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Monte Carlo results for binary multi-Yukawa mixtures. Evaluation of the accuracy of the mean spherical approximation for realistic hard-core potentials

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Monte Carlo (MC) simulations are used to determine the properties of two different binary multi-Yukawa mixtures studied previously through a quasianalytic Yukawa-MSA (mean spherical approximation) algorithm [Arrieta, Jedrzejek, and Marsh, *J. Chem. Phys.* **95**, 6806 (1991)]. These mixtures are composed of spherical hard-core molecules with multi-Yukawa interactions fitted (beyond the core diameters σ_{ij}^{LJ}) to Lennard-Jones potentials, including thus a significant repulsion (negative slope) interval. The characteristics of the first mixture were chosen to produce a nearly ideal solution, while those of the second mixture (large size difference between components, weak unlike-particle attractions) favored nonideal behavior. For a variety of compositions, densities (in the liquid range), and temperatures, the following properties are determined: configurational energy, pressure, and chemical potentials. The latter were obtained through a new implementation of Widom's particle insertion method. This simple implementation allowed the calculation of chemical potentials at high densities, where the usual procedures tend to fail. An analysis of the standard deviations and of the internal consistency of the MC data was used to confirm the general reliability of the simulation results. The good general agreement found between MC and MSA leads to the conclusion that the Yukawa-MSA quasianalytic algorithm provides not only a convenient but an accurate description of dense fluid mixtures, both ideal and nonideal.

I. INTRODUCTION

In 1978 Blum and Høye¹ showed that the mean spherical approximation (MSA) solution for mixtures of Yukawa fluids could be expressed as a simple system of nonlinear equations. In the preceding paper² we translated their theoretical analysis into a quasianalytic algorithm for multicomponent mixtures of multi-Yukawa fluids. Such an algorithm makes the MSA solution for mixtures of fluids with realistic potentials almost as convenient as that for hard-sphere fluids.

The qualitative capabilities of the Yukawa-MSA algorithm were investigated through an extensive study of two specific binary multi-Yukawa mixtures. These mixtures were composed of spherical hard-core molecules of diameter σ_i with multi-Yukawa interactions fitted, beyond the hard cores, to Lennard-Jones potentials. Thus the potentials used are essentially realistic even if positive [$\phi(r) > 0$] values (which the MSA has difficulty handling, see Ref. 2) are avoided. The interaction parameters of these two mixtures, designated as M1 and M2, are given in Table I of Ref. 2. Such parameters were chosen to produce a fairly ideal first mixture, M1, resembling argon-xenon, and a clearly nonideal second mixture, M2. The algorithm was shown able to determine the regions of thermodynamic instability due to both vapor-liquid and liquid-liquid separations.

Here we perform a quantitative evaluation of the

Yukawa-MSA algorithm (or, more properly and generally, of the MSA)—in particular, for the two mixtures studied in Ref. 2. Previous investigators have already confirmed the accuracy of the MSA-determined thermodynamic properties for pure components with a one-Yukawa potential (Henderson *et al.*³), with a hard-core plus attractive Lennard-Jones interaction [$\phi(r) = -\epsilon^{LJ}$ for $\sigma < r < r_{\min}$] (Stell and Weis,⁴) and for that same interaction fitted with a two-Yukawa potential (Konior and Jedrzejek⁵). However, apart from the hard cores, the interactions in all those fluids are strictly attractive.

This work determines the validity of the MSA for potentials which include a significant repulsion (negative slope) interval. In addition, we study the accuracy of the MSA for mixtures, with particular attention given to the chemical potentials of their components. A Monte Carlo study of structure and phase separation of Yukawa mixtures (only equidiameter system) was performed very recently by Hoheisel and Zhang.⁶

Monte Carlo (MC) simulations in the canonical ensemble, N, V, T , are carried out using the traditional Metropolis⁷ method. A variety of compositions, densities (in the liquid range), and temperatures are studied. Results for both the MC and MSA configurational energy, pressure, and chemical potentials are compared in Sec. II. A good general agreement is found between the theoretical (MSA) and “experimental” (MC) values. Furthermore, this agreement is

independent of the ideal or nonideal character of the mixture.

In the Monte Carlo (MC) simulations, the chemical potentials are calculated by means of a new implementation of Widom's method.⁸ The modification consists in substituting the traditional insertion points by insertion trajectories. This change allows (without significant additional effort) the calculation of chemical potentials at high densities, where the usual implementations of Widom's method fail.⁹ Details of this procedure are given in Sec. III.

Theoretically, MC simulation is able to determine the exact properties of any model fluid. However, given its statistical nature, its results may be greatly affected by any inadvertently introduced sampling bias. To ensure that is not the case, an analysis of the standard deviations and of the internal consistency of the MC data is performed in Sec. IV. The results of this analysis confirm the general reliability of those simulation data.

Finally, a summary of conclusions is presented in Sec. V.

II. COMPARISON BETWEEN MSA AND MONTE CARLO RESULTS

This section gives specific results for both the MSA and Monte Carlo (MC) thermodynamic properties of the two binary multi-Yukawa mixtures studied in Ref. 2. The Monte Carlo simulations were carried out using a total number of 864 particles. After equilibration, a minimum of 17.28 million configurations were sampled for the calculation of configurational energy and pressure. At least half as many configurations were sampled to obtain the chemical potentials.

Two different congruential random number generators, one of them with shuffling, were used; no apparent difference in the results was observed. Other details regarding these simulations are given in the next two sections. Table I gives results for the configurational energy and pressure and Table II lists the values of the chemical potentials. A variety of compositions, packing fractions, and temperatures were studied. In all cases, the MSA energy-derived properties were used. The hard-sphere contributions to those properties were calculated through the Carnahan–Mansoori–Starling–Leland (CMSL)¹⁰ equation of state. The figures given as \pm fluctuations in Table I are the standard deviations for the MC average values. The fluctuations for the chemical potentials are given as asymmetric intervals in Table II; the amplitude of these intervals is determined by the standard deviations of the corresponding Boltzmann factors γ_i , which are the quantities directly measured in the MC simulations (see Sec. III).

From a qualitative point of view, both the MSA and MC properties respond in a physical way to changing thermodynamic parameters. An increase in temperature augments the kinetic energy of the molecules, enabling them to move into configurations of higher potential energy (note the sign). At higher density the molecules are packed more closely, at distances of lower potential (or configurational) energy. Finally, because the second component in both mixtures has a larger (in absolute value) global potential energy, an increase in its mole fraction x_2 (decrease in x_1) results in higher configurational energy.

The variation of pressure is also consistent with the behavior of real fluids. Increases in either density or temperature lead (in the liquid region) to higher compressibility

TABLE I. Monte Carlo and MSA values for energy and pressure.

