

**LONG-RANGE CONTRIBUTION TO INVERSE-DISTANCE POWER
AND MORSE ENERGY AND PRESSURE TERMS OF A MOLECULAR LIQUID,
TESTED ON BENZENE**

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Abstract

Analytical expressions were derived to estimate the contribution to the intermolecular energy and pressure from pairs of rigid molecules farther than a cutoff distance; inverse power terms (like in the Lennard-Jones potential) and exponential terms (like in the Morse potential) were considered. The Lennard-Jones case was tested on liquid benzene at room temperature in the Gibbs ensemble using the cavity-biased technique. The density produced by simulations using the derived cutoff correction was found to be independent of the cutoff used.

1. Introduction

Liquid-state simulations generally involve a distance cutoff on the energy in order to reduce the computational effort. Too short a cutoff, however, affects the simulated structure. This is a particularly severe problem in the grand-canonical and isobaric ensembles [1] (including the Gibbs ensemble [2,3]) where even the simulated density will change with the introduction of a cutoff. Importantly, this effect can be largely circumvented by the inclusion of a reasonable estimate of the neglected long-range contributions.

For atomic fluids the long-range contributions are usually estimated under the assumption that atom pairs farther than the cutoff distance are uncorrelated and thus atoms beyond the cutoff distance are distributed uniformly in the space. It is easy to evaluate the resulting one-dimensional integral in most cases. For molecular liquids, however, the molecules will hold the atoms together in smaller clusters with a well defined structure. As a result, their distribution is not uniform beyond the cutoff distance thus the conditions for the application of the atomic formula are not met. This necessitated the search for different methods of estimating the long-range contributions in molecular liquids.

This paper presents analytical formulae for the estimate of the long-range contributions beyond a cutoff distance for rigid molecules that interact with site-site inverse power (of exponent larger than three), e.g., the Lennard-Jones potential, or with the Morse potential. In addition to the long-range correction to the energy the correction to the virial sum is also given up to third order for inverse power potentials. The effectiveness of the proposed estimate is demonstrated on the OPLS model [4] of liquid benzene. Note also that molecules with conformational freedom can be treated by assuming a mixture of fixed conformations.

In sharp contrast to their lengthy derivation the resulting formulae turned out to be of comparable simplicity to the formulae for the atomic fluid case thus their application is just as simple as the application of atomic fluid correction.

The formalism is developed for molecule-based cutoff, i.e., either all or none of the atoms of any two molecules interact. This method is commonly used in liquid simulations since not only does it reduce significantly the number of distances to be checked but it also eliminates possible artifacts that may arise when only a part of a molecule is 'visible' by an other in which case unphysical torques are generated. To avoid excessively long cutoffs, liquids of large or long molecules may be treated differently, e.g., by breaking them up into smaller parts for the purpose of the application of the cutoff — for such treatments our results are clearly not applicable.

2. Theory

For a fluid of rigid molecules that interact with each other via atom-atom pair potentials $E_{ij}(r)$ the contribution of molecules beyond a cutoff R_c to the energy of a selected

molecule M can be estimated under the assumption of no correlation (*vide supra*) as

$$C(M, M') = \frac{1}{2} \sum_i \rho \int_{R_c}^{\infty} \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \left[\sum_j \frac{1}{4\pi} \int_0^{2\pi} d\phi' \int_0^{\pi} \sin\theta' d\theta' [E_{i,j}(d_{i,j})] \right] r^2 dr \quad (1)$$

The summation over i represents the sites of the selected ‘central’ molecule M , the summation over j the sites of molecules M' beyond the cutoff R_c . r is the distance between the centers of the molecules M and M' on which the cutoff is based, $d_{i,j}$ is the distance between the sites i and j on molecule M and M' , respectively, and ρ is the number density of the liquid. The polar angles θ, ϕ are defined with respect to a coordinate system whose origin is the center of M and the site i is on the z axis. The origin of the coordinate system containing the polar angles θ', ϕ' is the center of M' , oriented in such a way that the site j (of molecule M') is on the z' axis of this system. The relative positioning of the two coordinate system is shown on Figure 1. Each molecule contributes to the total energy one half of its binding energy, hence the factor $\frac{1}{2}$. Averaging over all orientations of the M' molecules necessitated the normalization by 4π . Generalization to mixtures is straightforward.

