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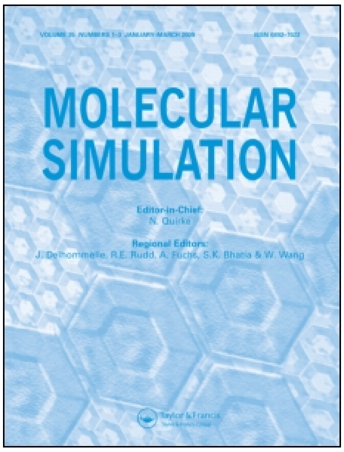

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A Grand-Canonical Ensemble Monte Carlo Study of the Effects of Change of Core Size on the Thermodynamic Properties of a Modified Lennard-Jones Fluid

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A GRAND-CANONICAL ENSEMBLE MONTE CARLO STUDY OF THE EFFECTS OF CHANGE OF CORE SIZE ON THE THERMODYNAMIC PROPERTIES OF A MODIFIED LENNARD-JONES FLUID

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It is shown by consideration of the fundamental theory that when dealing with potentials having hard cores the Grand Canonical Ensemble Monte Carlo (GCEMC) method should not introduce large errors of the type previously found in the use of the Shing-Gubbins (SG) method for estimation of the chemical potential. This is confirmed by making simulation runs using the GCEMC and the Canonical Ensemble Monte Carlo (CEMC) methods on similar systems having the hard-core Lennard-Jones intermolecular potential. Only when the hard-core parameter (α) (where the hard-core diameter is $\alpha\sigma$, σ being the Lennard-Jones length parameter) is increased from 0.9 to 0.95 are appreciable changes in density and reduced potential energy (for a given μ) found. Corresponding, though much larger, changes in the fluctuations quantities $f_{NN}(=\langle N^2\rangle - \langle N\rangle^2)$ and $f_{NU}(=\langle NU_N\rangle - \langle N\rangle\langle U_N\rangle)$, though not in f_{NU}/f_{NN}, also occur.

Keywords: Grand Canonical Monte Carlo methodology; hard core potential; fluctuations

1. INTRODUCTION

The Grand Canonical Ensemble Monte Carlo (GCEMC) method [1] has been used in a wide range of applications [2, 3]. The essential feature which distinguishes this technique from the more common Canonical Ensemble Monte Carlo (CEMC) method is that the chemical potential μ (or the activity z, where $\mu = \mu^\circ + kT \ln z$ and $\mu^\circ = kT \ln \Lambda^3, \Lambda$ being the thermal wave-length), is fixed and the number of particles N is allowed to vary, this

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being achieved by permitting creation and destruction of the particles. In GCEMC equilibration is reached when the rates of successful creation ($N-1 \Rightarrow N$) and destruction ($N \Rightarrow N-1$) moves are statistically in balance, although there will, of course, be fluctuations of N about this balance point. If there were to be an error in the formulation of either one of these two processes then an error in the estimated equilibrium value of N would obviously ensue.

In a recent paper [4], hereafter referred to as I, it has been shown that the usual implementation of the Shing-Gubbins method [5] for the estimation of the chemical potential from a CEMC simulation is in error if the intermolecular potential contains a hard-core component, whether explicit or implicit. (This had previously been suspected in studies of molecular dynamics simulations [6], though because of the more awkward ensemble involved in that method a proper quantitative reconciliation of the error found with the theory of that error was not obtained [7].) In I it was shown that

$$\exp[-\beta\mu] = \frac{Q_N}{Q_{N-1}} = \frac{V\int \delta_{\text{no}} \exp[-\beta U_{N-1}]\, d\tau^{N-1}\, d\tau_N}{N\int \exp[-\beta U_{N-1}]\, d\tau^{N-1}\, d\tau_N} \times \frac{\int \delta_{\text{no}} \exp[-\beta U_N]\, d\tau^N}{\int \delta_{\text{no}} \exp[-\beta U_{N-1}]\, d\tau^N} \tag{1}$$

where $\beta = 1/(kT)$, Q_N is the canonical partition function for N molecules at temperature T and volume V, $\delta_{\text{no}} = 1$ if there is no core overlap between the Nth and the remaining $N-1$ particles, otherwise $\delta_{\text{no}} = 0$; $d\tau^{N-1}$ and $d\tau^N$ indicate integration over the first $N-1$ particles and over all the N particles, respectively; and $d\tau_N$ indicates only over positions of the Nth particle. This leads to the result that

$$\mu = \mu^{\ominus} + kT \ln \rho - kT \ln\langle f_{\text{no}}\rangle + \mu'_{\text{SG}} \tag{2}$$

where

$$\mu'_{\text{SG}} = kT \ln \langle \exp [\beta U_N]\rangle'_{\text{SG}}$$

and $\langle f_{\text{no}}\rangle$ is the mean value of the fraction of successful attempts in trial insertions of a hard sphere with the appropriate core diameter into the system of $N-1$ particles averaged over the Boltzmann-weighted arrays of the $N-1$ particles. The term $\langle\rangle_{SG}$' is the value of the Shing-Gubbins average evaluated as it is done in practice, i.e. with some important terms omitted (see I).

With the aid of equation (2) it was shown that the error could be quantitatively explained for a system composed of Lennard-Jones molecules having a hard core ($u_{ij}=\infty$ if $r_{ij}<\sigma_{hc}=\alpha\sigma$) provided that α was sufficiently large ($\geqslant 0.875$ for $T^*=1$); for lower values of the core size parameter α the estimation of the chemical potential suffered from "poor statistics", in that some extremely rare events (close molecular encounters) would each make a large contribution to the estimate (these events are so rare that they do not occur at all in almost all runs of accessible length). The Widom method for the chemical potential [8,9] can also suffer from "poor statistics" of a kind rather similar to that described above; however, it does not incur any error corresponding to the systematic error which is the only source of error in the SG method for $\alpha\geqslant 0.875$ (see I). It turns out that, in order to avoid number overflow problems, workers usually impose a core-size in this upper range or make some equivalent assumption. It is shown in I that the systematic error in the SG method can, however, be readily calculated, and corrected for, during the same simulation which produces the normal, but erroneous, SG estimate of the chemical potential.