Mixture	x_1	η	kT/ϵ_{11}^L	$-U^c/N\epsilon_{11}^L$		$P/\rho kT$	
				MC	MSA	MC	MSA
M1	0.25	0.34	1.40	7.942 ± 0.003	7.730	-0.824 ± 0.012	-0.876
		0.34	1.70	7.794 ± 0.002	7.664	0.125 ± 0.015	0.113
		0.44	1.40	10.246 ± 0.001	10.003	1.921 ± 0.014	1.946
		0.44	1.70	10.155 ± 0.001	9.958	3.200 ± 0.021	3.141
	0.50	0.34	1.40	6.778 ± 0.003	6.634	-0.067 ± 0.011	-0.107
		0.34	1.70	6.679 ± 0.001	6.585	0.771 ± 0.009	0.754
		0.44	1.40	8.775 ± 0.001	8.598	3.014 ± 0.021	2.875
		0.44	1.70	8.701 ± 0.001	8.563	4.008 ± 0.040	3.902
	0.75	0.34	1.40	5.612 ± 0.001	5.530	0.708 ± 0.016	0.691
		0.34	1.70	5.561 ± 0.001	5.498	1.448 ± 0.009	1.421
		0.44	1.40	7.302 ± 0.001	7.182	3.985 ± 0.020	3.857
		0.44	1.70	7.244 ± 0.001	7.158	4.907 ± 0.023	4.714
M2	0.25	0.30	1.70	7.162 ± 0.008	6.908	-0.298 ± 0.008	-0.406
		0.30	2.10	6.933 ± 0.002	6.826	0.388 ± 0.009	0.374
		0.40	1.70	9.445 ± 0.001	9.268	1.080 ± 0.011	1.115
		0.40	2.10	9.363 ± 0.001	9.224	2.189 ± 0.013	2.168
	0.50	0.30	1.70	5.802 ± 0.002	5.691	0.232 ± 0.007	0.212
		0.30	2.10	5.708 ± 0.001	5.636	0.882 ± 0.007	0.871
		0.40	1.70	7.804 ± 0.001	7.673	1.882 ± 0.011	1.854
		0.40	2.10	7.743 ± 0.001	7.639	2.770 ± 0.014	2.734
	0.75	0.30	1.70	4.687 ± 0.001	4.624	0.851 ± 0.009	0.819
		0.30	2.10	4.637 ± 0.001	4.591	1.389 ± 0.008	1.370
		0.40	1.70	6.364 ± 0.001	6.273	2.653 ± 0.012	2.641
		0.40	2.10	6.314 ± 0.001	6.250	3.436 ± 0.014	3.369

TABLE II. Monte Carlo and MSA values for the chemical potentials.

Mixture	x_i	η	kT/ϵ_{ij}^{LJ}	μ_i^r/kT			μ_i^r/kT		
				MC	MSA	MC	MSA	MC	MSA
M1	0.25	0.34	1.40	-2.125 < -2.120 < -2.115	-2.179	-5.886 < -5.873 < -5.861	-5.900	-5.886 < -5.873 < -5.861	-5.900
		0.34	1.70	-0.926 < -0.921 < -0.917	-0.932	-3.743 < -3.733 < -3.722	-3.704	-3.743 < -3.733 < -3.722	-3.704
		0.44	1.40	0.304 < 0.342 < 0.383	0.209	-3.212 < -3.066 < -2.894	-3.238	-3.212 < -3.066 < -2.894	-3.238
		0.44	1.70	1.891 < 1.926 < 1.962	1.769	-0.275 < -0.152 < -0.013	-0.487	-0.275 < -0.152 < -0.013	-0.487
	0.50	0.34	1.40	-1.671 < -1.665 < -1.659	-1.695	-5.255 < -5.241 < -5.227	-5.216	-5.255 < -5.241 < -5.227	-5.216
		0.34	1.70	-0.456 < -0.450 < -0.445	-0.472	-3.059 < -3.045 < -3.032	-3.050	-3.059 < -3.045 < -3.032	-3.050
		0.44	1.40	1.125 < 1.166 < 1.208	1.059	-2.117 < -1.951 < -1.752	-2.014	-2.117 < -1.951 < -1.752	-2.014
		0.44	1.70	2.642 < 2.694 < 2.748	2.579	0.832 < 0.996 < 1.193	0.682	0.832 < 0.996 < 1.193	0.682
	0.75	0.34	1.40	-1.066 < -1.062 < -1.057	-1.079	-4.361 < -4.349 < -4.337	-4.338	-4.361 < -4.349 < -4.337	-4.338
		0.34	1.70	0.140 < 0.147 < 0.153	0.114	-2.224 < -2.207 < -2.191	-2.215	-2.224 < -2.207 < -2.191	-2.215
		0.44	1.40	2.256 < 2.320 < 2.389	2.149	0.116 < 0.323 < 0.585	-0.442	0.116 < 0.323 < 0.585	-0.442
		0.44	1.70	3.511 < 3.573 < 3.639	3.621	1.614 < 1.882 < 2.250	2.185	1.614 < 1.882 < 2.250	2.185
M2	0.25	0.30	1.70	-0.645 < -0.641 < -0.638	-0.692	-4.435 < -4.425 < -4.416	-4.486	-4.435 < -4.425 < -4.416	-4.486
		0.30	2.10	-0.047 < -0.046 < -0.045	-0.061	-2.620 < -2.616 < -2.611	-2.631	-2.620 < -2.616 < -2.611	-2.631
		0.40	1.70	0.209 < 0.214 < 0.219	0.197	-3.175 < -3.126 < -3.074	-3.103	-3.175 < -3.126 < -3.074	-3.103
		0.40	2.10	1.083 < 1.088 < 1.093	1.058	-0.552 < -0.502 < -0.451	-0.604	-0.552 < -0.502 < -0.451	-0.604
	0.50	0.30	1.70	-0.600 < -0.598 < -0.596	-0.613	-3.951 < -3.942 < -3.932	-3.954	-3.951 < -3.942 < -3.932	-3.954
		0.30	2.10	0.072 < 0.073 < 0.074	0.065	-2.054 < -2.047 < -2.039	-2.045	-2.054 < -2.047 < -2.039	-2.045
		0.40	1.70	0.509 < 0.516 < 0.523	0.479	-1.676 < -1.597 < -1.510	-1.882	-1.676 < -1.597 < -1.510	-1.882
		0.40	2.10	1.437 < 1.445 < 1.453	1.399	0.697 < 0.775 < 0.858	0.673	0.697 < 0.775 < 0.858	0.673
	0.75	0.30	1.70	-0.442 < -0.440 < -0.438	-0.448	-3.000 < -2.984 < -2.969	-2.976	-3.000 < -2.984 < -2.969	-2.976
		0.30	2.10	0.320 < 0.322 < 0.324	0.310	-0.956 < -0.941 < -0.925	-0.978	-0.956 < -0.941 < -0.925	-0.978
		0.40	1.70	1.085 < 1.096 < 1.107	1.046	0.135 < 0.345 < 0.611	0.401	0.135 < 0.345 < 0.611	0.401
		0.40	2.10	2.091 < 2.105 < 2.118	2.066	3.182 < 3.374 < 3.610	3.058	3.182 < 3.374 < 3.610	3.058

factors. Under some conditions, the intermolecular attractions bringing the molecules together prevail over their kinetic energy. As a result, an external force, a negative pressure, is necessary to take the molecules apart from one another, so that they will occupy the full volume specified by the density. This explains the appearance of negative pressures in Table I.

From a quantitative point of view, Table I shows a good general agreement between MSA and Monte Carlo. Even so, the MSA systematically underestimates the absolute value of the configurational energy and of its variation with temperature. The reason for this systematic deviation lies in the basic assumption of the MSA. A full discussion of this important matter is postponed to Sec. IV. The pressure is also underestimated, though to a lesser degree.

Table II shows the density residual values of the chemical potentials, i.e.,

$$\mu^r(\rho, T, x_i) = \mu(\rho, T, x_i) - \mu^*(\rho, T, x_i), \quad (1)$$

$\mu^*(\rho, T, x_i)$ being the corresponding perfect gas property. These results were obtained, in the Monte Carlo simulations, by means of a modified Widom's test particle method.⁸ This modification is explained in Sec. III.