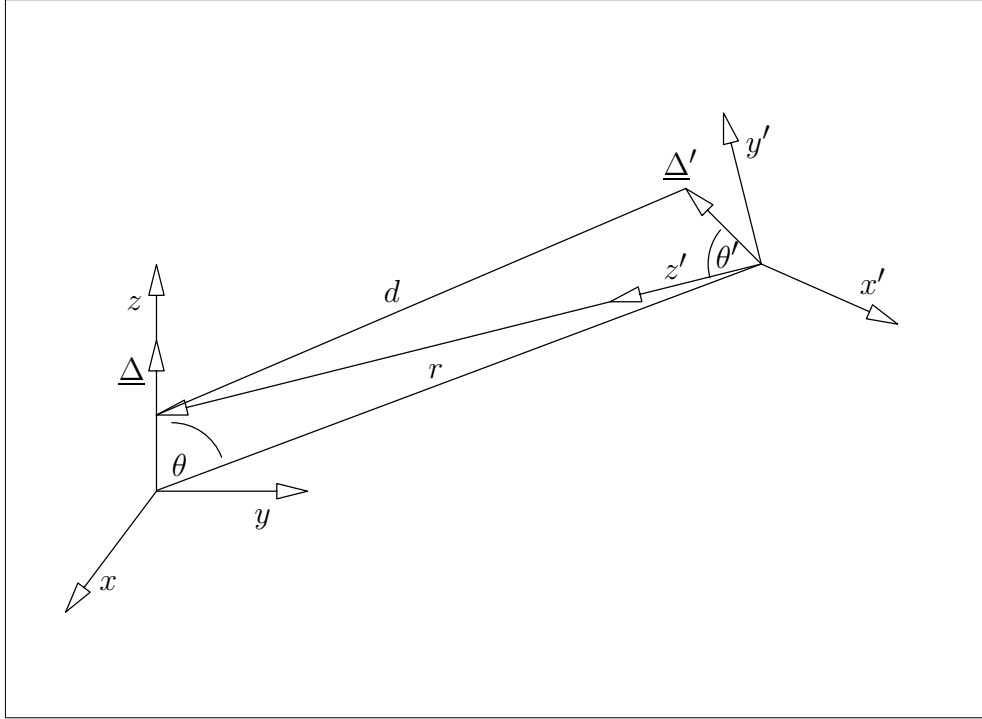


Fig. 1. Relative position of the molecular coordinate systems of two interacting molecules.

2.1 ENERGY CORRECTION FOR INVERSE POWER POTENTIALS

For inverse distance power interactions we have

$$E_{i,j}(d_{i,j}) = c_{i,j} d_{i,j}^{-k} \quad (2)$$

and integration with respect to ϕ and ϕ' gives

$$C(M, M') = \frac{\rho\pi}{2} \sum_i \sum_j c_{i,j} \int_{R_c}^{\infty} \int_0^{\pi} \int_0^{\pi} d_{i,j}^{-k} \sin\theta \sin\theta' d\theta d\theta' r^2 dr \quad (3)$$

By applying the law of cosines twice, the distance $d_{i,j}$ between the two sites can be expressed in terms of our integration variables:

$$d(r, \delta, \delta', \theta, \theta') = |\underline{\delta} - (\underline{r} + \underline{\delta}')|^{1/2} = \quad (4)$$

$$r^2 + \delta^2 - 2r\delta\cos\theta + \delta'^2 - 2\delta'(r^2 + \delta^2 - 2r\delta\cos\theta)^{1/2}\cos\theta'$$

Here the \underline{r} is the vector going from the center of molecule M to that of molecule M' , $\underline{\delta}$ and $\underline{\delta}'$ are the vectors from the center to the site in the M and M' molecule, respectively, and the scalars r , δ and δ' are their magnitudes.