Returning to the discussion of the GCEMC procedure, we note that its creation and destruction processes are similar, respectively, to the Widom and the Shing-Gubbins procedures for the chemical potential. Since the normal implementation of the SG procedure contains a serious error, this suggests that the destruction process of GCEMC may be in error also, and this would then lead to a shift of the value of N at which balance is achieved. It is the main purpose of this paper to examine whether such errors do occur in GCEMC. It may, of course, be argued that normal GCEMC procedures have been in use for many years and no suggestion has been made of serious errors in the results produced. However, reliance on such an argument seems to be very dangerous in view of the importance of being *sure* of the validity of the technique, which is here checked by several different studies. Apart from the direct impact of errors in the GCEMC technique, failures in it would almost certainly be repeated in the particle exchange process of the Gibbs Ensemble Monte Carlo method [10].

In this paper, the statistical mechanical equations which form the theoretical basis of GCEMC are recalled, and it is shown that there *should* be no error corresponding to the very large systematic errors which occur in SG determinations as usually carried out.

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Tests were then made to see whether errors of any other kind were introduced into GCEMC results by the actual implementation, as distinct from the principles, of the method. (It will be recalled [4] that the failure of the SG method in CEMC in the case of potentials with a hard-core arises not from the principles of the method, which were shown to be exactly true [5], but from the implementation.) To this end, GCEMC runs for two values of the chemical potential and four values of the core parameter α were then carried out and the results compared with those for the corresponding CEMC simulations with the same density [4]. In addition, two fluctuation quantities, which were chosen because of their tendency to be very sensitive to small changes in method, were examined.

A change of the core-size parameter α is, of course, a change of the physical system, but it is usual to assume that the consequent changes in the values of the thermodynamic properties, if correctly calculated, would be negligible. The final investigation was of the validity of this assumption.

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2. THE FUNDAMENTALS OF THE GCEMC METHOD

The basic principles of GCEMC have been examined in a general way previously [3]. These principles are here re-examined for the particular case of the hard-core Lennard-Jones potential used in I, lest there is some way in which the proofs of validity previously given should be inapplicable in the present situation. A case of this kind was discussed in I.

The potential energy of interaction (u_{ij}) for a pair of particles a distance apart r_{ij} is taken to be

$$\begin{aligned} u_{ij} &= \infty && \text{for} \quad r_{ij} < \alpha\sigma \\ &= 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] && \text{for} \quad \sigma \leqslant r_{ij} < r_{\mathrm{co}} \\ &= 0 && \text{for} \quad r_{\mathrm{co}} < r_{ij} \end{aligned} \tag{3}$$

where r_{co} is known as the cut-off distance.

For the creation attempts the criterion of acceptance may be formally written as

$$\xi \leqslant \min\left\{1, \frac{zV}{N+1}\exp\left[-\beta(U_{N+1,j} - U_{N,i})\right]\right\} \tag{4}$$

where ξ is a random number on the interval 0 to 1

$$\beta = (kT)^{-1}$$

$$z = \exp(\beta\mu)\,\Lambda^{-3}$$

$\Lambda =$ the thermal wave-length $= h(2\pi mkT)^{-1/2}$

V is the volume

and $U_{N+1,j}$ and $U_{N,i}$ are the potential energies of systems, respectively, with $N+1$ particles and in the j-th state and with N particles and in the i-th state.

Correspondingly, for destruction attempts the criterion for acceptance is

$$\xi \leqslant \min\left\{1, \frac{N}{zV}\exp\left[\beta(U_{N+1,j} - U_{N,i})\right]\right\} \tag{5}$$

This is the standard algorithm. Would any errors or difficulties arise if it were applied to a system of particles interacting according to the intermolecular potential of equation (3)?

For a creation step causing a core overlap $\Delta U_N = \infty$, and so the r.h.s. of equation (4) would be zero, and the proposed creation would necessarily be rejected. Likewise, for a destruction step involving the removal of a core overlap $\Delta U_N = \infty$ and therefore the r.h.s. of equation (5) would be ∞, and according to equation (5) the proposed change would be accepted. Thus it is clear that the normal implementation of GCEMC behaves entirely correctly with respect to hard-core overlaps: no configuration containing one or more overlaps would ever be the current state. The question that now arises is, How can this observation be reconciled with the fact that for the same type of hard-core potential the normal SG method, which is similar to a destruction trial in GCEMC, fails to give the correct answer [4]?

Consider now the equilibrium between those GCE states referred to in equations (4) and (5). The probabilities of finding the system in these particular states are written as *prob*$[N, i]$ and *prob*$[N+1, j]$, respectively. According to equation (4) the probability in one attempt of a transition from a particular N state to a particular $N+1$ state is

$$\text{prob}[N,i]\,\frac{\delta\tau_{N+1}}{V(N+1)}\min\left[1, \frac{zV}{N+1}\exp\left[-\beta\Delta U_N\right]\right] \tag{6}$$

where $\Delta U_N = U_{N+1,j} - U_{N,i}$

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$\delta\tau_{N+1}$ is the element of configuration space within which the $(N+1)$-th particle is known to be (this is the smallest definable element of space as determined by the computer) and the factor $1/(N+1)$ outside the argument of *min* represents the chance that the additional molecule is inserted in a particular position in the already existing sequence of N molecules.

The probability of the reverse process is, likewise,

$$\text{prob}[N+1,j]\,\frac{1}{N+1}\min\left[1,\frac{N+1}{zV}\exp[\beta\Delta U_N]\right] \tag{7}$$

Equating the probabilities of the forward and backward transitions leads to

$$\frac{\text{prob}\,[N+1,j]}{\text{prob}\,[N,i]}=\frac{z\,\delta\tau_{N+1}}{N+1}\exp[-\beta\Delta U_N] \tag{8}$$

whether $zV\exp[-\beta\Delta U_N]/(N+1)$ is $<\,=$ or >0.

