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Long-Range Corrections to Grand Canonical Ensemble Monte Carlo Calculations for Adsorption Systems

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Equations have been derived from which long-range corrections to molecular simulation results for both uniform and nonuniform systems can be calculated. An important feature in the latter is the distortion of the singlet distribution function which is a consequence of the finite system necessary for simulation. The theory has been applied to the calculation of long-range corrections in a physical adsorption system (12-6 Ar on "homogeneous" graphite at 120 K ($T^* = 1.002$)). The results of these calculations, using an augmented summation procedure with large cut off, are compared with those previously obtained using a faster standard procedure with small cut off. The greatest discrepancy was found when appreciable coverages occurred at distances from the surface larger than the cut-off distance; however, satisfactory accuracy can be achieved with the faster procedure for coverages less than about two statistical monolayers and no major modification to previous conclusions was found to be necessary.

1. INTRODUCTION

Molecular simulation calculations are usually carried out using a pair interaction potential with a finite cut off [1, 2]. The position of the cut off is determined by the size of the periodic cell and considerations of computation time needed to calculate the total pair interaction potential.

The machine averages are then corrected in an approximate manner to take account of the neglected long-range tail. Methods of applying this correction in the case of the canonical ensemble Monte Carlo [1] and molecular dynamics [2] calculations are well established and for liquid argon at $T^* \simeq 1$ and moderate pressures ($p^* \simeq 0.85$) with a pair potential cut off at about 2.5 atomic diameters the long-range correction [1] to the energy is of the order of 7 % and the correction to the pressure is about -0.56 reduced units. The estimated errors in the long-range correction terms are less than 2 % and 4 % for the energy and pressure, respectively.

In the grand ensemble (μ, V, T) MC calculations it is necessary to take account of the possible change of the long-range correction *at each step* in the simulation. This requirement was overlooked in earlier work on a homogeneous system [3] resulting in an apparent discrepancy between the grand ensemble results and those obtained by Hansen and Verlet [4] using a canonical ensemble method. Although it might appear natural to consider the correction to density at constant (μ, V, T) which results

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from these long-range effects, it is more convenient to determine instead the correction to μ necessary to maintain ρ and T constant. Barker and Miyazaki [5] have pointed out, and we have confirmed, that when this is done the discrepancy mentioned above is almost entirely eliminated. For nonuniform systems there is an additional problem because the long-range potential distorts the singlet distribution function.

The general problems arising for a nonuniform system are here illustrated by the case of a simple three-dimensional adsorption system involving a planar structure (continuum) adsorbent and a simple monatomic adsorbate. The adsorbate molecules interact with each other through a pairwise 12-6 potential and with the solid through a 9-3 potential acting normal to the surface. The results obtained for this system have already been described [6].

In Section 2 we give equations from which long-range corrections for the MC grand canonical ensemble calculations can be found. These are derived in a general form which is applicable to nonuniform as well as uniform systems. The singlet distribution function corrections are discussed in Section 3. The derived equations require several approximations and in Section 4 we examine the validity of these approximations by comparing the corrected results with those obtained from a more expensive augmented summation procedure [7] applied to a few selected points from the adsorption system previously examined [6].

2. GENERAL EQUATIONS FOR LONG-RANGE CORRECTIONS IN NONUNIFORM SYSTEMS

The full pair potential $\phi(r)$ is divided into the sum of a short-range part $\phi^{(0)}(r)$ and a long-range part $\xi\phi^{(1)}(r)$ where ξ is a coupling parameter which switches on the long-range part

$$\phi^{(0)}(r) \equiv [1 - H(R - r)]\, \phi(r), \tag{2.1a}$$

$$\phi^{(1)}(r) \equiv H(R - r)\, \phi(r), \tag{2.1b}$$

where R is the cut-off distance for the short-range potential and H is the Heaviside function.

The connection between the $\xi = 0$ system (short range only) and the $\xi = 1$ system (short range plus long range) is most readily made through the Helmholtz free energy (constant volume V, temperature T, and number of particles N).

A relation between the Helmholtz free energy $A^{(0)}$ of the $\xi = 0$ system and that of the $\xi = 1$ system, $A^{(0)} + A^{(1)}$ is obtained by the standard statistical mechanical technique of switching on the long-range part by increasing ξ, thus

$$A^{(1)} = \int_0^1 d\xi \langle U_N^{(1)} \rangle_{(N)}^{(\xi)} \tag{2.2a}$$

with

$$\langle X \rangle_N^{(\xi)} = \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \exp(-\beta U_N(\xi))\, X \Big/ \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \exp(-\beta U_N(\xi)), \tag{2.2b}$$

$$U_N(\xi) = U_N^{(0)} + \xi U_N^{(1)} + W_N^{(l)}, \tag{2.2c}$$

$$U_N^{(i)} = \sum_{k>j}^{N} \phi^{(i)}(r_{kj}), \qquad i = 0, 1, \tag{2.2d}$$

where $U_N^{(0)}$ and $U_N^{(1)}$ are the short- and long-range parts of the total pair potential energy, respectively. $\beta = 1/kT$ and $W_N^{(l)}$ is a potential associated with an external field which is the origin of the nonuniformity in the assembly of N molecules and which in our example is the molecule-wall potential.