For each pair i,j the integral depends only on r , δ_i , δ'_j :

$$S(\delta_i, \delta'_j) = \int_{R_c}^{\infty} r^2 I(\delta_i, \delta'_j, r) dr \quad (5)$$

where

$$I(\delta, \delta', r) = \int_0^{\pi} \int_0^{\pi} \frac{\sin\theta \sin\theta'}{d(\delta, \delta', \theta, \theta')^k} d\theta d\theta'. \quad (6)$$

We carry out the integration with respect to θ' with the substitution

$$u = r^2 + \delta^2 - 2r\delta\cos\theta + \delta'^2 - 2\delta'(r^2 + \delta^2 - 2r\delta\cos\theta)^{1/2}\cos\theta' \quad (7)$$

since $du = \sin\theta' d\theta'$ appears in the numerator. Next, the substitution

$$v = (r^2 + \delta^2 - 2r\delta\cos\theta)^{1/2} \quad (8)$$

transforms the integrand into the much simpler expression of $(v - s\delta')^{-k+2}$ (s may be -1 or +1) and this naturally leads to the subsequent substitution $w = v - s\delta'$.

Thus integration with respect to θ gives

$$I(\delta, \delta', r) = 1/[(-\frac{k}{2} + 1)(-k+3)(2\delta\delta')]. \quad (9)$$

$$r^{-1} \cdot [(r + \delta + \delta')^{-k+3} - (r - \delta + \delta')^{-k+3} - (r + \delta - \delta')^{-k+3} + (r - \delta - \delta')^{-k+3}]$$

Upon substituting into equation (5), each term of $I(\delta, \delta', r)$, yields an integral of the form

$$\int_{R_c}^{\infty} r \cdot (r + d)^{-k+3} dr \quad (10)$$

that can be evaluated with the substitution $t = r + d$. The final result is

$$S(\delta, \delta') = \int_{R_c}^{\infty} r^2 I(\delta, \delta', r) dr = -1 / [(-\frac{k}{2} + 1)(-k + 3)(2\delta\delta')]. \quad (11)$$

$$\sum_{s=-1,1} \sum_{s'=-1,1} ss' \left[\frac{(R_c + s\delta + s'\delta')^{-k+5}}{k-5} - (s\delta + s'\delta') \frac{(R_c + s\delta + s'\delta')^{-k+4}}{k-4} \right]$$

Note that integrating the terms of equation (9) with respect to r would result in divergent integrals when $k < 6$. Thus special treatment is necessary for $k = 4$ and $k = 5$, when the original integral in equation (3) is obviously finite. To get an analytical expression for S in these cases, we substitute the actual value of k into the equation (9) defining $I(\delta, \delta', r)$. This yields for $k = 4$

$$S(\delta, \delta') = \frac{1}{2\delta\delta'} \int_{R_c}^{\infty} \left[\frac{r}{(r + \delta + \delta')} - \frac{r}{(r - \delta + \delta')} - \frac{r}{(r + \delta - \delta')} + \frac{r}{(r - \delta - \delta')} \right] dr \quad (12)$$

and for $k=5$

$$S(\delta, \delta') = \frac{1}{12\delta\delta'} \int_{R_c}^{\infty} \left[\frac{r}{(r + \delta + \delta')^2} - \frac{r}{(r - \delta + \delta')^2} - \frac{r}{(r + \delta - \delta')^2} + \frac{r}{(r - \delta - \delta')^2} \right] dr \quad (13)$$

With finite upper limit, terms in equations (12) and (13) can be integrated easily. Now, these improper integrals can be obtained by integrating separately each of the four terms to the same finite upper limit b first and then taking the limit of the sum as the upper limit b of integration goes to infinity. This procedure yields for $k = 4$

$$S(\delta, \delta') = \frac{1}{2\delta\delta'} \left[(\delta + \delta') \ln \frac{R_c + \delta + \delta'}{R_c - \delta - \delta'} + (\delta - \delta') \ln \frac{R_c - \delta + \delta'}{R_c + \delta - \delta'} \right] \quad (14)$$

and for $k = 5$

$$S(\delta, \delta') = \frac{1}{12\delta\delta'} \left\{ \ln \frac{R_c^2 - (\delta - \delta')^2}{R_c^2 - (\delta + \delta')^2} + \frac{2(\delta + \delta')^2}{R_c^2 - (\delta + \delta')^2} + \frac{2(\delta + \delta')^2}{R_c^2(\delta + \delta')^2} \right\} \quad (15)$$

Substitution shows that for $k < 4$, the right hand side of equation (3) vanishes. Interestingly, in these cases the original integral in equation (1) is not expected to converge. This seeming paradox points to the conclusion that for systems interacting with these low exponents the decay of orientational correlation is at least as slow as the decay of the interaction

energy and thus the assumption of no orientational correlation that underlies equation (1), would be fundamentally false.