Within a homogeneous phase, the chemical potentials usually increase with higher density (at constant temperature and composition). On the other hand, an increase in temperature results in higher values of μ_i^r/kT . In all cases, an increase in the mole fraction of the smaller component (which, at constant packing fraction, augments the density) leads to higher chemical potentials.

The MSA chemical potentials agree surprisingly well with the MC values, often within statistical error (a slight

underestimating tendency notwithstanding). There are, though, a few clear exceptions. Section IV will examine these exceptions and will show that in those particular cases the MSA values are likely to be more reliable than the MC results.

In conclusion, despite some relatively minor differences, the overall agreement is sufficiently good to pronounce the MSA an accurate method for the description of realistic fluid mixtures (as long as no positive repulsions are involved). Moreover, the MSA appears to be equally valid for both ideal and nonideal mixtures.

III. CALCULATION OF CHEMICAL POTENTIALS BY MEANS OF INSERTION TRAJECTORIES

The calculation of chemical potentials in computer simulations is based on Widom's equation.⁸ This equation relates the density residual chemical potential for species i , μ_i^r , to the probability γ_i of accepting the insertion of one additional molecule of i (the test particle)

$$\mu_i^r = -kT \ln \langle \gamma_i \rangle, \quad (2)$$

where the overbar denotes an average over the whole volume for one configuration, and the $\langle \rangle$ sign indicates an average over all the configurations. The probability γ_i is in turn related (according to the fundamental principle of statistical mechanics) to the change in configurational energy produced by such an insertion ΔU_i ,

$$\gamma_i = \exp(-\Delta U_i/kT). \quad (3)$$

For a given configuration, this quantity should be averaged over the available volume, therefore

$$\bar{\gamma}_i = \frac{1}{V} \int_V d\mathbf{r}_i \exp(-\Delta U_i/kT), \quad (4)$$

where all possible insertion points \mathbf{r}_i in the simulation volume $V = L^3$ (L being the side of the cubic simulation cell) are included.

In the usual implementations of Widom's method, either a certain number (ranging from one to up to 10^4) random insertion points are selected for each configuration or a fixed array of insertion points is used every certain number of configurations. Neither technique gives a reliable average for any individual configuration ($\bar{\gamma}$) or group of configurations. But this is not a problem since the averaging process over the whole simulation run ($\langle \bar{\gamma} \rangle$) cancels out the individual errors. The problem occurs at high densities, where these techniques tend to fail. Their failure is most evident for hard-core molecules: an increase in density leads to a rapid decrease in the probability of finding a void space (a "hole") large enough to accept the additional molecule.

Therefore special sampling procedures are required for the determination of the chemical potentials in dense fluids. One way is the *umbrella* sampling method of Shing and Gubbins.⁹ This method uses energy-biased configurations to favor the presence of holes. The bias thus introduced is compensated by using properly selected (by trial and error) weights; however, this compensation is only effective for the chemical potentials. The biased series of configurations generated by umbrella sampling are not suitable for the calculation of any other properties. Therefore one must still run conventional simulations to determine energy, pressure, and correlation functions. One more serious inconvenience of umbrella sampling is that, unlike other implementations of Widom's method, it can be used in Monte Carlo simulations, but not in molecular dynamics.

For Lennard-Jones fluids, Shing and Gubbins⁹ found that umbrella sampling was required for pure components at packing fractions higher than $\eta = 0.42$, and for mixtures whenever the diameter ratio is such that $(\sigma_{12}/\sigma_{11})^3 > 1.5$. In this work, mixture M1 is being studied at $\eta = 0.44$ and mixture M2 exhibits a diameter ratio of $(\sigma_{12}/\sigma_{11})^3 = 1.95$. In addition, these mixtures exhibit a hard core at $r = \sigma_{ij}$ instead of the soft repulsion of the normal Lennard-Jones potential. This increases the difficulty of inserting the test particle.

The implementation of Widom's method presented here is based on the assumption that, except at the highest densities, procedures as complex as umbrella sampling are unnecessary. The holes exist, the problem is finding them. This can be done with the help of excluded volume map sampling (EVMS),¹¹ that uses the concepts used previously by Mezei¹² in his cavity-biased Monte Carlo. For a given configuration EVMS starts with finding the excluded volume map for this configuration. Next it uniformly samples the nonexcluded volume.

In this paper the usual random insertion points in the Widom's method are replaced with random insertion trajectories. These trajectories traverse (parallel to any of the axes) the simulation volume from side to side, detect the allowed insertion intervals, and place the additional molecule in an open, nonoverlapping point. The insertion proba-

bility for that point is then multiplied by the ratio of allowed to total interval lengths. The step-by-step procedure for the calculation of the density residual chemical potential of species i , μ_i^r , is as follows:

(1) Select a trajectory, in this case parallel to the x axis, by randomly choosing its coordinates y_i, z_i . This trajectory traverses the simulation cube L^3 from side to side, and thus its total length is L .

(2) Calculate the distances d_2 (two dimensions involved) from all the "regular" molecules to the trajectory,

$$\begin{aligned} d_2^2(k, l) &= (y_{k,l} - y_i)^2 + (z_{k,l} - z_i)^2, \\ k &= 1, 2, \dots, n, \\ l &= 1, 2, \dots, N_k, \end{aligned} \quad (5)$$

where k denotes the different chemical species present in the mixture and l specifies the individual molecules, the total number of molecules being $N = \sum_k N_k$.

(3) Find all forbidden (overlapped) intervals along the trajectory. That is, for all the molecules (k, l) inside the "collision tube," i.e., at a distance $d_2^2(k, l) < \sigma_{ik}^2$, the forbidden interval is $x_{k,l} \pm \sqrt{\sigma_{ik}^2 - d_2^2(k, l)}$.

(4) Determine by exclusion the allowed (nonoverlapped) intervals and find the total allowed length L_a . If there are no allowed intervals, $L_a = 0$, then $\bar{\gamma}_i = 0$ for this trajectory and the procedure is completed. If $L_a > 0$, continue with the following steps.

(5) Choose randomly a nonoverlapping point x_i within the allowed intervals where the additional molecule of i , the test particle, will be inserted.

(6) Compute the distances from all regular molecules to the additional molecule,

$$d_3^2(k, l) = d_2^2(k, l) + (x_{k,l} - x_i)^2. \quad (6)$$

(7) Evaluate the change in configurational energy ΔU_i produced by the insertion the additional molecule of i ,

$$\Delta U_i = \sum_{k=1}^n \sum_{l=1}^{N_k} \phi_{ik}[d_3(k, l)] + \delta U_i \quad \text{for } d_3(k, l) < L/2, \quad (7)$$

where the energy contribution from those molecules separated from the test particle by a distance larger than half the side of the simulation cube $L/2$ is not included directly; instead, a long-range tail contribution, δU_i , is used,

$$\delta U_i = 4\pi\rho \sum_{k=1}^n x_k \int_{L/2}^{\infty} \phi_{ik}(r) r^2 dr. \quad (8)$$

(8) Take as Boltzmann factor for this trajectory

$$\bar{\gamma}_i = \frac{L_a}{L} \exp(-\Delta U_i/kT). \quad (9)$$

Equation (9) approximates (if only one trajectory per configuration is used) the average of γ_i over the whole configuration with the average over one trajectory. Within this trajectory, Eq. (9) accounts exactly for the overlapped portion $(L - L_a)/L$, whose contribution to γ_i is zero; and it takes the ΔU_i for the randomly selected nonoverlapping point as the average over the whole allowed (nonoverlapped) portion. This is an obvious improvement over the selection of one random point (fastest implementation of

Widom's method) as representative of the whole configuration. Yet, it requires exactly the same effort as far as the computation of distances is concerned. (It is the calculation of those distances that consumes the bulk of the computation time.)