Substitution of (2.2d) into (2.2b) and standard manipulation of the integrals leads to[1]

$$\langle U_N^{(1)} \rangle_N^{(\xi)} = \tfrac{1}{2} \int d\mathbf{s}_1\, d\mathbf{s}_2\, \rho_N(\mathbf{s}_1\,;\xi)\, \rho_N(\mathbf{s}_2\,;\xi)\, g^{(2)}(\mathbf{s}_1\,, \mathbf{s}_2\,;\xi)\, \phi^{(1)}(s_{12}) \tag{2.3}$$

where the singlet distribution $\rho_N(\mathbf{r}_1\,;\xi)$ is defined by

$$\rho_N(\mathbf{r}_1\,;\xi) = N \int d\mathbf{r}_2 \cdots d\mathbf{r}_N \exp(-\beta U_N(\xi)) \Big/ \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \exp(-\beta U_N(\xi)). \tag{2.4}$$

A mean field approximation to $A^{(1)}$ is obtained from (2.3) by setting $g^{(2)}$ to unity for $s_{12} > R$. If we also assume $\rho_N(\mathbf{s}_1\,;\xi) = \rho_N(\mathbf{s}_1\,;0)$ we obtain

$$A_{\mathrm{MF}}^{(1)} = \tfrac{1}{2} \int d\mathbf{s}_1\, d\mathbf{s}_2\, \rho_N(\mathbf{s}_1\,;0)\, \rho_N(\mathbf{s}_2\,;0)\, \phi^{(1)}(s_{21}). \tag{2.5}$$

Taking appropriate derivatives of the long-range part of the Helmholtz free energy $A^{(1)}$ the additive long-range corrections to the energy $U^{(1)}$, chemical potential $\mu^{(1)}$, and diagonal components of the pressure tensor $p_\alpha^{(1)}$ can be obtained.

$$U^{(1)} = A^{(1)} + \beta \left(\frac{\partial A^{(1)}}{\partial \beta} \right)_{V,N}, \tag{2.6a}$$

$$p_\alpha^{(1)} = -\frac{l_\alpha}{V} \left(\frac{\partial A^{(1)}}{\partial l_\alpha} \right)_{N,\beta,l_\gamma}, \qquad \alpha = x, y, z, \quad V = l_x l_y l_z\,, \quad \alpha \neq \gamma; \tag{2.6b}$$

$$\mu^{(1)} = \left(\frac{\partial A^{(1)}}{\partial N} \right)_{V,\beta}. \tag{2.6c}$$

In the evaluation of these derivatives correlations of the type

$$\langle Y^{(1)} X \rangle_N^{(\xi)} - \langle Y^{(1)} \rangle_N^{(\xi)} \langle X \rangle_N^{(\xi)} \tag{2.7}$$

were set equal to zero. Here X is a phase function, usually dependent primarily on the short-range part of the system, and $Y^{(1)}$ is dependent only upon the long-range part

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[1] *Notation.* Symbols $\mathbf{r}_i$, where i is a numerical subscript, refer to the location of labeled particles $1 \cdots N$. Unsubscripted $\mathbf{r} = (r_x\,, r_y\,, r_z)$ and subscripted s are used to denote continuous variables.

of the interaction. It is interesting to note that this assumption, although unstated, is commonly made in the computation of long-range corrections. The actual correlations involved are given in full in Eqs. (A1.2a), (A1.6), (A1.8), and (A2.5). It is reasonable to suppose that the relative fluctuation of the long-range component in (2.7), $Y^{(1)}$, will be very small and it is justifiable therefore to replace this component by a mean value which can be factored out of the first bracket. Further justification for this assumption comes, a posteriori, from the agreement between augmented sum and corrected data discussed below. From the equations of Appendix I we have therefore

$$U^{(1)} = N\mu^{(1)}/2 = A_{\mathrm{MF}}^{(1)}, \tag{2.8a}$$

$$p_\alpha^{(1)} V = -\tfrac{1}{2} \int d\mathbf{s}_1\, d\mathbf{s}_2\, \rho_N(\mathbf{s}_1\,;0)\, \rho_N(\mathbf{s}_2\,;0) \frac{\alpha_{21}^2}{s_{21}} \frac{d\phi^{(1)}(s_{21})}{ds_{21}}. \tag{2.8b}$$

Using Eq. (2.1b) for $\phi^{(1)}(r)$, (2.8b) can be written

$$p_\alpha^{(1)} = p_{\alpha l} - p_{\alpha\delta}, \tag{2.9a}$$

$$p_{\alpha l} V = -\tfrac{1}{2} \int d\mathbf{s}_1\, d\mathbf{s}_2\, \rho_N(\mathbf{s}_1\,;0)\, \rho_N(\mathbf{s}_2\,;0)\, H(R - s_{21}) \frac{\alpha_{21}^2}{s_{21}} \frac{d\phi(s_{21})}{ds_{21}}, \tag{2.9b}$$

$$p_{\alpha\delta} V = \tfrac{1}{2} \int d\mathbf{s}_1\, d\mathbf{s}_2\, \rho_N(\mathbf{s}_1\,;0)\, \rho_N(\mathbf{s}_2\,;0)\, \delta(R - s_{21}) \frac{\alpha_{21}^2}{s_{21}} \phi(s_{21}). \tag{2.9c}$$