Taken with the fact that equation [8] can readily be derived from consideration of the Grand Partition Function written as

$$\Xi=\sum\frac{z^N}{N!}\int\exp[-\beta U_N]d\tau^N \tag{9}$$

this provides the standard justification of the GCEMC method.

Now consider the potential energy of equation (3) as the limit of a potential energy with $u_{ij}=\varepsilon$ for $r<r_{hc}$ as $\varepsilon\rightarrow\infty$. Suppose that in state $N+1,j$ there is a core overlap and that the state N,i has no core overlaps. Then $\Delta U_N=\sim\varepsilon$, where ε is large but not infinite. Equation (8) then gives

$$\frac{\text{prob}\,[N+1,j]}{\text{prob}\,[N,i]}=\sim\frac{z\,\delta\tau_{N+1}}{N+1}\exp[-\beta\varepsilon] \tag{10}$$

Taking the limit as $\varepsilon\rightarrow\infty$, this leads correctly to $prob[N+1,j]=0$. Thus it can be seen that there should be no discrepancy of the kind found for the SG procedure between the actual implementation and the statistical mechanical treatment of the GCEMC. (It will be recalled (see I) that the discrepancy found for the SG procedure between the actual implementation and the statistical mechanical treatment was clearly exposed when the potential function with hard core was considered as the limiting case of a potential with a large, but finite, potential for overlaps.)

In the Introduction (§1) the observation was made of the similarity between the Widom and the normal form of the SG methods for the evaluation of the

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chemical potential, on the one hand, and the creation and destruction procedures of GCEMC, on the other. Yet, it has now been shown that whereas the normal implementation of the SG method gives grossly incorrect values with the intermolecular potential of equation (3), the creation-destruction procedures of GCEMC together should lead to correct results for the same potential. What is the essential difference between the two pairs of procedures? An essential difference is that, whereas in GCEMC for the potential of equation (3) it is perfectly correct for states with overlapping cores never to be accepted, it is necessary in order to obtain correct values of chemical potential from the SG method to consider particle removal from some states having core overlap, even though such states would never be the current state in either CEMC or GCEMC simulation. Apart from the detailed correction given in I for this error in normal SG evaluations, there was also given there a brief verbal explanation. This was as follows. Consider the simple hard-core potential as the limiting case of a potential which was very large (ε), though non-infinite, at distances less than the core-diameter. The probability of occurrence of a simple core overlap is a very small quantity $\sim \exp[-\beta\varepsilon]$. However, when virtual elimination of the overlapping particle is considered in the SG procedure there is a further contributary factor of $\sim \exp[\beta\varepsilon]$. The overall contribution from such occurrences is, therefore, $\sim \exp[-\beta\varepsilon+\beta\varepsilon] = \sim 1$. When the limit as $\varepsilon \to \infty$ is taken the answer remains ~ 1 and is therefore not negligible. If such an argument is applied to the GCEMC situation then, with the core-overlap potential at ε, the chance of occurrence of the overlap would again be $\sim \exp[-\beta\varepsilon]$, which would be very small, though non-zero. At the first attempted move which, if accepted, would eliminate the overlap, there would be a very high chance (nearly 1) of acceptance. So the overlap would have only a very small chance of being created and would exist for only a very short time. As $\varepsilon \to \infty$ the chance of occurrence of the overlap $\to 0$ and the life-time would also $\to 0$. During these limitingly short sojourns in the overlapping state there would not be any correspondingly large contributions to the sum from which $\langle N \rangle$ is obtained. This may be summarised as follows. In SG the small negative exponential factor is multiplied by a factor with a corresponding large positive exponential factor; in GCEMC the chance of acceptance of the destruction, and consequently the second factor, is limited to being very close to 1. Therein lies the essential reason why it would be expected that the normal GCEMC would not be subject to severe errors for the hard-core Lennard-Jones potential of equation (3), even though it is known that the normal SG procedure does experience such problems.

Thus a convincing argument has been presented that the normal GCEMC method is valid for hard-core potentials of the type of equation

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(3). However, it must be remembered that, what appeared to be a convincing argument for the validity of the normal SG method was presented [5], yet it ignored the common misimplementation which was only shown up by careful comparison of results from the normal SG method with those from the more securely based Widom method [8]. Implementation of the GCEMC algorithm for the potential of equation (3) is now examined to test whether there are any errors, large or small, which may have escaped the theoretical analysis of §2.

3. METHOD

The starting configuration was in each case the empty box, the size of the system being chosen so that the equilibrium number of particles would be ~ 500. The acceptance rates for translational, creation and destruction moves were $\sim 28\%$, $\sim 1.9\%$, and $\sim 1.9\%$, respectively when $\rho^* \approx 0.635$, and $\sim 26\%$, $\sim 0.3\%$ and $\sim 0.3\%$ when $\rho^* \approx 0.75$.

In addition to $\langle N \rangle$ and $\langle U_N \rangle$, which were needed for the test of consistency with the CEMC results [4], values for the fluctuation quantities $f_{NN} = \langle N^2 \rangle - \langle N \rangle^2$ and $f_{NU} = \langle NU_N \rangle - \langle N \rangle \langle U_N \rangle$ were collected. These were examined because it was felt that they might be more sensitive to errors or to real changes brought about by alterations in the core size parameter α. These quantities are, of course, also related to the isothermal compressibility and an energy of vaporisation, respectively, and so do have immediate application. Furthermore, the corresponding quantities for adsorption systems provide the main route for obtaining isosteric heats of adsorption [2].

In order that the results can be directly compared with those obtained and reported for the CEMC results in I, no long-range corrections were applied. This is because the present paper is concerned with the testing of the methodology, rather than with attempting to reproduce experimental or other data for which the inclusion of long-range contributions would have been necessary.