The use of trajectories instead of points results in higher sampling efficiency at any density. But the improvement is most dramatic at high densities, where the main problem is to find void spaces where the additional molecule can be inserted. In this regard, the capacity of one single trajectory to find those voids is equivalent, in theory, to that of an infinite number of random points. As an example of the difference in sampling efficiency, when both techniques were applied to the larger component of mixture M1 at $\eta = 0.44$ and $T = 1.70$, out of 1.728×10^6 tries, only four insertion points avoided overlapping while, on the other hand, 1.375×10^3 insertion trajectories gave meaningful ($\bar{\gamma}_i \neq 0$) statistics.

In the interest of expediency, only one nonoverlapping point per trajectory and one trajectory per configuration were used in determining the chemical potentials in Table II. Moreover, for the binary mixtures studied here, both components shared the same insertion trajectories. This way most or all of the calculations in the four first steps of the procedure were common to both components.

This trajectory procedure, although particularly well suited to spherical, hard-core molecules, can be easily adapted to soft cores and to nonspherical shapes (for which analogous random rotations could be used). The precision and accuracy of the simulation measurement of chemical potentials could be further improved by combining the trajectory procedure with the restricted umbrella¹⁰ or the f - g sampling methods.^{10,11,13} (On the other hand, the addition of insertion trajectories would extend considerably the range of applicability of these sampling methods.) In the case of restricted umbrella sampling, the test particle would be allowed to move around within one of the voids found by the insertion trajectory, improving the sampling of the ΔU_i energy. In the case of f - g sampling, the change in energy produced by the addition of the test molecule would be combined with that resulting from the elimination of one of the regular molecules, giving a better, more balanced value of ΔU_i . This latter technique would be especially useful for soft-core potentials. Recently, Deitrick *et al.*¹¹ showed that among the three f - g sampling methods proposed by Widom,⁸ Shing and Gubbins,⁹ and Bennett,¹³ the Bennett's method estimates fugacity coefficient with the least variance.

IV. ANALYSIS OF MONTE CARLO RESULTS

The objective of this subsection is to determine the reliability of the Monte Carlo results given in Tables I and II. Given the statistical nature of Monte Carlo simulation, the average values it yields can be trusted only in the absence of any sampling bias. Also important in this regard are the equilibration of the system and the sample size, i.e., the number of configurations considered. The adequacy of the equilibration, a sample size, and convergence will be determined

by examining the standard deviations, and any possible sampling bias will be detected by analyzing the consistency among the energy, pressure, and chemical potential measurements.

For each composition, the point corresponding to higher density and temperature was started from a face-centered crystalline configuration. Usually, the Yukawa interactions were disregarded (treating the system as a hard-sphere mixture) during a short, initial equilibration stage. This first stage lasted until the system lost all crystalline characteristics. After adding the Yukawa interactions (and also whenever the density or temperature of the system was reduced), a few short runs of typically 400 iterations (400×864 configurations) were used to adjust the acceptance ratio for the moves of both kinds of molecules to between 0.40 and 0.50. Once this was achieved, a series of standard runs, all 2000 iterations long, was started. The length of the equilibration process was determined *a posteriori*. After a minimum of ten standard runs were completed, the values of the equilibrated averages and fluctuation ranges were assessed for the energy and the compressibility factor. The initial runs yielding values in disagreement with such an assessment were not taken into account for the final averages. The number of iterations thus discarded varied between 2400 and 8500, with the faster equilibrations normally corresponding to changes in temperature.

The necessity of the analysis presented below stems from the fact that not only molecular dynamical variables but also Monte Carlo variables can be correlated (biased). Particles in a dense fluid do not move independently, in particular, when several quasiergodic regions exist.¹⁴ In extreme cases, such as quantum Monte Carlo simulation of the Anderson model the covariance matrix is far from diagonal (practically dense¹⁵).

Each standard run j was subdivided in ten groups of 200 iterations. For every property Y , each of these groups yielded a sample average y_{ji} , $i = 1, \dots, 10$. These values were used to calculate the average for the run \bar{y}_j and the standard deviation σ_j of that average: $\sigma_j^2 = \sum_i (y_{ji} - \bar{y}_j)^2 / 90$. However, the averages for successive runs were often separated by an interval larger than the sum of the corresponding standard deviations. Very similar behavior was observed by Caillol *et al.*¹⁶ in the Monte Carlo simulation of an ion-dipole mixture.

Whether these differences were due to lack of convergence or to acceptable statistical fluctuations can be determined by comparing the "internal" and "external" estimates of the standard deviations. The first one is given by the average of the σ_j^2 variances from each run: $\sigma_{\text{int}}^2 = \sum_j \sigma_j^2 / m$, where m is the number of runs contributing to the final averages ($m \geq 10$ for energy and pressure, $m \geq 5$ for the chemical potentials). The external estimate is calculated directly by comparing the different runs: $m\sigma_{\text{ext}}^2 = \sum_j (\bar{y}_j^2 - \bar{y}^2) / (m - 1)$, where \bar{y} is the final or overall average. [The standard deviations, σ , of the overall averages, \bar{y} , given as \pm half-intervals in Table I, are based on the total number of 200 iteration groups, and hence $(10m - 1)\sigma^2 = (10 - 1)\sigma_{\text{int}}^2 + (m - 1)\sigma_{\text{ext}}^2$.] These two values represent the "short-" (σ_{int}^2) and the "long-period" (σ_{ext}^2) variabilities of property

Y . If each standard run/samples the whole range of Y , and if the total simulation run is sufficiently long to smooth out the long-period fluctuations and yield a reliable average, then one would expect $\sigma_{\text{int}} > \sigma_{\text{ext}}$. On the other hand, if for lack of equilibration property Y exhibits a monotonic trend, then the result would be $\sigma_{\text{int}} < \sigma_{\text{ext}}$.

There exist several methods of calculation of variance of a mean of time (or Monte Carlo "time") correlated data. The most lucid presentation of two methods: an autocovariance integration method and a block-variance method can be found in the excellent work of Deitrick *et al.*¹¹ Our estimate is related to the block-variance method. It is not clear that the method is reliable once autocorrelation time exceeds the block length.^{17,18}

Table III compares σ_{int} and σ_{ext} for energy, compressibility factor, $Z = P/\rho kT$, and the Boltzmann factors, $\gamma_i = \exp(-\mu_i^*/kT)$. With very few exceptions, σ_{int} is observed to be larger than σ_{ext} , and even for the exceptions $\sigma_{\text{int}} \approx \sigma_{\text{ext}}$. Therefore we can assume that the systems were properly equilibrated and that the total simulation length was adequate.