The term $p_{\alpha\delta}$ arises from the differentiation of the Heaviside function. Note that $p_\alpha^{(0)}$, the pressure of the short-range $\xi = 0$ system is defined by

$$\begin{aligned} p_\alpha^{(0)} V &= -l_\alpha \left(\frac{\partial A^{(0)}}{\partial l_\alpha}\right)_{N,\beta,l_\gamma} \\ &= N/\beta - \left\langle \sum_{i>j}^{N} \frac{\alpha_{ij}^2}{r_{ij}} \frac{d\phi^{(0)}(r_{ij})}{dr_{ij}} \right\rangle_N^{(0)} - \left\langle \sum_i \boldsymbol{\alpha}_i \cdot \frac{d\psi_l(\mathbf{r}_i)}{d\mathbf{r}_i} \right\rangle_N^{(0)}. \end{aligned} \tag{2.10}$$

Here $\psi_l(\mathbf{r}_i)$ is the interaction of a molecule at $\mathbf{r}_i$ with the wall, i.e., $W_N^{(l)}$ in (2.2c) is $\sum_i \psi_l(\mathbf{r}_i)$ and using (2.1a) for $\phi^{(0)}$ we obtain

$$p_\alpha^{(0)} = p_\alpha^{(\mathrm{MC})} + p'_{\alpha\delta}, \tag{2.11a}$$

$$p_\alpha^{(\mathrm{MC})} V = N/\beta - \left\langle \sum_{j>i}^{N} \{1 - H(R - r_{ij})\} \frac{\alpha_{ij}^2}{r_{ij}} \frac{d\phi(r_{ij})}{dr_{ij}} \right\rangle_N^{(0)}, \tag{2.11b}$$

$$p'_{\alpha\delta} V = \left\langle \sum_{i>j}^{N} \delta(R - r_{ij}) \frac{\alpha_{ij}^2}{r_{ij}} \phi(r_{ij}) \right\rangle_N^{(0)}. \tag{2.11c}$$

The term $p_\alpha^{(MC)}$, defined by Eq. (2.11b), is the pressure calculated by molecular simulation methods using a truncated potential and the term $p'_{\alpha\delta}$ in Eq. (2.11c) is equal to $p_{\alpha\delta}$ of Eq. (2.9c) in the mean field approximation. Thus using Eqs. (2.10) and (2.11) the total pressure, $p_\alpha^{(0)} + p_\alpha^{(1)}$, for the full potential is given by

$$p_\alpha^{(0)} + p_\alpha^{(1)} = p_\alpha^{(MC)} + p_{\alpha l}\,. \tag{2.12}$$

We note for $\phi(r) \sim 1/r^6$ for $r \geqslant R$ that

$$(p_{xl} + p_{yl} + p_{zl})V = 6A^{(1)}. \tag{2.13}$$

3. The Singlet Distribution Function

In [4, Part I], where no long-range corrections were applied to the activity or distribution functions it was stated that the average density in the MC cell remote from the adsorbing surface was in good agreement with the density of the 12-6 gas (five virial coefficients) [8] at the activity. At low activities this implied that $\bar\rho_{\text{end}}(0)$ is equal to $Z(0)$, the activity $(2\pi\hbar^2\beta/m)\exp(\beta\mu)$ where

$$\bar\rho_{\text{end}}(\xi) = \frac{1}{aV}\int_{r_z > al_z} d\mathbf{r}\,\rho_N(\mathbf{r};\,\xi), \tag{3.1}$$

and a is a parameter in the range $(0.5 \leqslant a < 1)$ used to define the fraction of the box to be taken as comprising the "end."

However, for the thermodynamic and mechanical equilibrium of the adsorbate with the bulk gas it is required that $\bar\rho_{\text{end}}(1)$ should be equal to the density of the 12-6 gas at the activity $Z(1)$, i.e., for low activities $\bar\rho_{\text{end}}(1)$ should be equal to $Z(1)$. This implies that the long-range corrections must distort the singlet distribution function.

An approximate equation for $\rho_N(\mathbf{r};\,1)$ in terms of $\rho_N(\mathbf{r};\,0)$ is derived in Appendix II using the assumption of Eq. (2.7). From Eqs. (A2.7) and (3.1) we have

$$\begin{aligned}\bar\rho_{\text{end}}^{(1)} &= \bar\rho_{\text{end}}^{(0)}\{1 + \ln(Z(1)/Z(0))\}\\ &\quad - \beta(1/aV)\int d\mathbf{s}\,\rho_N(\mathbf{s};\,0)\int d\mathbf{s}_1\,\rho_N(\mathbf{s}_1\,;\,0)\,\phi^{(1)}(|\,\mathbf{s}_1 - \mathbf{s}\,|), \qquad r_z > al_z\,.\end{aligned} \tag{3.2}$$

It is clear that Eq. (3.2) gives the correct dependence of $\bar\rho_{\text{end}}(1)$ on $Z(1)$ at low activities $(\rho_N(\mathbf{r};\,0) \to 0,\ r_z > al_z)$ when the last term can be neglected. We then have for $Z((1)/Z(0) \simeq 1$,

$$\bar\rho_{\text{end}}(1) \simeq \bar\rho_{\text{end}}(0)\,Z(1)/Z(0), \tag{3.3}$$

which is the required result.

In the next section it will be shown that Eq. (3.2) gives the correct $\bar\rho_{\text{end}}(1)$ for higher activities when the gas is nonideal.

4. RESULTS FOR ADSORPTION

Periodic boundary conditions were imposed such that eight replicas of the MC box were generated contiguous to it in the xy plane, which is the plane parallel to the adsorbent surface. In [6] the cut-off distance for the pair potential was half of the side l_x of the cell and the minimum image method was used to calculate the pair interaction potential. In the new (L) results presented here the cut-off distance used was $3l_x/2$ and the pair interaction potential was calculated by summing the interaction of each particle with all the other particles and their eight images within the cut-off distance. This is the "augmented summation" procedure of Wood and Parker [7]. Long-range corrections are still necessary in these calculations but are very much smaller than those for the smaller box (cf. $\beta U^{(1)}/\mathscr{A}$ values in the table).

