infinite dilution of the two solute particles.

Excellent analytical approaches exist for computing the effective potential of the hard-sphere model. Comparison with results obtained from these constitutes thus a stringent test of the accuracy of the method. To illustrate this point, we computed the potential of the mean force between two hard-sphere solutes in a bath of hard-sphere solvent with size ratio $R = 5$ and $R = 10$. Bulk packing fractions are fixed to $\eta_b = 0.1$ and $\eta_b = 0.2$. We considered thus $N_s = 5280$ and $N_s = 10560$, respectively, in a cubic box of $L = 30D_s$ for $R = 5$ and simply doubled the size of the box for $R = 10$. In contrast to other Monte Carlo methods for computing the effective interaction, this method needs no extrapolation [23] and

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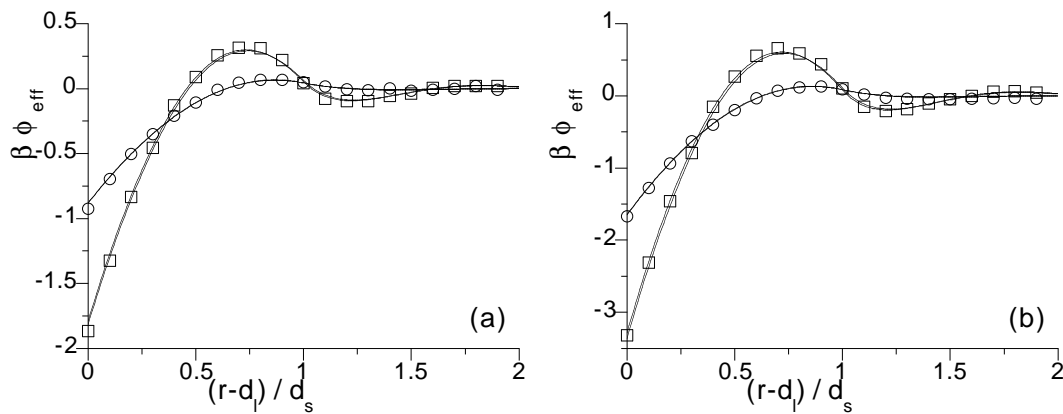


Figure 4. Potential of the mean force for hard-sphere mixture with $R = 5$ (a) and $R = 10$ (b); *symbols*: Selective-pivot sampling; *lines*: DFT and RHNC/fundamental measure functional; *circles*: bulk packing fraction $\eta_b = 0.1$; *squares*: $\eta_b = 0.2$. DFT result are obtained with the density functional theory presented in [16,17]. RHNC/FMF are obtained using integral equations with the same bridge functional (see [5]).

has no adjustable parameter [24]. For both size ratios, the Monte Carlo data agree very well with the potential of the mean force obtained from the Ornstein-Zernike equation with the Rosenfeld fundamental measure closure [25,26] (for alternative closures see for example [27]) and from density functional theory [16,17] which are barely distinguishable (see Fig. 4). Results of Fig. 4 for $R = 10$ may be compared with those presented in Fig. 2 of [28]. Even for $\eta_b = 0.2$, the presented DFT approach did not perfectly reproduce simulation data from [29] near contact and in the region of the first minimum. The precision of the simulation data from [29] did not permit to go farther in the analysis. Our simulation data are accurate enough (precision of the order of the dots in Fig. 4) to allow comparison at a quantitative level. They confirm that the DFT from [28] slightly overestimates the attraction at contact while the improved version of the functional [16,17] corrects this problem. From a technical point of view, our sampling method gives again higher precision data in reasonable time (a few hours per point on a workstation for $R = 10$ and a precision of 1%) compared to what can be obtained with standard simulation schemes.

4 Selective-pivot sampling for models with general pair interactions

Our sampling method can be directly generalized to more general interactions, which can also be handled by the pivot-cluster algorithm (see [12,13]). As an illustration we study the effect of solvation forces in a binary mixture of colloids with size ratio $R = 5$, and a Yukawa tail for unlike pairs of colloids added to the hard-sphere interaction:

$$u_{1s}(r) = \begin{cases} \infty & r < D_{1s} \\ -\epsilon_{1s} \exp\{-z_{1s}(r - D_{1s})\}/r & r \geq D_{1s} \end{cases} \quad (4)$$

We used a value of $0.5k_B T$ for the depth of the attractive well, which correspond to $\epsilon_{1s}^* = \epsilon_{1s} D_s / (k_B T) = 3/2$, and considered two values for the inverse range of the attraction force, $z_{1s}^* = z_{1s} D_s = 10$ and $z_{1s}^* = 2.5$. In Fig. 5 we see that data obtained from selective-pivot sampling and from standard cluster algorithm agree very well. As mentioned elsewhere (see [12]), we simply notice here that the contact value of the radial distribution function decreases when the range of the attraction between small and large particles increases, because the solvation forces create a thin shell of small colloids which counterbalances the depletion between the large ones. The