2.2 ENERGY CORRECTION FOR THE MORSE POTENTIAL

For the Morse potential

$$E_{i,j}(d_{i,j}) = D_{i,j} \exp[-2A_{i,j}(d_{i,j} - r_{i,j}^o)] - 2D_{i,j} \exp[-A_{i,j}(d_{i,j} - r_{i,j}^o)] \\ \sum_{f=1,2} (3f-5) D_{i,j} \exp[-fA_{i,j}(d_{i,j} - r_{i,j}^o)] \quad (16)$$

In analogy with the previous derivation we introduce the quantity S for the ‘hard’ part of the integral:

$$C(M, M') = \frac{\rho\pi}{2} \sum_i \sum_j S(\delta_i, \delta'_j, A_{i,j}, r_{i,j}^o, D_{i,j}) \quad (17)$$

As the success previously was not affected by the particular form of the function $E_{i,j}$ we can employ the same sequence of substitutions to obtain the final result:

$$S(\delta, \delta', A, r^o, D) = \\ \sum_{s=-1,1} \sum_{s'=-1,1} \sum_{f=1,2} s s' (3f-5) D \exp(-fA(R_c - s'\delta - s\delta' - r^o)) / [(fA)^3 \delta \delta'] \cdot \\ [(2R_c - s'\delta - s\delta')(R_c - s'\delta - s\delta') + (\frac{9}{2}R_c - s'\delta - s\delta')/(fA) + \frac{5}{2(fA)^2}] / [\delta \delta' (fa)^2] \quad (18)$$

2.3 PRESSURE CORRECTION TO INVERSE POWER POTENTIALS.

The liquid pressure can be obtained from the ensemble average of the virial sum V

$$V = \sum_{i < j} V_{i,j}(d_{i,j}, r) \quad (19)$$

where $V_{i,j}$ is the contribution of the atom pair (i,j) to the virial sum, given by

$$V_{i,j}(d_{i,j}, r) = \left(\left(\frac{\partial E}{\partial \underline{r}} \right) \cdot \underline{r} \right) = \left(\frac{\partial E}{\partial d_{i,j}} \right) \left(\left(\frac{\partial d_{i,j}}{\partial \underline{r}} \right) \cdot \underline{r} \right) = \\ \left(\frac{\partial E}{\partial d_{i,j}} \right) \left(\frac{\partial d_{i,j}}{\partial r} \right) \left(\left(\frac{\partial r}{\partial \underline{r}} \right) \cdot \underline{r} \right) = \left(\frac{\partial E}{\partial d_{i,j}} \right) \left(\frac{\partial d_{i,j}}{\partial r} \right) r \quad (20)$$

since

$$\left(\frac{\partial r}{\partial \underline{r}} \right) = \left\langle \frac{x}{r}, \frac{y}{r}, \frac{z}{r} \right\rangle. \quad (21)$$

When the energy expression involves an inverse-power so will $\left(\frac{\partial E}{\partial d_{i,j}}\right)$ also and the partial derivative of $d_{i,j}$ with respect to r is

$$\begin{aligned} \left(\frac{\partial d}{\partial r}\right) &= \\ [2r - 2\delta\cos\theta - 2\delta'\frac{1}{2}(r^2 + \delta^2 - 2r\delta\cos\theta)^{-1/2} \cdot (2r - 2\delta\cos\theta)\cos\theta'] \cdot \\ (r^2 + \delta^2 - 2r\delta\cos\theta + \delta'^2 - 2\delta'(r^2 + \delta^2 - 2r\delta\cos\theta)^{1/2}\cos\theta')^{-1/2}/2 = \\ [r - \delta\cos\theta - \delta'(r - \delta\cos\theta)\cos\theta'(r^2 + \delta^2 - 2r\delta\cos\theta)^{-1/2}]/(\alpha + \beta\cos\theta')^{1/2}. \end{aligned} \quad (22)$$