The details of the MC procedure and parameters for the Ar-homogeneous "graphite" system used are described in [6]. The final configurations for the runs 4, 6–8 at $T^* = 1.002$ from [6] were used as starting points for runs $4L$, $6L$, $7L$, and $8L$ reported in the table. The computing time for each configuration from these runs was a factor of about 1.7 greater than that for the original calculations, which required about 2.0 msec per configuration on a CDC 7600. $Z(0)$ was chosen using Eqs. (2.3) and (2.8a) with the $\rho_N(\mathbf{s}_1\,; 0)$ taken from the $l_x/2$ runs, so that it gave the same corrected activity $Z(1)$ using the cut-off $3l_x/2$ as the corresponding original $l_x/2$ cut-off run.

The table gives the number of configurations used for averaging, together with the coverage θ, and the uncorrected energy and layer coverages. The long-range corrections $Z(1)/Z(0) = \exp(\beta\mu^{(1)})$ and $U^{(1)}$ to the activity and energy were calculated using Eqs. (2.8a) and (2.5). The integral of Eq. (2.5) was simplified by using the fact that $\rho_N(\bar{r}; 0)$ is a function only of the distance r_z from the adsorbing wall and that $\phi^{(1)}(s_{21}) \simeq 4/s_{21}$ for $s_{21} > R$ giving

$$A_{\mathrm{MF}}^{(1)} = \mathscr{A}\pi \int ds_{z1}\, \rho_N(s_{z1}\,; 0) \left\{ \int_{|s_{z2}-s_{z1}|<R} ds_{z2}\, \frac{\rho_N(s_{z2}\,; 0)}{R^4} \right.$$

$$\left. + \int_{|s_{z2}-s_{z1}|<R} ds_{z2}\, \frac{\rho_N(s_{z2}\,; 0)}{(s_{z2} - s_{z2})^4} \right\}, \qquad \mathscr{A} = l_x l_y\,. \tag{4.1}$$

This integral was evaluated numerically using tabulated values of the grand canonical ensemble singlet distribution function from previous MC runs for $\rho_N(\mathbf{s}; 0)$ [6].

The quantity $\theta_t(i)$ in the table gives a measure of the coverage in the ith layer and was calculated with the assumption that each layer had the spacing of the (111) planes in fcc Ar at 0K. This choice for layer thickness differs from that used to calculate $\theta(i)$ in [6] and avoids the need to determine limits from minima in the singlet distribution which is particularly difficult for the outer layers at $T^* = 1.002$. The difference between $\theta_t(i)$ and $\theta(i)$ is more marked the greater the distance from the surface since layer structure no longer provides a very adequate description of the adsorbate.

Figure 1 shows the mean end density $\bar{\rho}_{\mathrm{end}}(0)$ plotted against $Z(0)$ for the runs 1–8 of [6]. This figure also illustrates the variation of $\bar{\rho}_{\mathrm{end}}(1)$ with $Z(1)$ for the runs 4,

TABLE I

Results for MC Runs at $T^* = 1.002$ and the Long-Range Corrections[a]

Run	$Z(0)/10^{-2}$	$Z(1)/10^{-2}$	States/10^6	$-\beta U^{(0)}/\mathscr{A}$	$-\beta U^{(1)}/\mathscr{A}$	$-\beta\langle W^{(1)}\rangle^*/\mathscr{A}$	θ	$\theta_t(1)$	$\theta_t(2)$	$\theta_t(3)$	$\theta_t(4)$	$\theta_t(5)$
45	1.168	1.093	2.25	11.93	0.05	7.54	1.769	0.900	0.512	0.158	0.038	0.020
4*L*	1.094	1.093	3.10	11.69	0.0007	7.39	1.724	0.884	0.496	0.153	0.038	0.019
6	1.635	1.504	1.75	13.99	0.09	7.77	2.272	0.902	0.654	0.343	0.111	0.045
6*L*	1.507	1.505	2.05	14.57	0.001	7.82	2.358	0.909	0.664	0.381	0.144	0.054
7	1.869	1.687	1.50	16.40	0.13	8.05	2.769	0.919	0.729	0.521	0.237	0.097
7*L*	1.690	1.687	2.65	16.83	0.002	8.09	2.820	0.934	0.714	0.529	0.267	0.116
8	2.103	1.859	3.05	19.24	0.19	8.34	3.381	0.951	0.752	0.633	0.418	0.240
8*L*	1.860	1.856	4.85	20.31	0.003	8.10	3.623	0.915	0.754	0.667	0.492	0.335

[a] The pair potential cut off for the two runs was $3\mathscr{A}^{1/2}/2$ and the augmented summation procedure was used. The cut off for the other runs [6] was $\mathscr{A}^{1/2}/2$. $\theta_t(i)$ values are calculated from uncorrected singlet distributions.