The ratio $\sigma_{\text{ext}}/\sigma_{\text{int}}$ is generally larger for energy than for Z or either γ_i . This is normal, since these latter quantities can change rapidly from one configuration to another, while the change in energy is always gradual and slow. That is, the whole range of pressure and chemical potential values can be sampled in a relatively short run, whereas sampling all possible energy values requires longer runs. For energy, the higher values of both standard deviations as well as of their $\sigma_{\text{ext}}/\sigma_{\text{int}}$ ratios appear normally at the lower densities and temperatures. The likelihood of having included nonequilib-

rium configurations is minimal in this case (after three equilibration processes, the first starting from a crystalline configuration, the second following a reduction in density, and the third after a decrease in temperature). Instead, those high values are due to physical reasons: at lower densities, there is a much larger variety of configurations available to the molecules, taking longer runs to sample them; at lower temperatures, a given positive change in energy ΔU^c between two configurations has greater effect, taking more tries to generate a random number n such that $n < \exp(-\Delta U^c/kT)$. The appearance of these higher ratios also is correlated to the larger values of both σ_{int} and σ_{ext} for the Boltzmann factors, which indicate a higher natural variability for those conditions.

Table IV presents the relative values of the overall standard deviations given in Tables I and II, that is, σ/\bar{P} . (The compressibility factor is not included in this table because $Z = 0$ cannot be taken as a reference point.) Again the higher values for the energy correspond to the combination of lower densities and temperatures. For the Boltzmann factors, however, the relative standard deviations are larger at the higher densities; the denser the fluid, the more difficult it is to find a nonoverlapping position for the additional molecule, and the lower the sampling efficiency becomes. Observe also (by comparing results for M1 and M2) that the ratio of the value for γ_2 over the value for γ_1 is clearly correlated to the difference in molecular sizes.

Table V lists the relative errors of the MSA results, as compared to the MC values; for a given thermodynamic property Y , these errors are given as $(Y_{\text{MSA}} - Y_{\text{MC}})/|Y_{\text{MC}}|$. Comparing Tables IV and V it is obvious that there is a

TABLE III. Monte Carlo estimates of the standard deviations.

Mixture	x_1	η	kT/ϵ_{11}^L	$-U^c/N\epsilon_{11}^L$		$P/\rho kT$		γ_1		γ_2	
				σ_{int}	σ_{ext}	σ_{int}	σ_{ext}	σ_{int}	σ_{ext}	σ_{int}	σ_{ext}
M1	0.25	0.34	1.40	0.0079	0.0058	0.031	0.028	0.111	0.055	12.687	4.026
		0.34	1.70	0.0040	0.0031	0.039	0.031	0.030	0.008	1.090	0.399
		0.44	1.40	0.0035	0.0020	0.041	0.018	0.075	0.026	9.233	2.085
		0.44	1.70	0.0039	0.0018	0.070	0.023	0.013	0.005	0.370	0.153
	0.50	0.34	1.40	0.0065	0.0078	0.034	0.016	0.073	0.066	6.350	4.437
		0.34	1.70	0.0036	0.0012	0.032	0.012	0.023	0.010	0.730	0.340
		0.44	1.40	0.0036	0.0015	0.068	0.023	0.039	0.011	3.914	0.873
		0.44	1.70	0.0038	0.0021	0.138	0.038	0.010	0.003	0.173	0.071
	0.75	0.34	1.40	0.0031	0.0017	0.053	0.012	0.043	0.018	3.029	1.007
		0.34	1.70	0.0025	0.0013	0.030	0.008	0.013	0.007	0.372	0.112
		0.44	1.40	0.0032	0.0022	0.060	0.031	0.017	0.008	0.444	0.158
		0.44	1.70	0.0038	0.0015	0.080	0.024	0.004	0.003	0.111	0.061
M2	0.25	0.30	1.70	0.0116	0.0120	0.027	0.013	0.011	0.014	1.807	0.943
		0.30	2.10	0.0067	0.0026	0.029	0.010	0.003	0.000	0.129	0.082
		0.40	1.70	0.0034	0.0012	0.036	0.010	0.009	0.002	2.459	1.562
		0.40	2.10	0.0039	0.0012	0.045	0.011	0.004	0.002	0.203	0.086
	0.50	0.30	1.70	0.0063	0.0048	0.024	0.009	0.007	0.008	0.998	1.011
		0.30	2.10	0.0047	0.0013	0.024	0.008	0.003	0.001	0.128	0.057
		0.40	1.70	0.0028	0.0012	0.037	0.015	0.010	0.004	0.949	0.149
		0.40	2.10	0.0029	0.0012	0.043	0.015	0.004	0.002	0.083	0.035
	0.75	0.30	1.70	0.0032	0.0024	0.030	0.008	0.007	0.004	0.727	0.420
		0.30	2.10	0.0026	0.0013	0.026	0.010	0.003	0.001	0.088	0.034
		0.44	1.70	0.0026	0.0012	0.043	0.014	0.008	0.005	0.371	0.273
		0.44	2.10	0.0026	0.0009	0.045	0.014	0.004	0.002	0.017	0.009

TABLE IV. Relative standard deviations for MC properties (%).

Mixture	x_1	η	kT/ϵ_{11}^L	$(U^c/N\epsilon_{11}^L)^a$	γ_1	γ_2
M1	0.25	0.34	1.40	3.63	0.49	1.25
		0.34	1.70	1.97	0.47	1.06
		0.44	1.40	1.18	3.96	15.81
		0.44	1.70	1.24	3.54	12.99
	0.50	0.34	1.40	4.52	0.62	1.40
		0.34	1.70	1.60	0.56	1.34
		0.44	1.40	1.29	4.15	18.07
		0.44	1.70	1.42	5.33	17.82
	0.75	0.34	1.40	1.86	0.49	1.24
		0.34	1.70	1.50	0.64	1.64
		0.44	1.40	1.60	6.61	23.07
		0.44	1.70	1.58	6.40	30.77
M2	0.25	0.30	1.70	6.77	0.32	0.98
		0.30	2.10	3.02	0.11	0.44
		0.40	1.70	1.11	0.47	5.02
		0.40	2.10	1.20	0.47	5.04
	0.50	0.30	1.70	3.83	0.20	0.95
		0.30	2.10	2.37	0.12	0.74
		0.40	1.70	1.08	0.74	8.28
		0.40	2.10	1.24	0.77	8.02
	0.75	0.30	1.70	2.48	0.20	1.56
		0.30	2.10	1.89	0.19	1.53
		0.44	1.70	1.28	1.07	23.32
		0.44	2.10	1.26	1.34	21.10

^a %10².

general correlation between the relative standard deviations for the MC values and the relative errors for the MSA results. These relative errors are of particular interest in the case of the energy, because they allow an evaluation of the reliability of the MC data. Most of the characteristics of the MSA can be understood from the approximation it introduces at the zero density limit: the exact RDF

$$g(r) = \exp[-\phi(r)/kT], \quad (10)$$

is substituted by the approximate MSA RDF

$$g(r) = 1 - \phi(r)/kT. \quad (11)$$

This explains why the MSA systematically underestimates negative interactions at any density (and why it overestimates positive interactions). Because the potentials used in this work are strictly negative, the MSA energies are sure to be higher (lower in absolute value) than the real ones. It can be seen that in all cases U_{MC}^c is more negative than U_{MSA}^c , as it should be. The change in magnitude of the relative errors for U^c is consistent with the difference between Eqs. (10) and (11): whenever the temperature increases, the relative errors diminish; whenever the mole fraction of the first component increases [lower overall $-\phi(r)$], the relative errors decrease.