The integral that combines equations (21) and (22) and averages over all mutual orientations and distances (beyond the cutoff) can again be evaluated with the same sequence of substitutions (although the derivation is lengthier than for the energy corrections). Besides the type of integrals that we had to deal with above, integrals of expressions of the type $(x+t)^{-m}x^{-1}$, and $(x+t)^{-m}x^{-2}$ are also needed for which we resorted to power series expansion. First note that integration by parts reduces the problem of calculating the second type to the problem of calculating the first since

$$\int (x+t)^{-m}x^{-2}dx = -(x+t)^{-m}x^{-1} - \int (-1)(-m)(x+t)^{-m-1}x^{-1}dx. \quad (23)$$

To evaluate the first integral we substitute $y = x+t$ and use the geometric series:

$$\begin{aligned} \int y^{-m}(y-t)^{-1}dy &= \int \frac{y^{-m-1}}{1-t/y}dy = \\ \int y^{-m-1} \left[1 + \frac{t}{y} + \left(\frac{t}{y}\right)^2 + \dots \right] dy &= \left[\frac{y^{-m}}{-m} + \frac{ty^{-m-1}}{-m-1} + \frac{t^2y^{-m-2}}{-m-2} \dots \right] = \\ \frac{-(x+t)^{-m}}{m} - \frac{t(x+t)^{-m-1}}{(m+1)} - \frac{t^2(x+t)^{-m-2}}{m+2} - \dots \end{aligned} \quad (24)$$

The final result for the contribution to the virial sum beyond the cutoff distance (up to third order) for $k > 5$ is

$$\frac{\rho\pi}{2} \sum_{i,j} S(\delta_i, \delta_j) \quad (25)$$

where

$$\begin{aligned}
S(\delta, \delta') = \sum_{s,s'=-1,1} \frac{s'sk}{4\delta\delta'} & \left\{ 4(R_c + s'\delta - s\delta')^{-k+5} \frac{2k^2 - 2k - 4}{k(k-1)(k-2)(k-3)(k-5)} + \right. \\
& (R_c + s'\delta - s\delta')^{-k+4} (s'\delta - s\delta') \frac{3k^3 - 10k^2 - k + 20}{k(k-1)(k-2)(k-3)(k-4)} + \\
& \left. (R_c + s'\delta - s\delta')^{-k+3} \frac{\delta^2(-2k^2 + 2k + 4) + \delta'^2(-8k + 16) + ss'\delta\delta'(2k^2 + 6k - 20)}{k(k-1)(k-2)(k-3)} \right\}.
\end{aligned} \tag{26}$$

3. Calculations

The OPLS [4] model for benzene was simulated in the Gibbs ensemble [2,3] at 300K temperature, using cutoffs ranging from 10 Å to 17 Å. The Gibbs ensemble simulations included a total of 300 molecules. The simulations used the cavity biased technique [5] to improve the success rate of exchanging molecules between the liquid and vapor phase. Further enhancement in the success rate was obtained by selecting a large combined volume, 843750 Å³, as suggested in [6]. Such choice generates the vapor phase with large enough volume to require the presence of more than one molecule there increasing the likelihood of the acceptance of exchange attempts. Each simulation involved 4 million attempted displacements (in each system). Molecule exchanges were attempted at every 10th step and volume exchanges at every 100th step. The estimate of the contributions to the energy beyond the cutoff was incorporated in the manner described in [5].

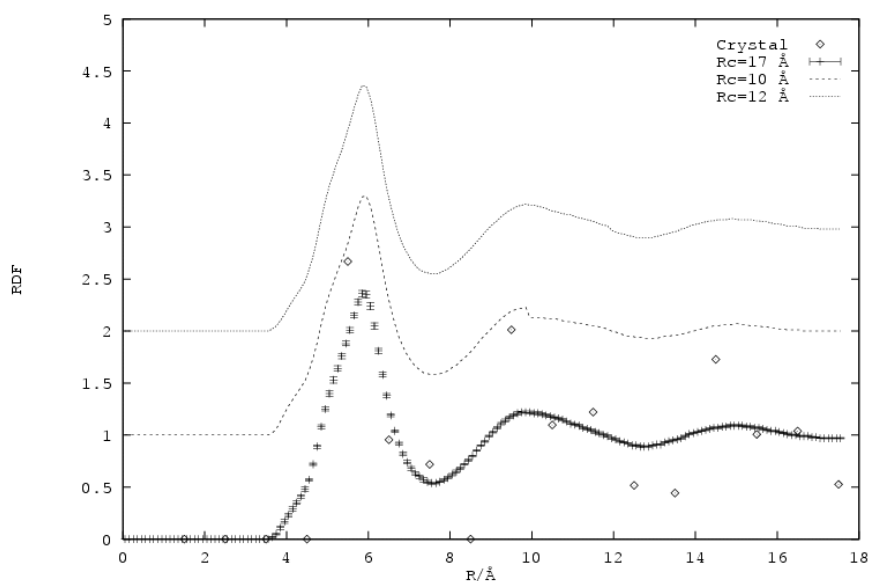
Table 1. Simulation results with different cutoffs at 300 K.