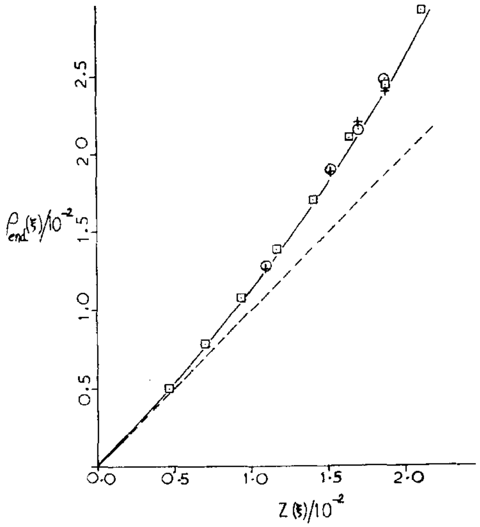

FIG. 1. Plots of $\bar{\rho}_{\text{end}}(\xi)$ against $Z(\xi)$ for $T^* = 1.002$. $\bar{\rho}_{\text{end}}(\xi)$ is defined by Eqs. (3.1–3.2). The solid curve is the density activity plot for a 12-6 gas using up to the fifth virial coefficient [8] and the dotted line is for an ideal gas. □, $\xi = 0$ for runs 1–8 [6], $a = \frac{1}{2}$; ○, $\xi = 1$ for runs 4, 6–8; +, $\xi = 1$ for runs 4L, 6L–8L, $a = 7/8$.

6–8 and 4L, 6L–8L together with the line for a 12–6 gas (five virial coefficients). The $\bar{\rho}_{\text{end}}(0)$ points were calculated with $a = \frac{1}{2}$ in Eq. (3.1). For the corrected densities deviations from 1 % (4, 4L) up to 5 % (8, 8L) of the virial density were found for $a = \frac{1}{2}$ but this deviation was negligible for $a > 0.87$. The decrease of $\bar{\rho}_{\text{end}}(1)$ with increasing a showed consistent trends for all runs and indicates that the adsorbent field still has a measurable effect at considerable distances from the wall and becomes negligible only in the final eighth of the box.

Figure 2 shows plots of the singlet distribution functions $\rho(r_z\,;\,\xi)$ against the distance r_z from the adsorbent. The uncorrected ($\xi = 0$) and corrected ($\xi = 1$) distribution functions for the system of reference [6] (with cut off $l_x/2$ and using nearest image interactions) are plotted and can be seen to differ significantly only at distances from the surface greater than $r_z = 3$, and even then only for higher degrees of coverage. The effect of using the $\xi = 1$ distribution function in run 8 to calculate $\theta_t(i)$ is to produce an increase, as compared with the corresponding L runs of 0.005, 0.008, 0.008, 0.006, and 0.006 for layers $i = 1, 2, 3, 4, 5$, respectively. These deviations are comparable with the sampling errors of 0.005, 0.006, 0.007, 0.005, and 0.004, respectively.

It can be seen from Fig. 2 that the main difference between 4, 6–8 and 4L, 6L–8L distribution functions is in the fourth and higher layers, and the quantitative change is shown in Fig. 3 where the increased coverage of the L runs $\Delta\theta_t(i)$ for layer i is plotted against $\theta_t(i)$. Test runs show that the deviations $\Delta\theta_t(i)$ at $T^* = 0.668$ for the runs reported in [4] have a similar magnitude for a given $\theta_t(i)$ to the deviations at $T^* = 1.002$ reported here.

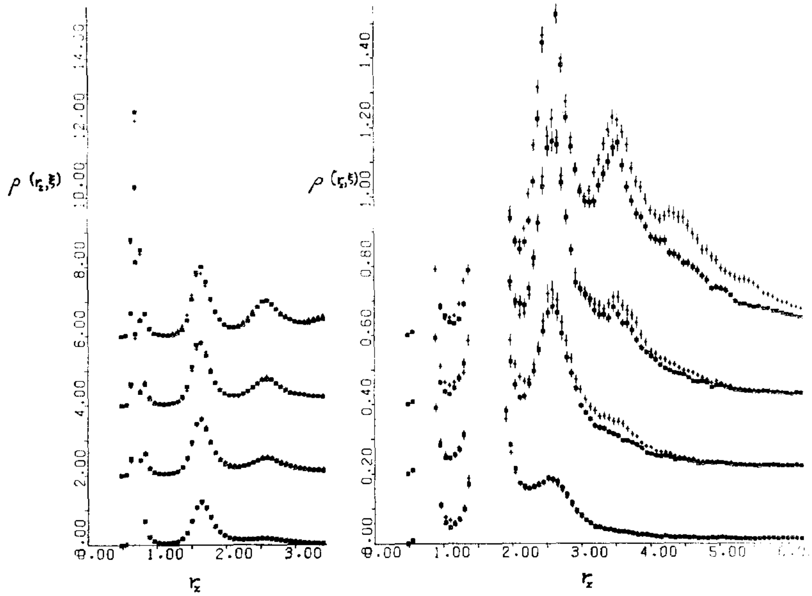

FIG. 2. The singlet distribution $\rho(r_z\,;\,\xi)$ as a function of r_z, the distance from the adsorbent for $\xi = 0(\square)$ and $\xi = 1(+)$ at $T^* = 1.002$. The curves in ascending order are for runs 4, 6, 7, and 8 and successive curves are displaced by 2.0 and 0.2 ordinate units on the left- and right-hand figures, respectively. The right-hand figure illustrates the variation of density beyond $r_z = 2.00$ and most of the points at $r_z < 2.00$ have been omitted for greater clarity.