4. RESULTS AND DISCUSSION

Throughout this paper all lengths and energies are given in units of σ and kT, respectively. Results obtained from GCEMC simulations at two activities chosen from a knowledge of the chemical potentials calculated in I so as to give fluids of reduced density ~ 0.65 and ~ 0.75, respectively, are given in

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Table I. For the four runs at the lower activity the cubic simulation box was of edge (9.235) such that the number of particles would be ~ 500; for the same reason the box edge for the runs at the higher activity was 8.805.

Table II shows CEMC results on systems with $N=512$ and the same final density as four of the eight runs for which results are presented in Table I. Values of the residual chemical potential as obtained by the Widom and the Modified Shing-Gubbins methods (see I), together with the components which make up the latter, are shown. In column 9 are given the values of the residual chemical potential equivalent to the activity used in the GCEMC runs of Table I which resulted in mean densities identical to the fixed densities used in these CEMC runs. If the GCEMC method is free from errors these values should be equal to those obtained by the CEMC + Widom (μ_w) and, for $\alpha=0.95$ but not for $\alpha=0.7$, by the CEMC + Modified Shing-Gubbins ($\mu_{SG}' + \Delta\mu$) methods. The discrepancies found

TABLE I GCEMC results for the number density (ρ^*), mean potential energy per molecule ($\langle U_N\rangle/\langle N\rangle\varepsilon$) and $\kappa_T kT/V = [\langle N^2\rangle - \langle N\rangle^2]/\langle N\rangle^2$ for two activities and four values of the core diameter parameter (α)

α	$\langle N\rangle$	ρ^*	$-\frac{\langle U_N\rangle}{\langle N\rangle\varepsilon}$	$10^4 F_{NN}$	$10^3 F_{NU}$	$\frac{F_{NU}}{F_{NN}}\frac{\langle U_N\rangle}{\langle N\rangle\varepsilon}$	$\frac{Run}{10^6}$
z = 0.02928							
0.7	501.01	0.6361	4.1293	7.695	1.497	8.052	72
0.8	501.00	0.6361	4.1280	7.348	1.423	8.008	72
0.9	500.47	0.6354	4.1246	7.690	1.511	8.042	120
0.95	495.47	0.6291	4.1058	9.116	1.757	7.957	128
(all the above runs are for a cubic box of edge 9.235)							
z = 0.08649							
0.7	516.29	0.7563	4.8683	1.838	0.3545	9.446	65
0.8	515.86	0.7557	4.8653	1.830	0.3528	9.395	60
0.9	514.48	0.7537	4.8533	1.837	0.3506	9.243	68
0.95	512.67	0.7510	4.8854	1.364	0.2653	9.537	76
(all the above runs are for a cubic box of edge 8.805)							

TABLE II CEMC results on systems with $N=512$ and the same density as the final density in the corresponding runs by GCEMC. Comparison with the residual chemical potential used in the GCEMC simulations

α	ρ^*	$-\frac{\langle U_N\rangle}{\langle N\rangle\varepsilon}$	μ_w	μ_{SG}'	$\Delta\mu$	$\mu_{SG}'+\Delta\mu$	μ_{GCE}	δ_w	δ_{SG}	$\frac{Run}{10^6}$
0.70	0.6361	4.1262	−3.075	−6.594	1.499	−5.096	−3.078	−.003	-	16
0.95	0.6291	4.1127	−3.079	−7.224	4.161	−3.062	−3.067	+.012	−.005	12
0.70	0.7568	4.8715	−2.175	−7.500	2.080	−5.420	−2.169	−.001	-	21
0.95	0.7510	4.8834	−2.185	−8.766	6.608	−2.156	−2.161	+.024	−.005	20

respectively for ($\rho^* \approx 0.635$, $\alpha = 0.7$), ($\rho^* \approx 0.635$, $\alpha = 0.95$), ($\rho^* \approx 0.75$, $\alpha = 0.7$), and ($\rho^* \approx 0.75$, $\alpha = 0.95$) were -0.0034, $+0.0119$, -0.0006 and $+0.0199$ for μ_w and (2.0174), -0.0049, (2.7668), and $+0.0363$ for $\mu_{SG}' + \Delta\mu$. Values from the Modified SG method with $\alpha = 0.7$ are given in brackets because, as shown in I, the Modified SG method is not applicable for $\alpha \leqslant 0.875$ and so agreement with the GCEMC results would not be expected.

In Figure 1 the reduced density is plotted against the core parameter for each of the two activities for which GCEMC data were obtained. At the lower activity, which gives densities near to 0.635 there is very little change in ρ^* up to and including $\alpha = 0.9$; however, on increasing α to 0.95, ρ^* falls by $\sim 1.1\%$. The higher activity, giving densities of ~ 0.75, shows an accelerating fall-off over the whole range, the total fall being $\sim 0.7\%$. To convert these falls in density into equivalent falls in residual chemical potential we need to know $(\partial\mu^r/\partial\rho^*)_T$. From a plot of μ^r against ρ^*, using values taken from I and from unpublished work at higher densities, we find that $(\partial\mu^r/\partial\rho^*)_T$ is $\sim 4.0\,kT$ at $\rho^* = 0.635$ and $\sim 12.5\,kT$ at $\rho^* = 0.75$. We thence

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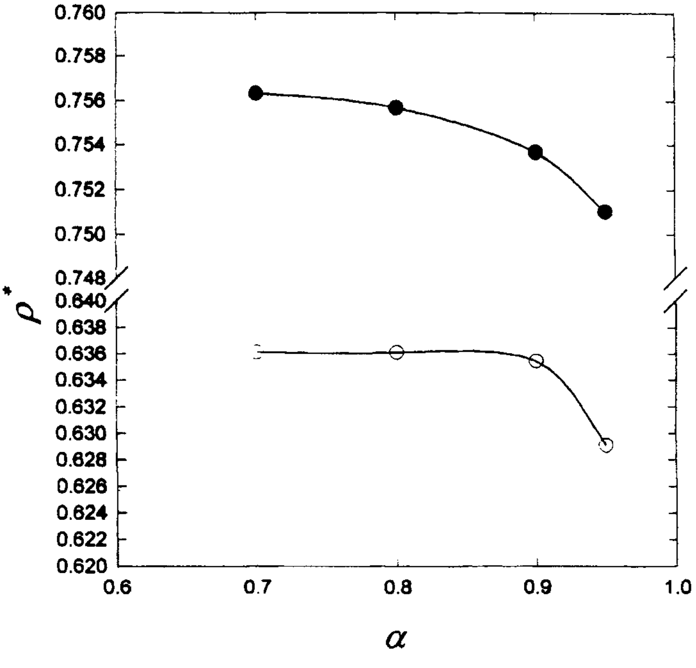