$R_c/\text{Å}$	$\rho_l/(\text{g/ml})$	$\rho_v(\text{g/ml})$	$E_l/(\text{kJ/mol})$	$E_C(\text{kJ/mol})$
10	0.8617±0.0037	0.00053±0.00009	-30.811±0.079	-1.929
12	0.8690±0.0030	0.00040±0.00006	-31.547±0.079	-1.084
17	0.8706±0.0034	0.00051±0.00008	-31.929±0.114	-0.366
10	0.8468±0.0036	0.00113±0.00009	-28.280±0.075	0.0
12	0.8597±0.0026	0.00050±0.00005	-30.150±0.075	0.0
17	0.8645±0.0062	0.00067±0.00014	-32.564±0.075	0.0

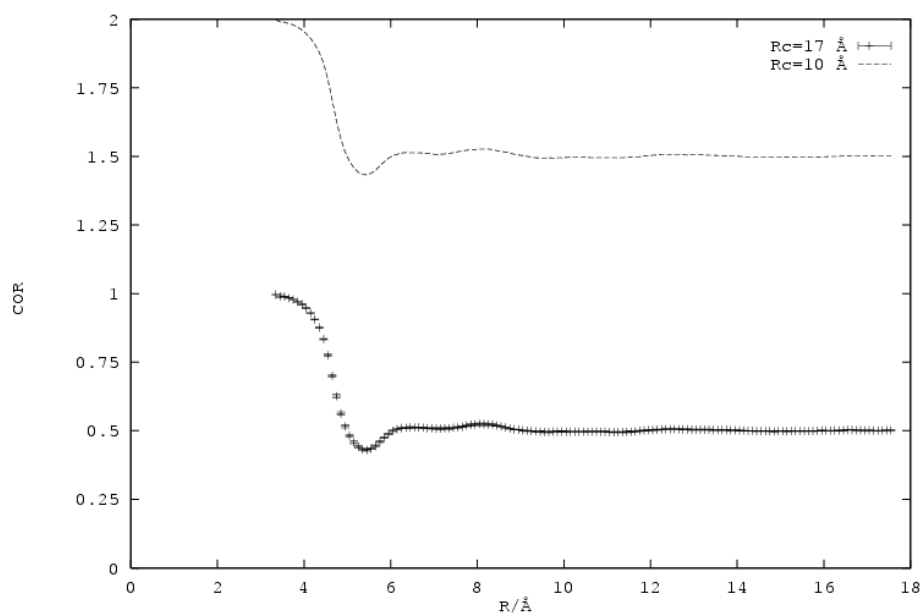
R_c is the energy cutoff used, ρ_l and ρ_v are the liquid and vapor densities, E_l is the internal energy of the liquid, and the entry in the column marked E_C gives the cutoff correction (zero indicates that it was not employed), included into E_l . Error estimates represent 95% confidence intervals (2σ).

4. Results and discussion

The degree of consistency of the liquid structure calculated with different cutoffs as well as the deviation from uniform distribution beyond the cutoff distance (assumed in the



2. Center-of-mass radial distribution functions (RDF) of the liquid and solid phase. +++: $R_c=17\text{\AA}$, ---: $R_c=10\text{\AA}$, ...: $R_c=12\text{\AA}$. Errorbars (2σ) are provided only for the $R_c=17\text{\AA}$ curve. The curves are shifted from one another for clarity. The RDF derived from the crystal structure is shown with the diamond symbols.



3. Mean absolute correlation COR of the normals to the molecular plane as a function of intermolecular distance. +++: $R_c=17\text{\AA}$, ---: $R_c=10\text{\AA}$. Errorbars (2σ) are provided only for the $R_c=17\text{\AA}$ curve. The two curves are shifted from one another for clarity.

derivation of the cutoff correction) can be characterized by the liquid density and by various distribution functions.