The correct systematic differences between the MC and MSA energies (the essential property in MC simulations) is evidence of the general reliability of the MC data given here. This evidence provides further support for the conclusion drawn from the analysis of the internal and external estimates of the standard deviations: the simulated systems were properly converged, and the sample sizes (the number of configurations) were sufficiently large to yield sample averages representative of the population means.

TABLE V. Relative errors^a for MSA properties (%).

Mixture	x_1	η	kT/ϵ_{11}^L	$U^c/N\epsilon_{11}^L$	γ_1	γ_2
M1	0.25	0.34	1.40	2.66	6.03	2.71
		0.34	1.70	1.67	1.10	-2.86
		0.44	1.40	2.38	14.22	18.82
		0.44	1.70	1.94	17.08	39.69
	0.50	0.34	1.40	2.12	3.09	-2.56
		0.34	1.70	1.41	2.22	0.47
		0.44	1.40	2.03	11.24	6.51
		0.44	1.70	1.58	12.10	37.01
	0.75	0.34	1.40	1.46	1.75	-1.11
		0.34	1.70	1.13	3.31	0.77
		0.44	1.40	1.64	18.73	114.87
		0.44	1.70	1.19	-4.72	-26.17
M2	0.25	0.30	1.70	3.55	5.15	6.21
		0.30	2.10	1.54	1.51	1.55
		0.40	1.70	1.87	1.75	-2.24
		0.40	2.10	1.49	3.07	10.67
	0.50	0.30	1.70	1.91	1.56	1.19
		0.30	2.10	1.26	0.76	-0.11
		0.40	1.70	1.68	3.77	33.01
		0.40	2.10	1.33	4.68	10.64
	0.75	0.30	1.70	1.35	0.82	-0.88
		0.30	2.10	1.00	1.20	3.79
		0.40	1.70	1.43	5.11	-5.47
		0.40	2.10	1.02	3.92	37.05

^a The relative error for property Y is defined as $(Y_{MSA} - Y_{MC})/|Y_{MC}|$.

In order to check the internal consistency of the MC results, the following differential expression of the density residual Helmholtz free energy is used:

$$d\left(\frac{A'}{kT}\right) = -\frac{U^c}{(kT)^2} d(kT) - \frac{P^r}{kT} dV + \sum_i \frac{\mu_i^r}{kT} dN_i. \quad (12)$$

Since A'/kT is a property of state, the cross derivatives in this equation must be equal. All these derivatives can be evaluated approximately from the MC data. It should be noted, however, that the derivatives must be approximated with finite differences, and that these differences are not exact but have some statistical error. Therefore the resolution of this internal consistency test is limited, and hence its only aim is the detection of values clearly out of line.

Beginning with energy and pressure, their cross derivatives can be written, after changing from volume to density ($dV = -Nd\rho/\rho^2$), as

$$-\frac{\rho^2}{(kT)^2} \left[\frac{\partial(U^c/N)}{\partial\rho} \right]_{T,x} = \left[\frac{\partial(P^r/kT)}{\partial(kT)} \right]_{\rho,x}, \quad (13)$$

where the subindex x denotes that the composition remains constant (constant N is not needed since all quantities involved are intensive properties). Dividing by ρ , the differential of pressure is transformed into $\partial Z' = \partial Z$, since the compressibility factor for perfect gases is constant, $Z^* = 1$. The ρ remaining on the left-hand side can be converted into packing fractions, as compositions and molecular diameters are constant. Therefore Eq. (13) may be expressed as

$$-\eta \left[\frac{\partial(U^c/N)}{\partial\eta} \right]_{T,x} = (kT)^2 \left[\frac{\partial Z}{\partial(kT)} \right]_{\eta,x}. \quad (14)$$

For each composition, Table I gives U^c/N and Z for four

points forming a square in the temperature vs packing fraction diagram. Taking the η and T for the central point of that square, and using the finite differences between the middle points of opposite sides (with the properties at those middle points evaluated by averaging the data at the corners), all quantities in Eq. (14) can be calculated approximately. The results are displayed in Table VI. This table also gives the same derivatives for the MSA properties. The MSA values are included as an indication of the degree of agreement to be expected between the cross derivatives. (Because all MSA properties given here are energy derived, the MSA cross derivatives would have been exactly equal had they been calculated without introducing approximations.) For both mixtures, the agreement is quite reasonable. Since the reliability of the energy values has already been established, Table VI lends confidence to the pressure measurements.

Equating the energy and chemical potential cross derivatives, the following relation results:

$$\left[\frac{\partial(\mu'_i/kT)}{\partial(kT)} \right]_{T,V,N_i} = - \frac{1}{(kT)^2} \left[\frac{\partial U^c}{\partial N_i} \right]_{T,V,N_j} \quad (15)$$

For this equation, the left-hand side is evaluated directly from the temperature differences (at constant composition and packing fraction) in Table II. The right-hand side can be computed through the energy derivatives with respect to composition and packing fraction. However, a more direct approach is possible. Noting that the configurational energy is given by

$$U^c = 2\pi\rho \sum_i N_i \sum_j x_j \varphi_{ij}, \quad (16)$$

where

$$\varphi_{ij} = \int_{\sigma_{ij}}^{\infty} \phi_{ij}(r) g_{ij}(r) r^2 dr, \quad (17)$$

it can be assumed that the addition of one molecule of component i will not change any of the φ_{ij} integrals significantly. Thus, limiting the effect of such an addition to the number of molecules, the mole fractions and the density, the following approximation is obtained:

$$\left(\frac{\partial U^c}{\partial N_i} \right)_{T,V,N_j} \approx 4\pi\rho \sum_j x_j \varphi_{ij}. \quad (18)$$

The values of φ_{ij} can be calculated from Table VII, which gives the contributions to the total configurational energy from the different interactions U^c_{ij} . The specific form of

these contributions is such that, for these binary mixtures,

$$U^c = U^c_{11} + U^c_{12} + U^c_{22}, \quad (19)$$

and therefore

$$U^c_{ii}/N = 2\pi\rho x_i^2 \varphi_{ii} \quad (i = 1, 2), \quad (20)$$

$$U^c_{12}/N = 4\pi\rho x_1 x_2 \varphi_{12}. \quad (21)$$

Thus making the appropriate substitutions, Eq. (15) becomes

$$\left[\frac{\partial(\mu'_i/kT)}{\partial(kT)} \right]_{T,x} = - \frac{1}{(kT)^2} \frac{2U^c_{ii}/N + U^c_{ij}/N}{x_i}. \quad (22)$$

Table VIII gives the specific results for both sides of this equation, or of Eq. (15). The values on the right-hand side were averaged between the low and high temperatures. The MSA results are included again to estimate the error introduced by Eq. (18) and by replacing derivatives with difference ratios. The agreement between the two MC derivatives and between the corresponding MC and MSA values is generally very reasonable; especially for the smaller component, and also for the larger component at the lower packing fractions—for the cases that allow a more precise MC determination of the chemical potentials. However, there is an obvious problem with the MC derivatives of the chemical potentials for M1 at $x_1 = 0.75$ and $\eta = 0.44$, especially for the larger component. Observe that if the MC value of μ'_2/kT for these conditions and $T = 1.40$ had been similar to the corresponding MSA value, the MC agreement in Table VIII would have been much better. (Instead, the difference between these MC and MSA chemical potentials produces a maximum relative error for the Boltzmann factor γ_2 of 114.87%, see Table V.)