FIGURE 1 The reduced density ρ^* against the core parameter α for two activities. o: $z = 0.02928$; ●, $z = 0.08649$.

find that the total falls in ρ^* as α increases from 0.7 to 0.95 are equivalent to falls in μ^r of $\sim 0.04kT$ and $\sim 0.09kT$ for $\rho^* \approx 0.635$ and 0.75, respectively. Such changes in μ^r may be significant if, for example, accurate calculations of the vapour pressure of a dense fluid were being attempted. In that case, an error of 0.1 kT in the chemical potential of the dense phase would need a shift in the chemical potential of the gaseous phase of $0.1kT$ in order for equilibrium to be preserved. If, for simplicity, the gaseous phase is assumed to be an ideal gas, that phase would need to change its density by a factor f such that $kT \ln f = 0.1kT$ or $f \approx 1.1$. This represents a 10% change in vapour pressure. For many other purposes, however, the error of $0.1kT$ incurred on raising α to 0.95 would be acceptable.

Figure 2 shows plots of $\langle U_N \rangle / \langle N \rangle \varepsilon$ against α for the two activities. The behaviour at the lower activity is very similar to that shown in Figure 1 for ρ^*. There is a very slow decrease in $-\langle U_N \rangle / \langle N \rangle \varepsilon$ up to $\alpha = 0.9$, but a much more rapid decrease thereafter. The explanation for this decrease is essentially that it arises partly from the change in $\langle N \rangle$ described immediately above and partly directly from the change in α, these two effects being in opposition (see I). The magnitudes of these effects can be determined, respectively, from $(\partial U_N / \partial \rho^*)_{T^*,\alpha}$ taken with $\delta\rho^*$ and from the CEMC results

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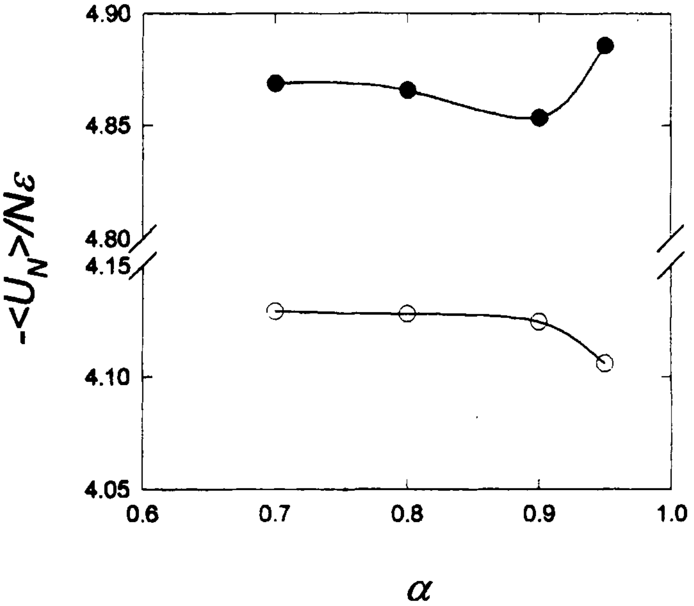

FIGURE 2 As Figure 1 but for the mean potential energy $\langle U_N \rangle$ per molecule (in units of ε).

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in I. At the lower density the fall in $-\langle U_N\rangle/\langle N\rangle\varepsilon$ of 0.043 due to the fall in density is partly offset by a direct rise of 0.035 due to the increase in α; at the higher density the fall in $-\langle U_N\rangle/\langle N\rangle\varepsilon$ of 0.029 due to the fall in density is more than compensated by the direct increase of 0.050 due to the increase in α. We have used here the interesting observation made in I that the direct effect of a rise in α is a rise in $-\langle U_N\rangle/\langle N\rangle\varepsilon$, that is a fall in the mean potential energy. As a fall in the corresponding free energy would be forbidden this requires that the direct effect of the change in α must include an entropy fall which is sufficiently large to more than compensate for the fall in the potential energy. (As the number of molecules is unchanged in the direct effect it would not include any change in kinetic energy.)

Figure 3 shows plots of the fluctuation quantities $F_{NN}=[\langle N^2\rangle-\langle N\rangle^2]/[\langle N\rangle^2]$ and $F_{NU}=[\langle NU_N\rangle-\langle N\rangle\langle U_N\rangle]/[\langle N\rangle\langle U_N\rangle]$ against the core parameter α for the two activities employed. Error bars were calculated by dividing the converged part of the run into 5–7 sections and determining the uncertainty in the overall mean from the variance of the values obtained for these sections; unfortunately, for two of the 18 points shown the required