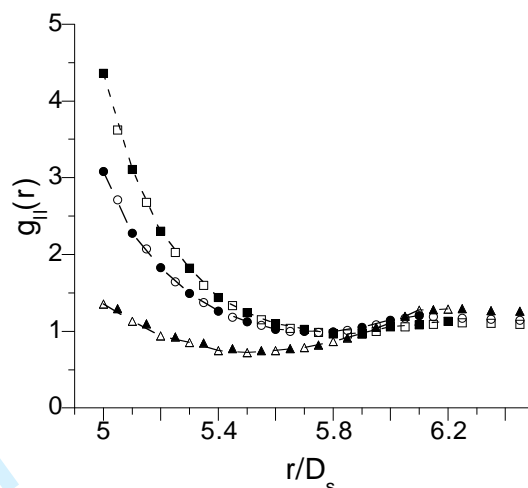


Figure 5. Pair distribution function of solute particles for $R = 5$, $\eta_s = 0.11$ and $\eta_l = 0.12$. *Empty symbols*: standard sampling method; *filled symbols*: selective-pivot sampling; *squares*: hard-sphere; *circles*: Yukawa interaction with $z_{1s}^* = 10$; *triangles*: with $z_{1s}^* = 2.5$.

advantages and the applications mentioned in the previous section carry over. This method is particularly relevant for models beyond asymmetric hard sphere because reliable analytical approaches, even for computing the potential of the mean force (see [26, 30]), are still needed.

5 Conclusion

In this paper, we have presented a selective sampling cluster algorithm which allows to obtain the radial distribution function, including the contact value in a much more accurate manner than standard sampling method. It also yields the pair potential of the mean force between two solutes due to the presence of the solvent. The algorithm solves a sampling problem for observables with very rich structure on a small scale, but does not overcome the remaining limitation of cluster algorithms for liquid simulations, namely the restriction to moderate densities. Even if releasing this restriction is an important task for the future, we show that the particular efficiency of our sampling algorithm may help for validating analytical methods or for studying specific models of asymmetric liquid mixtures.

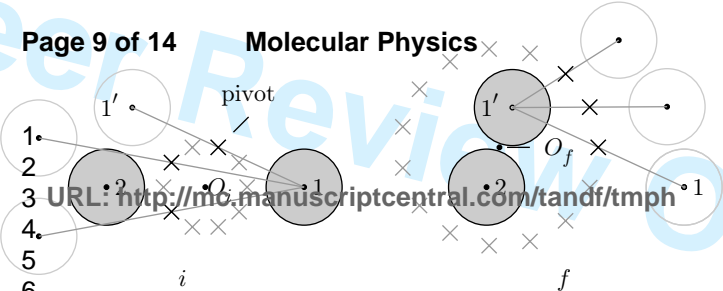
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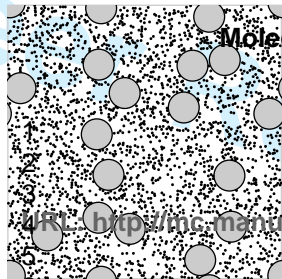
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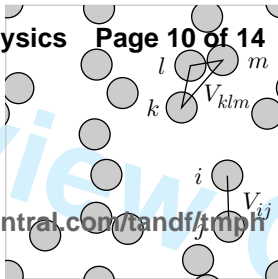
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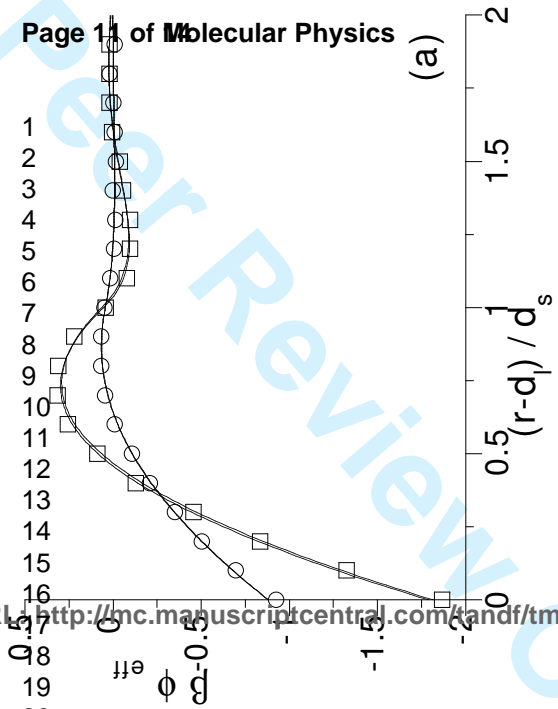
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binary hard-sphere mixture



effective fluid



(b)