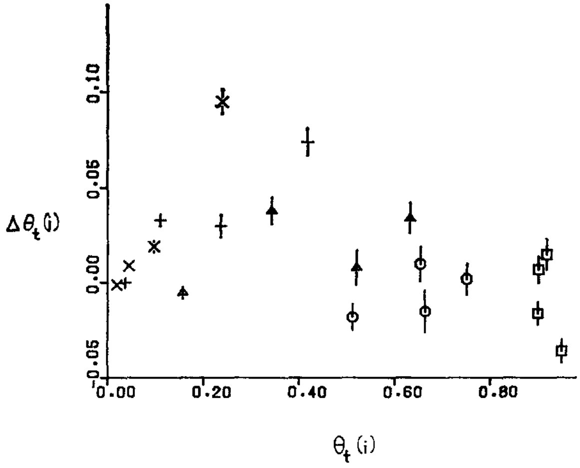

FIG. 3. The increase in coverage for various i for the corrected L runs as a function of the total coverage in a layer. The symbols $\square$, $\bigcirc$, $\triangle$, $+$ and $\times$ are $i = 1, 2, 3, 4$, and 5. $\theta_t(i)$ values for each run are given in the table. All values refer to $T^* = 1.002$.

Comparison of the pair contributions to the internal energy per particle between the runs 4*L*, 6*L*–8*L* and the 4, 6–8 shows agreement to within the sampling errors. The magnitude of the pair contribution to the potential energy per particle of run 7*L* is $\simeq 1\%$ above that of run 7 and the long-range correction to run 7 is $\simeq 1.6\%$ of the pair part of the potential energy.

The run 8*L* is anomalous in that the coverage in the first layer is significantly lower than for run 8. This difference is equivalent to one and a half particles over the area of the square periodic surface of the MC box. We attribute this anomaly to the formation of a metastable state in the first layer and conjecture that the existence of this state is related to the geometry and small size of the basic cell. The magnitude of the pair contribution to the potential energy per particle of run 8*L* is $\simeq 3\%$ above that of run 8 and the long-range correction to run 8 is $\simeq 1.8\%$ of the pair part of the potential energy.

5. DISCUSSION

The calculation of the long-range correction by means of an augmented summation procedure requires a substantial increase in computer time compared with the correction method used in [6]. For uniform systems an accurate correction can be made without resort to the augmented summation method, but for nonuniform systems this is not the case because of the distortion of the singlet distribution function. This difficulty would arise in both canonical ensemble and grand ensemble methods and it is therefore important to know whether serious error is entailed in carrying out the less expensive calculations.

An important conclusion from the present study is that the two methods give identical results, to within the limits of sampling error, when coverage is lower than approximately two statistical monolayers. This observation is associated with low occupation in the fourth and higher layers. When the density in this region of the adsorbate becomes appreciable considerable distortion of the singlet distribution function occurs (Fig. 2). This in turn is related to the cut-off distance of $R = l_x/2 = 3.39$ which can be compared with the distance of 2.75 between the fourth and first layers. For example if the cut-off distance in a fcc structure is changed from $R = 3l_x/2$ to $R = l_x/2$ the interaction between a particle in layers 2, 3, 4, and 5 with the first layer would be decreased by 1, 7, 27, and 100%, respectively.

The correction to the singlet distribution functions, Eq. (3.2), is adequate at large distances from the adsorbent wall where the distribution function is uniform, but does not provide a large enough correction in the region of the fourth and fifth layers when they have a significant coverage.

One possibility would be to replace the spherical cut off for the pair interaction potential by a cut off with cylindrical symmetry so that the most significant part of the interlayer interaction was always included in the MC simulation. However, this would invalidate the comparison with data for 12-6 argon which have been derived for a spherical cut off and in turn reduce the compensation for three-body interactions.

A larger system with a longer range of spherical cut off could contain, on average, a greater number of particles and the consequent increase in computer time (and storage) required for a significant improvement is even greater than that needed for the augmented summation procedure.

An indication of the consistency of the long-range corrections can be obtained by comparing Eq. (2.6c) and Eq. (2.8a). These equations imply that plots of $\ln(-\beta U^{(1)}/\mathscr{A})$ against $\ln\theta$ should be linear with a slope of 2.0. The data give good straight lines with slopes of 1.943 ($T^* = 1.002$, runs 1–8), 2.008 ($T^* = 1.002$, runs 4*L*, 6*L*–8*L*), and 1.996 ($T^* = 0.668$, runs 1–19[4]).

Values of θ for the *L* runs in this work and the corrected runs previously reported in [4] can be compared in the table. The new values do not lead to any serious modification of the conclusions in the earlier work. Thus Polanyi plots, the comparison of MC, cell, and lattice models, q_{st} plots, and internal energy data are only slightly modified and no significant qualitative change is observed. There is no improvement to the BET equation fit when the *L* runs are used in place of the previous ones and FHH plots indicate a reduction (of the order of 15 %) in the θ exponent *s*. The low value of *s* compared with that expected from the FHH theory was discussed in [4].

It can be concluded that the long-range corrections can be applied, without the augmented summation procedure, without generating appreciable error, for coverages up to about two statistical monolayers. At higher coverages, there is a distortion in the singlet distribution function due to long-range interaction which is not adequately corrected by Eq. (A2.7). This distortion leads to small increases in the coverage in fourth and subsequent layers but has a negligible effect on the pair interaction energies per molecule.