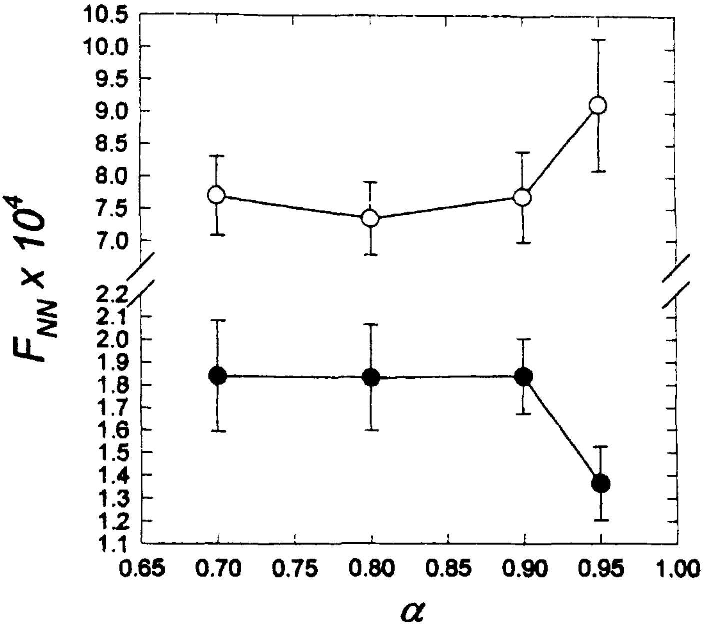

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FIGURE 3 The fluctuation quantities $F_{NN}=[\langle N^2\rangle-\langle N\rangle^2]/[\langle N\rangle^2]$ and $F_{NU}=[\langle NU_N\rangle-\langle N\rangle\langle U_N\rangle]/[\langle N\rangle\langle U_N\rangle]$ against the hard core parameter α for two activities. o, $z=0.02928$; ●, $z=0.08649$.

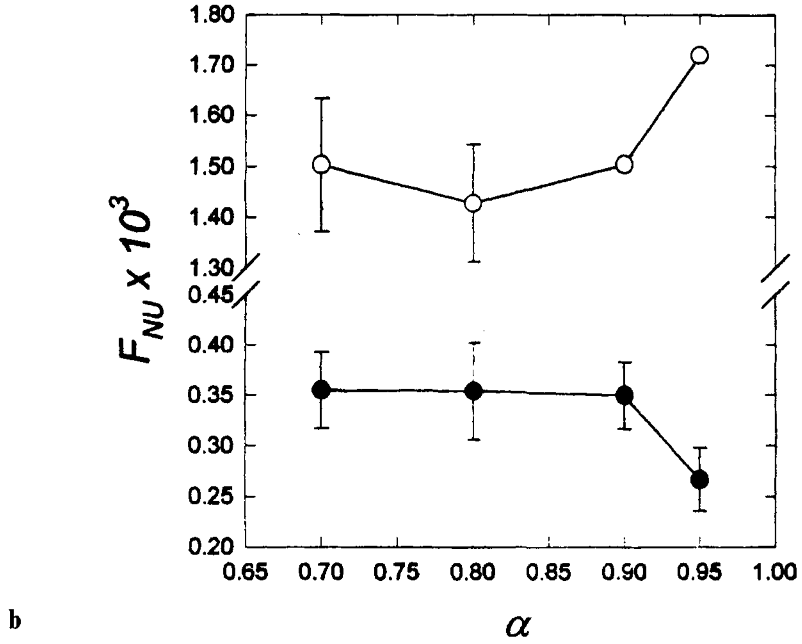

FIGURE 3 (*Continued*).

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intermediate data to enable this process to be carried out had not been saved. All four curves show behaviour which is similar to that found for $\langle N\rangle$ in that there is little change between $\alpha = 0.7$ and 0.9, but a large change between 0.9 and 0.95 ($\sim 20\%$, $\sim 30\%$, $\sim 20\%$, $\sim 32\%$ for F_{NN} for $z = 0.02928$ and 0.08649 and for F_{NU} for 0.02928 and 0.08649, respectively. These relative "shifts" are very much larger than the corresponding changes found for $\langle N\rangle$ (0.7–1.0%). It is also noteworthy that in this latter range of α for both fluctuation quantities the sign of the shift is different for the two activities.

In the Grand Ensemble it is easy to show that

$$\frac{\langle N^2\rangle - \langle N\rangle^2}{kT} = \left(\frac{\partial N}{\partial \mu}\right)_{T,V} \tag{11}$$

and that

$$\frac{\langle NU_N\rangle - \langle N\rangle\langle U_N\rangle}{kT} = \left(\frac{\partial\langle U_N\rangle}{\partial \mu}\right)_{T,V} = \left(\frac{\partial\langle U_N\rangle}{\partial N}\right)_{T,V}\left(\frac{\partial N}{\partial \mu}\right)_{T,V} \tag{12}$$

It follows that

$$\frac{\langle NU_N\rangle - \langle N\rangle\langle U_N\rangle}{\langle N^2\rangle - \langle N\rangle\langle N\rangle} = \left(\frac{\partial\langle U_N\rangle}{\partial N}\right)_{T,V} \tag{13}$$

From column 7 of Table I and Figure 4 it is seen that the variation in the left-hand side of equation (13) is only ~ 1.2% and ~ 3.2% over the full range of α for the lower and the higher density sets, respectively. Thus the anomalous behaviours of F_{NN} and F_{NU} are so similar that by virtue of their cancellation their ratio is virtually without anomaly, suggesting that the same effect is responsible for the anomalies in F_{NN} and F_{NU} (and, correspondingly, in f_{NN} and f_{NU}).

Considering first the fluctuations in N, and bearing in mind the statistical mechanical relationship:

$$F_{NN} = \frac{\langle N^2\rangle - \langle N\rangle^2}{\langle N\rangle^2} = \frac{\kappa_T kT}{V} \tag{14}$$

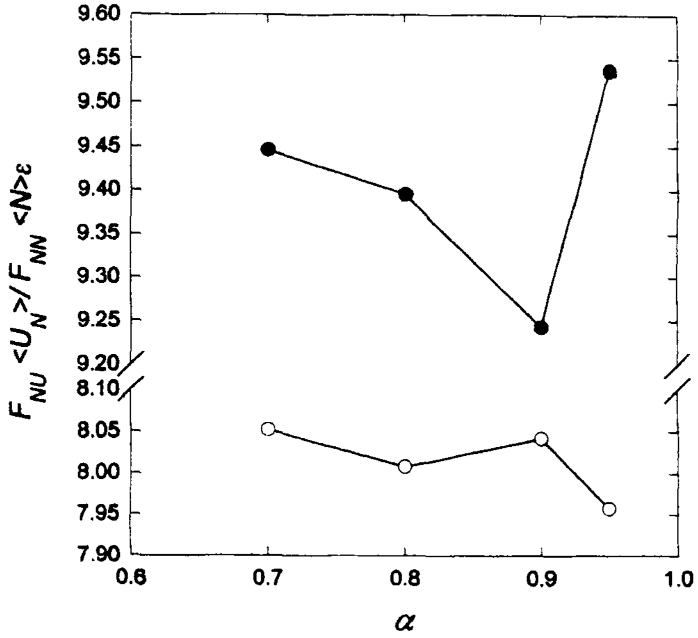

FIGURE 4 The ratio of F_{NU} to F_{NN} (normalised by $\langle N\rangle\varepsilon/\langle U_N\rangle$) against the hard core parameter α for two activities. o, $z = 0.02918$; ●, $z = 0.08649$.