The liquid and vapor densities, obtained from simulations using different cutoffs with and without the cutoff corrections are shown in Table 1, along with the calculated internal energies and the correction terms.

The liquid densities calculated with the cutoff corrections show remarkable consistency, indicating that the proposed cutoff correction is successful in keeping the density at the infinite cutoff value. They compare well, too, with the experimental value 0.8787 g/ml. The corrected energies still show some cutoff dependence but much less than the energies obtained from simulations without the cutoff correction. This deviation is reasonable since the calculated radial distribution function (RDF) shows (*vide infra*) that for $r < 12$ Å the density deviates significantly from the bulk density, violating the assumption of the derivation of our cutoff correction. Comparing the two calculations at the 17 Å cutoff, the difference in the calculated energies is very close to the estimated correction.

Figure 2. shows the calculated RDF's as a function of the center-of-mass distance for the runs with different cutoffs. The only visible effect of the cutoff — whether or not using the correction — is the small discontinuity in the RDF at $r=R_c$ for $R_c \leq 12$ Å. This can be easily eliminated by a graduated cutoff, that is commonly used in molecular dynamics simulations to avoid warming up the system. As there were no other visible differences between the RDF's (with or without the cutoff correction) only the RDF's from the run with correction are shown. Also, as the error estimates were similar for all RDF's, so they are shown only for the 17 Å cutoff run.

Point by point comparison of the calculated RDF's shows little variation. The RDF's from runs with the 12 Å cutoff and the 17 Å cutoff are within the error limits, and the largest RDF difference between the 10 Å and the 17 Å cutoff runs was 0.11 . With and without the correction, RDF's with the same cutoff run agreed with each other within the estimated error, although at the 10 Å cutoff the RDF without the correction deviated slightly more from the 17 Å standard than the one with the correction.

The mean absolute correlation of the normals to the molecular planes, COR, is shown on Figure 3 as a function of the center-of-mass distance for the 10 Å run and the 17 Å run (with the correction). As the relative orientations randomize after 6 Å, it shows no perceptible sensitivity to either the cutoff length or the correction.

The calculated RDF is very similar to the RDF's obtained in earlier simulations [7,8] using a different Lennard-Jones parametrization [9], although the two pronounced shoulders found in these former calculations around 5 Å are barely perceptible in our results. The fast decay of the correlation of normals is also seen in Ref. 8.

It has not been pointed out, however, that the calculated RDF is unusual in that the spacing between the peaks varies significantly from peak to peak — an indication that benzene is not a simple liquid. This is all the more interesting since, on the other hand, the orientational correlation between the molecules at the second peak distance is essentially

random (vide supra) and integration of the RDF to its first minimum indicates about 13 neighbours — these characteristics would suggest a simple liquid.

The positions of the RDF peaks appear to support the suggestion of Katzoff [10] and Narten [11] based on their X-ray diffraction data that the liquid structure is similar to the solid structure. On Figure 2 we also displayed the RDF obtained from the crystal structure (using 1 Å wide bins). The positions of the first and second liquid peaks correspond very well with those obtained from the crystal structure [12,13]. Unfortunately, X-ray diffraction experiments give the carbon-carbon RDF only where the various interatomic contributions largely cancel [10,11,14]. The resulting very broad and very low peaks can hardly serve to differentiate among proposed liquid structures.

The fast decay of the orientational correlations has some experimental support too: Tohji and Murata studied the change in the X-ray diffraction pattern during melting and their data seems to suggest that there is a significant increase in molecular rotation even before melting [15].

The comparison with experimental data is to be considered in the context of the findings of Williams and Xiao [16] who showed that for the proper characterization of orientational preferences of the benzene dimer it is essential to have a somewhat polar C-H bond in the model. Such model has, in fact, been recently added to the OPLS potential library [17].

The calculated liquid energy, -31.8 kJ/mol, compares favorably with the experimental heat of vaporization, 30.8 kJ/mol [18].

Finally, we would like to point out that our successful test of the proposed cutoff correction not only demonstrates the usefulness of the derived correction expression but also shows how such Gibbs-ensemble simulations can serve as an effective testing ground for corrections corresponding to other different types of interactions, e.g., the long-range contributions to the electrostatic terms (when present in the potential).

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