APPENDIX I: DERIVATIVES OF $A^{(1)}$

(i) From the mean field approximation of Eq. (2.5) we obtain

$$\left(\frac{\partial A^{(1)}_{\mathrm{MF}}}{\partial\beta}\right)_{N,V} = \int d\mathbf{s}_1\, d\mathbf{s}_2\, \rho_N(\mathbf{s}_1\,;0)\left(\frac{\partial\rho_N(\mathbf{s}_2\,;0)}{\partial\beta}\right)_{N,V}\phi^{(1)}(s_{21}). \qquad \text{(A1.1)}$$

And using the definition of $\rho_N(\mathbf{r};0)$ Eq. (2.4),

$$\left(\frac{\partial A^{(1)}_{\mathrm{MF}}}{\partial\beta}\right)_{N,V} = -\int d\mathbf{s}_1\,\rho_N(\mathbf{s}_1\,;0)\{\langle\eta^{(1)}_N(\mathbf{s}_1)U^{(0)}_N\rangle^{(0)}_N - \langle\eta^{(1)}_N(\mathbf{s}_1)\rangle^{(0)}_N\langle U^{(0)}_N\rangle^{(0)}_N\}, \qquad \text{(A1.2a)}$$

$$\eta^{(i)}_N(\mathbf{s}_1) = \sum_j^N \phi^{(i)}(|\,\mathbf{s}_1 - \mathbf{r}_j\,|) - (i-1)\,\psi_I(\mathbf{s}_1), \qquad i = 0, 1. \qquad \text{(A1.2b)}$$

(ii) Taking the derivative of Eq. (2.5) with respect to *N* we have

$$\left(\frac{\partial A^{(1)}_{\mathrm{MF}}}{\partial N}\right)_{V,\beta} = \int d\mathbf{s}_1\, d\mathbf{s}_2\, \rho_N(\mathbf{s}_1\,;0)\left(\frac{\partial\rho_N(\mathbf{s}_2\,;0)}{\partial N}\right)_{V,\beta}\phi^{(1)}(s_{21}) \qquad \text{(A1.3)}$$

and from Eq. (2.4)

$$\left(\frac{\partial \rho_N(\mathbf{s}_2\,;0)}{\partial N}\right)_{V,\beta} = \rho_{N+1}(\mathbf{s}_2\,;0) - \rho_N(\mathbf{s}_2\,;0)$$

$$= \frac{\rho_N(\mathbf{s}_2\,;0)}{N} + \frac{Z(0)}{N}\int d\mathbf{r}\left\{\left\langle\sum_i^N \delta(|\,\mathbf{s}_2 - \mathbf{r}_i\,|)\,\mathrm{Exp}(-\beta\eta_N^{(0)}(\mathbf{r}))\right\rangle_N^{(0)}\right.$$

$$\left. - \left\langle\sum_i^N \delta(|\,\mathbf{s}_2 - \mathbf{r}_i\,|)\right\rangle_N^{(0)} \langle\mathrm{Exp}(-\beta\eta_N^{(0)}(\mathbf{r}))\rangle_N^{(0)}\right\} \qquad \text{(A1.4)}$$

where we have used the equation

$$\frac{N+1}{Z(0)} = \int d\mathbf{r}\langle\mathrm{Exp}(-\beta\eta_N^{(0)}(\mathbf{r}))\rangle_N^{(0)} \qquad \text{(A1.5)}$$

for the activity $Z(0)$ of the short-range system [9].

Using (A1.4) and (A1.3) we have

$$\left(\frac{\partial A_{\mathrm{MF}}^{(1)}}{\partial N}\right)_{V,\beta} = \frac{2A_{\mathrm{MF}}^{(1)}}{N} + \frac{Z(0)}{N}\int d\mathbf{r}\int d\mathbf{s}_1\,\rho_N(\mathbf{s}_1\,;0)\{\langle\eta_N^{(1)}(\mathbf{s}_1)\,\mathrm{Exp}(-\beta\eta_N^{(0)}(\mathbf{r}))\rangle_N^{(0)}$$

$$- \langle\eta_N^{(1)}(\mathbf{s}_1)\rangle_N^{(0)}\langle\mathrm{Exp}(-\beta\eta_N^{(0)}(\mathbf{r}))\rangle_N^{(0)}\}. \qquad \text{(A1.6)}$$

(iii) Starting from Eq. (2.2a) for $A^{(1)}$ and Eq. (2.6b) we have

$$p_\alpha^{(1)}V = -\int_0^1 d\xi\left[\left\langle\sum_{i>j}^N \frac{\alpha_{ij}^2}{r_{ij}}\frac{d\phi^{(1)}(r_{ij})}{dr_{ij}}\right\rangle_N^{(\xi)}\right.$$

$$+ \beta\left\{\left\langle U_N^{(1)}\sum_{i>j}^N \frac{\alpha_{ij}^2}{r_{ij}}\frac{d}{dr_{ij}}(\phi^{(0)}(r_{ij}) + \xi\phi^{(1)}(r_{ij}))\right\rangle_N^{(\xi)}\right.$$

$$\left.\left. - \langle U_N^{(1)}\rangle_N^{(\xi)}\left\langle\sum_{i>j}^N \frac{\alpha_{ij}^2}{r_{ij}}\frac{d}{dr_{ij}}(\phi^{(0)}(r_{ij}) + \xi\phi^{(1)}(r_{ij}))\right\rangle_N^{(\xi)}\right\}\right]. \qquad \text{(A1.7)}$$