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where κ_T is the isothermal compressibility, the behaviour between $\alpha = 0.9$ and 0.95 indicates that κ_T increases for the liquid of lower density and decreases for that of higher density. Certainly, at sufficiently high densities it would be expected that the compressibility would decrease as the core size is increased. The opposite shift at the lower density is counter-intuitive.

In the GCEMC simulations the change in κ_T as α increases towards 0.95 may be attributed to two effects. Firstly, there is the direct effect of the reduction in "softness" of the potential, which might be expected to reduce κ_T. Secondly, there is the effect which is associated with the change in density which accompanies the change in α at constant chemical potential. Thus

$$\left(\frac{\partial \kappa_T}{\partial \alpha}\right)_\mu = \left(\frac{\partial \kappa_T}{\partial \alpha}\right)_{\rho^*} + \left(\frac{\partial \kappa_T}{\partial \rho^*}\right)_\alpha \left(\frac{\partial \rho^*}{\partial \alpha}\right)_\mu \tag{15}$$

Figure 5 shows κ_T^* for the fluctuation computations versus the resultant density. The points are, of course, clustered in two regions corresponding to the two values of z_{act} for which simulations were carried out; within each of these clusters there is a spread of densities arising from the variation of α. To get a good estimate of the importance of the indirect effect a plot is also given for the widely used fitted equation for Lennard-Jones systems of Nicolas *et al.*, with the parameters of Johnson *et al.* (NJ) [11, 12]. The NJ equation refers to systems in which corrections have been made so that long-range interactions are included. These results are seen to be higher than the fluctuation results for all members of the "cluster" near $\rho^* = 0.63$; for the higher density "cluster" the NJ and the GCEMC results are in good accord for $\alpha = 0.7$–0.9, but not for $\alpha = 0.95$.

Results from the NJ equation were then adjusted so as to be appropriate for the system with a long-range cut-off at $r = 2.5\sigma$, as in the simulation studies performed here (see Appendix). This gave results ($\kappa_{T,\mathrm{NJ-lrc}}^*$) which were lower than the fluctuation values for all cases except that with $\rho^* \approx 0.75$, $\alpha = 0.95$. This suggests that the NJ equation provides quite a good qualitative explanation of the variations of κ_T^* observed. Turning to the direct effect of the change in α, it would be expected that this would cause the simulation results to fall below the corresponding $\kappa_{T,\mathrm{NJ-lrc}}^*$ values and to have a larger relative effect at the higher densities. Such a correction for $\rho^* \approx 0.75$, $\alpha = 0.95$ would tend to bring that point into accord with the points at lower values of α; inclusion of this effect would, however, tend to affect adversely the agreement at $\rho^* \approx 0.635$ although the changes might be very weak at that density. Results for κ_T^* from fluctuation computations

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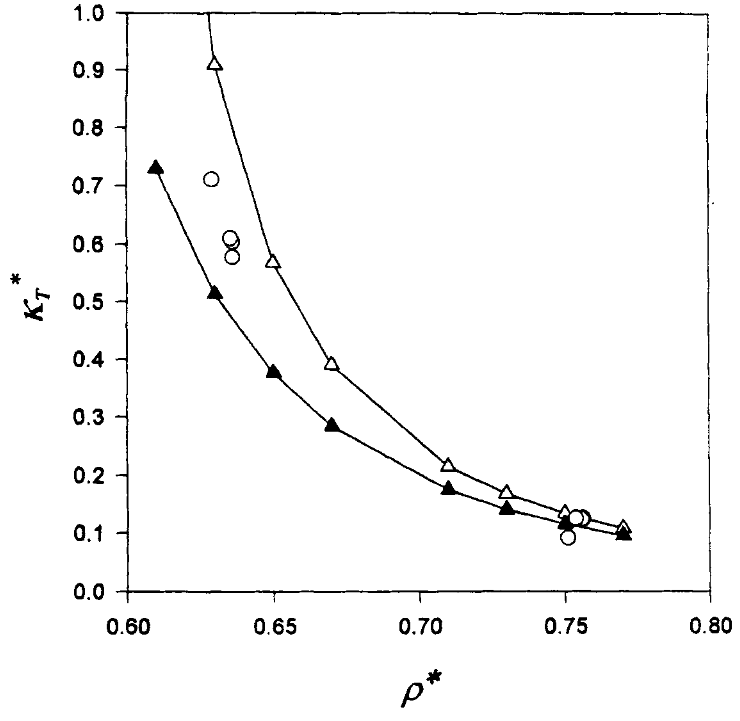

FIGURE 5 Reduced isothermal compressibility (κ_T^*) against reduced density (ρ^*). △, from NJ equation for LJ system: ▲, from NJ equation with contribution from long-range interactions deducted; o, GCEMC results for LJ system with long-range interactions omitted (present work).

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would thus appear to be consistent with the two effects (direct and indirect) proposed.