Finally, the equality of the pressure and chemical potential cross derivatives requires, after replacing $dV = -Nd\rho/\rho^2$,

$$\rho \left[\frac{\partial(\mu'_i/kT)}{\partial\rho} \right]_{T,x} = \frac{N}{\rho} \left[\frac{\partial(P'/kT)}{\partial N_i} \right]_{T,V,N_j}. \quad (23)$$

Density can be substituted by packing fraction on the left-hand side. For the right-hand side, a strategy similar to that followed in Eqs. (16) through (18) is possible but not advisable. The compressibility factor is given by

$$Z = \frac{P}{\rho kT} = 1 + \frac{2\pi}{3} \rho \sum_{ij} x_i x_j \psi_{ij}, \quad (24)$$

where

TABLE VI. Relation between energy and pressure derivatives.

Mixture	x_1	MC		MSA	
		$-\eta(\partial U^c/\partial\eta)$	$(kT)^2[\partial Z/\partial(kT)]$	$-\eta(\partial U^c/\partial\eta)$	$(kT)^2[\partial Z/\partial(kT)]$
M1	0.25	9.099	8.919	8.905	8.747
	0.50	7.836	7.337	7.685	7.559
	0.75	6.576	6.652	6.457	6.358
M2	0.25	8.248	8.099	8.327	8.273
	0.50	7.065	6.942	6.975	6.943
	0.75	5.869	5.959	5.790	5.774

TABLE VII. Energy contributions from different (*ij*) interactions.

Mixture	<i>x</i> ₁	<i>η</i>	$\frac{kT}{\epsilon_{11}^{LJ}}$	$-U_{11}^c/N\epsilon_{11}^{LJ}$		$-U_{12}^c/N\epsilon_{11}^{LJ}$		$-U_{22}^c/N\epsilon_{11}^{LJ}$	
				MC	MSA	MC	MSA	MC	MSA
M1	0.25	0.34	1.40	0.195 ± 0.001	0.195	2.106 ± 0.002	2.066	5.640 ± 0.003	5.470
		0.34	1.70	0.194 ± 0.001	0.195	2.092 ± 0.002	2.061	5.507 ± 0.002	5.409
		0.44	1.40	0.270 ± 0.001	0.259	2.763 ± 0.002	2.721	7.213 ± 0.002	7.023
		0.44	1.70	0.259 ± 0.001	0.259	2.763 ± 0.002	2.713	7.133 ± 0.002	6.987
	0.50	0.34	1.40	0.877 ± 0.002	0.864	3.085 ± 0.004	3.061	2.816 ± 0.003	2.709
		0.34	1.70	0.870 ± 0.001	0.862	3.086 ± 0.004	3.049	2.724 ± 0.003	2.674
		0.44	1.40	1.154 ± 0.001	1.143	4.094 ± 0.003	4.003	3.528 ± 0.002	3.452
		0.44	1.70	1.130 ± 0.001	1.140	4.106 ± 0.003	3.991	3.464 ± 0.002	3.432
	0.75	0.34	1.40	2.200 ± 0.001	2.181	2.641 ± 0.003	2.585	0.772 ± 0.002	0.764
		0.34	1.70	2.193 ± 0.001	2.174	2.603 ± 0.003	2.571	0.765 ± 0.002	0.753
		0.44	1.40	2.903 ± 0.001	2.865	3.410 ± 0.003	3.352	0.989 ± 0.002	0.966
		0.44	1.70	2.876 ± 0.001	2.858	3.404 ± 0.003	3.340	0.964 ± 0.002	0.959
M2	0.25	0.30	1.70	0.100 ± 0.000	0.097	1.255 ± 0.002	1.236	5.807 ± 0.005	5.575
		0.30	2.10	0.098 ± 0.000	0.096	1.245 ± 0.001	1.234	5.589 ± 0.002	5.496
		0.40	1.70	0.143 ± 0.001	0.136	1.735 ± 0.002	1.713	7.567 ± 0.002	7.419
		0.40	2.10	0.141 ± 0.001	0.135	1.724 ± 0.002	1.709	7.498 ± 0.002	7.380
	0.50	0.30	1.70	0.496 ± 0.001	0.484	2.098 ± 0.002	2.071	3.208 ± 0.003	3.136
		0.30	2.10	0.491 ± 0.001	0.480	2.080 ± 0.002	2.067	3.137 ± 0.002	3.089
		0.40	1.70	0.703 ± 0.001	0.678	2.871 ± 0.003	2.849	4.231 ± 0.002	4.146
		0.40	2.10	0.679 ± 0.001	0.673	2.885 ± 0.002	2.846	4.179 ± 0.001	4.121
	0.75	0.30	1.70	1.490 ± 0.001	1.458	2.102 ± 0.002	2.095	1.095 ± 0.002	1.071
		0.30	2.10	1.468 ± 0.002	1.448	2.106 ± 0.003	2.090	1.064 ± 0.002	1.053
		0.40	1.70	2.069 ± 0.001	2.022	2.853 ± 0.002	2.846	1.442 ± 0.002	1.405
		0.40	2.10	2.036 ± 0.002	2.011	2.872 ± 0.003	2.846	1.407 ± 0.002	1.393

$$\psi_{ij} = \sigma_{ij}^3 g_{ij}(\sigma_{ij}) - \frac{1}{kT} \int_{\sigma_{ij}}^{\infty} \phi'_{ij}(r) g_{ij}(r) r^3 dr. \quad (25)$$

[The energy-derived MSA compressibility factor has a different form, see Eq. (39) of Ref. 2.] While it was reasonable to assume that the change in the RDF produced by the addition of one molecule did not alter ϕ_{ij} significantly, the same cannot be presumed for ψ_{ij} . Such an addition would have considerable effect on both the RDF contact value, $g_{ij}(\sigma_{ij})$, and the integral in Eq. (25), as $\phi'_{ij}(r)$ changes much faster with distance than $\phi_{ij}(r)$. Therefore the right-hand side in Eq. (23) must be calculated as follows:

$$\left[\frac{\partial(P'/kT)}{\partial N_i} \right]_{T,V,N_j} = \left[\frac{\partial(P'/kT)}{\partial N_i} \right]_{T,\eta,N_j} + \left(\frac{\partial \eta}{\partial N_i} \right)_{T,V,N_j} \left[\frac{\partial(P'/kT)}{\partial \eta} \right]_{T,x}, \quad (26)$$

where

$$\left[\frac{\partial(P'/kT)}{\partial N_i} \right]_{T,\eta,N_j} = \left(\frac{\partial x_1}{\partial N_i} \right)_{N_j} \left[\frac{\partial(P'/kT)}{\partial x_1} \right]_{T,\eta} = \left(\frac{\partial x_2}{\partial N_i} \right)_{N_j} \left[\frac{\partial(P'/kT)}{\partial x_2} \right]_{T,\eta}. \quad (27)$$

TABLE VIII. Relation between chemical potential and energy derivatives.