Taking the mean field approximation in the first term of Eq. (A1.7) (i.e., neglecting ξ dependence of the integral and setting $g^{(2)}$ to unity) we obtain

$$p_\alpha^{(1)}V = -\tfrac{1}{2}\int d\mathbf{s}_1\,d\mathbf{s}_2\,\rho_N(\mathbf{s}_1\,;0)\,\rho_N(\mathbf{s}_2\,;0)\,\frac{\alpha_{21}^2}{s_{21}}\frac{d\phi^{(1)}(s_{21})}{ds_{21}}$$

$$+ \beta\int_0^1 d\xi\left\{\left\langle U_N^{(1)}\sum_{i>j}^N \frac{\alpha_{ij}^2}{r_{ij}}\frac{d}{dr_{ij}}(\phi^{(0)}(r_{ij}) + \xi\phi^{(1)}(r_{ij}))\right\rangle_N^{(\xi)}\right.$$

$$\left. - \langle U_N^{(1)}\rangle_N^{(\xi)}\left\langle\sum_{i<j}^N \frac{\alpha_{ij}^2}{r_{ij}}\frac{d}{dr_{ij}}(\phi^{(0)}(r_{ij}) + \xi\phi^{(1)}(r_{ij}))\right\rangle_N^{(\xi)}\right\}. \qquad \text{(A1.8)}$$

APPENDIX II: Distortion of the Singlet Distribution Function

From the definition of $\rho_N(\mathbf{r};\xi)$, Eq. (2.4) and using Eqs. (A1.2b) and Eq. (2.2b) we can show

$$\rho_N(\mathbf{r};\xi) = N\langle \operatorname{Exp}(-\beta\eta_{N-1}(\mathbf{r};\xi))\rangle_{N-1}^{(\xi)} \Big/ \int d\mathbf{r}\langle \operatorname{Exp}(-\beta\eta_{N-1}(\mathbf{r};\xi))\rangle_{N-1}^{(\xi)} \tag{A2.1}$$

where

$$\eta_N(\mathbf{r};\xi) = \eta_N^{(0)}(\mathbf{r}) + \xi\eta_N^{(1)}(\mathbf{r}). \tag{A2.2}$$

Using the expression

$$\frac{N}{Z(\xi)} = \int d\mathbf{r}\langle \operatorname{Exp}(-\beta\eta_{N-1}(\mathbf{r};\xi))\rangle_{N-1}^{(\xi)} \tag{A2.3}$$

for the activity $Z(\xi)$ we can write

$$\begin{aligned} \rho_N(\mathbf{r};\xi) &= Z(\xi)\langle \operatorname{Exp}(-\beta\eta_{N-1}(\mathbf{r};\xi))\rangle_{N-1}^{(\xi)} \\ &\cong Z(\xi)\langle \operatorname{Exp}(-\beta\eta_N(\mathbf{r};\xi))\rangle_N^{(\xi)}. \end{aligned} \tag{A2.4}$$

Differentiating Eq. (A2.4) with respect to ξ and then integrating from 0 to 1 with respect to ξ we obtain

$$\begin{aligned} \rho_N(\mathbf{r};1) - \rho_N(\mathbf{r};0) = {} & -\beta\int_0^1 d\xi\, Z(\xi)\langle \eta_N^{(1)}(\mathbf{r}) \operatorname{Exp}(-\beta\eta_N(\mathbf{r};\xi))\rangle_N^{(\xi)} \\ & -\beta\int_0^1 d\xi\, Z(\xi)\{\langle U_N^{(1)} \operatorname{Exp}(-\beta\eta_N(\mathbf{r};\xi))\rangle_N^{(\xi)} \\ & - \langle U_N^{(1)}\rangle\langle \operatorname{Exp}(-\beta\eta_N(\mathbf{r};\xi))\rangle_N^{(\xi)}\} \\ & + \int_0^1 d\xi\, \frac{\partial Z(\xi)}{\partial\xi}\langle \operatorname{Exp}(-\beta\eta_N(\mathbf{r};\xi))\rangle_N^{(\xi)}. \end{aligned} \tag{A2.5}$$

Using Eq. (2.7) on the first two members of the right-hand side of Eq. (A2.5) and employing Eqs. (A2.1) and (A2.4) it is straightforward to obtain

$$\rho_N(\mathbf{r};1) \cong \rho_N(\mathbf{r};0) + \int_0^1 d\xi\, \rho_N(\mathbf{r};\xi)\left\{\frac{\partial \ln Z(\xi)}{\partial\xi} - \beta\langle \eta_N^{(1)}(\mathbf{r})\rangle_N^{(\xi)}\right\}. \tag{A2.6}$$

Making a mean field approximation and ignoring the ξ dependence of $\rho_N(\mathbf{r};\xi)$ on the right-hand side of Eq. (A2.6) we have

$$\rho_N(\mathbf{r};1) \cong \rho_N(\mathbf{r};0)\left\{1 + \ln(Z(1)/Z(0)) - \beta\int d\mathbf{s}_1\, \rho_N(\mathbf{s}_1;0)\, \phi^{(1)}(|\mathbf{s}_1 - \mathbf{r}|)\right\}. \tag{A2.7}$$

We note that this approximation for $\rho_N(\mathbf{r}; 1)$ in terms of $\rho_N(\mathbf{r}; 0)$ conserves the number of particles N, since by integrating both sides over all $\mathbf{r}$ we obtain

$$N = N(1 + \ln(Z(1)/Z(0)) - 2\beta A_{\mathrm{MF}}^{(1)},$$

which is equivalent to Eq. (2.8a) when we have $\beta\mu^{(1)} \equiv \ln(Z(1)/Z(0))$.

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