Figure 5 shows that the values of κ_T^* from the N-J equation are greatly altered as a result of the deduction of the long-range part of the interaction, although very little of this change is due to the repulsive interaction. The values from the GCEMC fluctuations lie between the (rather widely separated) curves for the N-J equation with and without long-range corrections. One possible explanation is that the Allen-Tildesley long-range method, which is of the mean-field type, overestimates the long-range correction. Another possible explanation is that in the region of $\rho^* \approx 0.635$ the N-J equation itself is incorrect, and indeed it is found that that equation gives a curve for P^* versus ρ^* which has a sigmoid shape and is nearly horizontal at that point (Fig. 6). Converting this behaviour into the effect on κ_T^*, it is found that κ_T^* is very large and has an unrealistic sigmoid shape.

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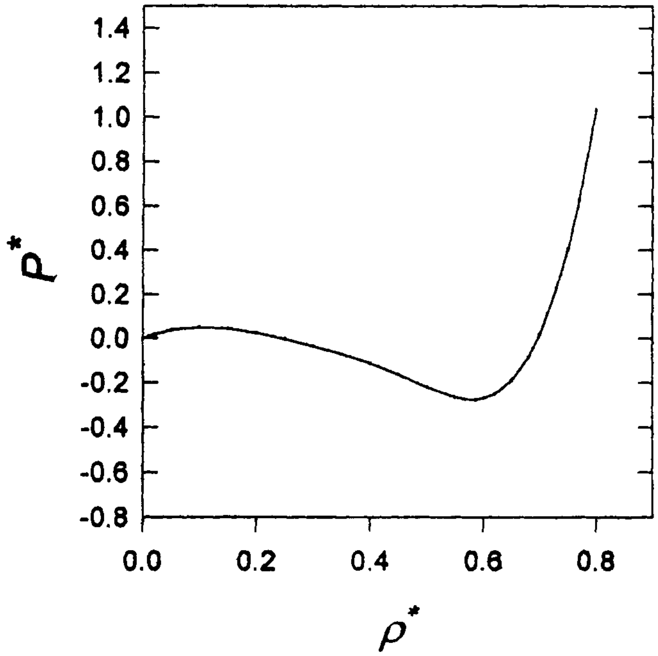

FIGURE 6 Reduced pressure-reduced density isotherm for $T^* = 1$ from NJ equation.

Thus a large part of the "anomaly" in $\kappa_T{}^*$ (and therefore in F_{NN} and, indeed, in F_{NU}, also) for the points near $\rho^* = 0.635$ can be explained in terms of the indirect effect of the change in α on the density, which in turn affects $\kappa_T{}^*$. At the higher densities ($\rho^* \approx 0.75$) the change in density would produce little change in $\kappa_T{}^*$ and, indeed, would act in the opposite direction to the observed fall in $\kappa_T{}^*$ as $\alpha \to 0.95$; the direct effect, due to the increase in repulsive interactions, would be expected to cause $\kappa_T{}^*$ to fall, as is observed.

5. CONCLUSIONS

It would appear that GCEMC simulation, at least as normally applied, does not contain the same type of error as was found for the Shing-Gubbins method. It would, therefore, seem unlikely that the exchange trials of the Gibbs Ensemble Monte Carlo are vulnerable to that type of error either.

As α is increased from 0.9 to 0.95 changes in the computed properties are observed which can be assigned to changes in the real Hamiltonian of the system. The changes in ρ^* at constant μ (or of μ at constant ρ^*), representing as they do departures from the behaviour of the simple Lennard-Jones potential (without a hard-core), may be acceptable as approximations to the properties of the simple Lennard-Jones in the majority of circumstances, though not where careful reproduction of high quality data is being attempted. The corresponding changes in κ_T and $(\partial U/\partial N)_{T,V}$, both obtained by fluctuation calculations, are, at first sight, far more significant (20–30%). However, at the lower activity at least this anomalous behaviour is largely accounted for by the change of density which accompanies the change in α in a GCEMC simulations.

APPENDIX

LONG RANGE CORRECTIONS TO κ_T FOR A LENNARD-JONES SYSTEM

As a starting point the equation for the long-range correction to the pressure given by Allen and Tildesley [3] is taken:

$$P_{\text{tot}} = P_{\text{tr}} - \frac{16\pi N^2\sigma^6\varepsilon}{3V^2 r_c^3} + \frac{32\pi N^2\sigma^{12}\varepsilon}{9V^2 r_c^9} \tag{A.1}$$

where P_{tot} and P_{tr} are the pressures for the systems with the total and the truncated Lennard-Jones potentials, respectively.

Differentiating equation (A.1) with respect to V at constant T yields

$$\left(\frac{\partial P_{\text{tot}}}{\partial V}\right)_T = \left(\frac{\partial P_{\text{tr}}}{\partial V}\right)_T + \frac{32\pi N^2\sigma^6\varepsilon}{3V^3 r_c^3} - \frac{64\pi N^2\sigma^{12}\varepsilon}{9r_c^9} \tag{A.2}$$

or

$$-\frac{1}{V\kappa_T} = -\frac{1}{V\kappa_{T,\text{tr}}} + \frac{32\pi N^2\sigma^6\varepsilon}{3V^3 r_c^3} - \frac{64\pi N^2\sigma^{12}\varepsilon}{9V^3 r_c^9} \tag{A.3}$$

$$\text{where } \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P_{\text{tot}}}\right)_T$$

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$$\kappa_{T,\mathrm{tr}} = -\frac{1}{V}\left(\frac{\partial V}{\partial P_{\mathrm{tr}}}\right)_T \tag{A.4}$$

Rearranging equation (A.3) yields

$$\kappa_{T,\mathrm{tr}} = \frac{1}{\dfrac{1}{\kappa_T} + \dfrac{32\pi\rho^{*2}\varepsilon}{3r_c^3} - \dfrac{64\pi\rho^{*2}\sigma^6\varepsilon}{9r_c^9}} \tag{A.5}$$

For $T^* = kT/\varepsilon = 1$, with which this paper is concerned, and writing equation (A.5) in units of kT and σ, this becomes

$$\kappa_{T,\mathrm{tr}} = \frac{1}{\dfrac{1}{\kappa_T} + \dfrac{32\pi\rho^{*2}}{3r_c^3} - \dfrac{64\pi\rho^{*2}}{9r_c^9}} \tag{A.6}$$

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