Mixture	<i>x</i> ₁	<i>η</i>	MC		MSA		MC		MSA	
			$\frac{\partial(\mu_1^c/kT)}{\partial(kT)}$	$-(kT)^{-2} \frac{\partial U^c}{\partial N_1}$	$\frac{\partial(\mu_1^c/kT)}{\partial(kT)}$	$-(kT)^{-2} \frac{\partial U^c}{\partial N_1}$	$\frac{\partial(\mu_2^c/kT)}{\partial(kT)}$	$-(kT)^{-2} \frac{\partial U^c}{\partial N_2}$	$\frac{\partial(\mu_2^c/kT)}{\partial(kT)}$	$-(kT)^{-2} \frac{\partial U^c}{\partial N_2}$
M1	0.25	0.34	3.997	4.142	4.155	4.084	7.136	7.352	7.322	7.182
	0.25	0.44	5.280	5.481	5.197	5.385	9.711	9.495	9.172	9.283
	0.50	0.34	4.049	4.023	4.078	3.980	7.320	7.180	7.218	7.025
	0.50	0.44	5.094	5.315	5.068	5.228	9.826	9.234	8.987	9.058
	0.75	0.34	4.028	3.893	3.977	3.847	7.139	6.924	7.076	6.819
	0.75	0.44	4.175	5.098	4.908	5.033	5.196	8.924	8.757	8.776
M2	0.25	0.30	1.489	1.604	1.577	1.582	4.524	4.671	4.637	4.545
	0.25	0.40	2.184	2.231	2.152	2.196	6.558	6.203	6.248	6.098
	0.50	0.30	1.676	1.704	1.696	1.680	4.738	4.673	4.770	4.595
	0.50	0.40	2.322	2.360	2.301	2.326	5.928	6.253	6.388	6.158
	0.75	0.30	1.904	1.869	1.895	1.846	5.109	4.724	4.994	4.672
	0.75	0.40	2.522	2.573	2.550	2.541	7.571	6.327	6.642	6.253

Evaluating the derivatives of the mole fractions and the packing fraction with respect to N_i , and taking the results of Eqs. (26) and (27) to Eq. (23) one gets

$$\eta \left[\frac{\partial(\mu_i'/kT)}{\partial\eta} \right]_{T,x} = \frac{x_j}{\rho} \left[\frac{\partial(P'/kT)}{\partial x_i} \right]_{T,\eta} + \frac{\pi}{6} \sigma_{ij}^3 \left[\frac{\partial(P'/kT)}{\partial\eta} \right]_{T,x}, \quad (28)$$

where $i \neq j$. Table IX gives values for both sides of this equation, or of Eq. (23). The values of η and ρ outside the derivatives correspond to the average density. The calculation of the pressure derivative with respect to composition was based on the difference between two successive x_1 values; except for $x_1 = 0.50$, where the differences centered in this composition were used. The agreement between the MC chemical potential and pressure derivatives is generally similar to that for the "control" MSA values. Given the parallelism between the MC and MSA pressure derivatives, one would expect an analogous equivalence between the chemical potential derivatives. That is generally the case. There are, however, two clear exceptions, corresponding to the larger component in mixture M1 at $x_1 = 0.75$. Table II shows that the problem lies in the chemical potentials at the higher packing fraction, $\eta = 0.44$. Since the energy and pressure values for these points seem entirely correct, there is no reason to doubt the validity of these MC runs. Perhaps these conditions require a more careful determination of the chemical potentials, using more than one nonoverlapping point per trajectory and more than one trajectory per configuration. It may also be that these points are slightly beyond the density range where the method of insertion trajectories is reliable. In this case the method of Deitrick *et al.*¹¹ that constructs the excluded volume (encompassing the whole space) map is expected to be more accurate.

In summary, from the analysis of standard deviations, energy differences with respect to the MSA, and internal consistency of the MC properties, it can be concluded that the values given in Tables I and II correspond to converged

systems and adequate sample sizes, and that the MC results are generally reliable, with clear exceptions only for the chemical potentials in mixture M1 at the maximum packing fraction $\eta = 0.44$ and mole fraction $x_1 = 0.75$ (the maximum density considered in this work). For these exceptions, Tables VIII and IX show that the MSA μ_i' are probably more accurate than the MC chemical potentials, because they produce cross derivatives in better agreement with the MC energy and pressure results.

V. CONCLUSIONS

Extensive Monte Carlo (MC) simulations have been carried out for two multi-Yukawa mixtures previously studied in the MSA by means of a quasianalytic Yukawa-MSA algorithm.² Through these molecular simulations, the energy, pressure, and chemical potentials have been determined for a variety of composition, density, and temperature points. These points have been chosen to constitute a representative array of dense fluid conditions. The efficient determination of chemical potentials at these conditions has been made possible by a new implementation of Widom's test particle method.⁸ New procedures also have been devised to determine the reliability of the MC results. These procedures have given credence to the MC data presented by this work. Unreliable values were found only for the chemical potentials at the highest density considered.

The Monte Carlo results were used to evaluate the quantitative accuracy of the MSA thermodynamic properties. The good general agreement between the two sets of values indicates that the MSA can describe realistic interaction potentials with considerable accuracy, for both pure components and mixtures. In particular, this work establishes—for the first time—the accuracy of the MSA for the representation of fluids with repulsive (though not positive) interactions, and also for the determination of chemical potentials in mixtures. Moreover, the accuracy of the MSA is found to be independent of the character (ideal or nonideal) of the mixtures it describes.

TABLE IX. Relation between chemical potential and pressure derivatives.

Mixture	x_1	T	MC		MSA		MC		MSA	
			$\frac{\partial(\mu_1'/kT)}{\eta \partial\eta}$	$\frac{N}{\rho} \frac{\partial(P'/kT)}{\partial N_1}$	$\frac{\partial(\mu_1'/kT)}{\eta \partial\eta}$	$\frac{N}{\rho} \frac{\partial(P'/kT)}{\partial N_1}$	$\frac{\partial(\mu_2'/kT)}{\eta \partial\eta}$	$\frac{N}{\rho} \frac{\partial(P'/kT)}{\partial N_2}$	$\frac{\partial(\mu_2'/kT)}{\eta \partial\eta}$	$\frac{N}{\rho} \frac{\partial(P'/kT)}{\partial N_2}$
M1	0.25	1.40	9.604	10.181	9.314	10.082	10.950	10.281	10.382	10.691
	0.25	1.70	11.106	11.534	10.533	11.270	13.962	13.028	12.546	12.824
	0.50	1.40	11.039	11.652	10.742	11.201	12.831	13.330	12.484	12.827
	0.50	1.70	12.261	12.758	11.901	12.341	15.763	15.265	14.554	14.866
	0.75	1.40	13.190	13.273	12.588	12.839	18.222	16.680	15.195	15.967
	0.75	1.70	13.362	14.638	13.677	13.918	15.949	18.750	17.162	17.884
M2	0.25	1.70	2.995	3.713	3.110	3.866	4.549	4.382	4.839	4.945
	0.25	2.10	3.969	4.784	3.915	4.726	7.396	7.196	7.095	7.160
	0.50	1.70	3.898	4.277	3.822	4.246	8.208	7.391	7.251	7.317
	0.50	2.10	4.802	5.210	4.669	5.110	9.874	9.660	9.516	9.539
	0.75	1.70	5.375	5.183	5.230	5.210	11.653	12.691	11.819	12.799
	0.75	2.10	6.240	6.240	6.147	6.078	15.100	15.589	14.127	15.218

However, much more work is required to determine statistical efficiency, i.e., cost function weighting precision against computational cost of estimated property. Nature of correlation decays of Monte Carlo variables need to be revealed in a systematic way.¹⁸ Validity of estimates as functions of run "time," block length, and decay time of correlation needs to be systematically studied. Investigating main sources of error will help to develop more accurate Monte Carlo algorithms.

The combination of computational convenience and accuracy in the treatment of realistic dense fluid mixtures makes the quasianalytic Yukawa-MSA algorithm a most promising tool for the use of statistical mechanics in practical, engineering applications.

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