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Electron Diffraction and Monte Carlo Studies of Liquids. 3. Supercooled Benzene

Lawrence S. Bartell,* Leo R. Sharkey, and Xianqian Shi

Contribution from the Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109. *Received March 21, 1988*

Abstract: Monte Carlo simulations of supercooled liquid benzene have been carried out with two aims. The first was to investigate, specifically, whether such treatments can significantly augment the interpretation of electron diffraction patterns of large, cold, liquid clusters grown in supersonic flow. The second and more general aim was to determine the degree to which currently feasible treatments of molecular liquids as complex as benzene can be considered to be realistic. For a treatment to qualify as realistic, it is proposed that the intermolecular interaction potential for a given substance be able to account for (1) the detailed crystal structure, (2) the crystal binding energy, (3) the liquid structure (especially for the supercooled liquid), and (4) the thermodynamic properties of the liquid. All prior simulations for benzene modeled to fit criterion 4 had incorporated simplified potential functions. These were found to be inadequate in reproducing criteria 1–3. Two promising potentials that had been developed in paper I of this series were examined in detail. One, the LJ12-2 model, was derived from a very successful formulation in crystallography constructed by Williams and Starr. The other, a (12-10-6-2) model, was based upon quantum calculations by Karlström et al. for the benzene dimer. Both models were rescaled to satisfy criteria 1 and 2 and simplified to be suitable for long simulations. Both were considerably better than all prior potentials in representing criterion 3 with the (12-10-6-2) model demonstrating a distinct superiority; for criterion 4 the (12-10-6-2) model was much better. Virtues and deficiencies of the present approach are analyzed. Certain similarities between cold benzene and amorphous aggregates of spheres were noted. Despite the fact that the Monte Carlo simulation had passed through the glass transition, it succeeded in accounting for cold clusters of benzene far better than did RISM computations. Results confirmed but improved upon earlier broad estimations of the properties of microdrops of benzene generated in supersonic expansions and indicated the advantages of studying liquids in their supercooled state.

I. Introduction

The aim of this paper is to investigate the degree to which molecular liquids can be considered to be understood, in a practical sense, in systems as complex as benzene. It is well-known that properties of monatomic liquids are reproduced with convincing accuracy in Monte Carlo (MC) and molecular dynamics (MD) computer simulations.[1-3] There can be no doubt that the liquid state, by far the most formidable of the common phases of matter to treat, is theoretically well-understood, at least in the sense that quantum chemistry is well-understood on the basis of Schroedinger's successful treatment of the hydrogen atom. The required ingredients for treatments of monatomic liquids, the interatomic interactions, are quite well-established. Pair-interaction energies between rare-gas atoms have been measured accurately in molecular beam experiments,[1,4-6] and the leading term in many-body interactions is known well enough to provide the modest corrections needed.[2] Quantum corrections are neither large nor difficult to estimate for atoms as heavy as argon.[2] Furthermore, the simplicity of the system makes it possible to derive experimental structural information with precision from diffraction patterns of liquids.[7-9] Such measurements provide additional benchmark tests that theoretical calculations have passed quite well, although small anomalies remain.[9,10]

Diatomic molecular systems are more complex. Quite accurate interaction potentials for some of them have been derived from experiments and quantum calculations.[11] Although certain problems remain in the understanding of their condensed phases, considerable progress has been made.[12]

Polyatomic molecular systems offer a more elusive target. Intermolecular interaction laws are much more poorly known. Certain rules-of-thumb have been popularly invoked, some of which are examined in this series of papers.[13] Little practical knowledge exists about the form and magnitude of the relevant many-body interactions. Although Evans and Watts took three-body interactions into account in a treatment of benzene crystals,[14] all simulations to date on liquids as complex as benzene have been based on two-body interactions parameterized in many cases to include three-body interactions in some average way.[13-20]

Fragments of organic molecules are lighter than neon, a system requiring appreciable quantum correction.[2] Such corrections, nevertheless, are probably smaller than errors associated with the incompletely established interaction potential. Intramolecular vibrations introduce complications not encountered in monatomic systems. Appreciable isotope effects for benzene, in such properties as the surface tension and molar volume, confirm their significance.[21] In the case of benzene, it is clear that it is the mass dependence of rather large amplitudes of vibration instead of a translational mass effect that is involved.[21] A further obstacle to simulations for molecular liquids is that, for a given sample size and level of rigor, computations for polyatomic molecular systems are enormously more time-consuming than for atomic systems.

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(1) See, for example: Maitland, G. C.; Rigby, M.; Smith, E. B.; Wakeham, W. A. *Intermolecular Forces*; Clarenden Press: Oxford, 1981; Chapter 9.

(2) Barker, J. A.; Fisher, R. A.; Watts, R. O. *Mol. Phys.* **1971**, *21*, 657.

(3) Barker, J. A.; Klein, M. L. *Phys. Rev. B.* **1973**, *7*, 4707.

(4) Scoles, G. *Annu. Rev. Phys. Chem.* **1980**, *31*, 81, and references therein.

(5) Barker, J. A.; Watts, R. O.; Lee, J. K.; Schafer, T. P.; Lee, Y. T. *J. Chem. Phys.* **1974**, *61*, 3081.

(6) Beneventi, L.; Casavecchia, P.; Volpi, G. G. *J. Chem. Phys.* **1986**, *84*, 4288.

(7) Powles, J. G. *Adv. Phys.* **1973**, *22*, 1.

(8) Pings, C. J. In *Physics of Simple Liquids*; Temperley, H. N. V., Ed.; North-Holland: Amsterdam, 1968; Chapter 10.

(9) Egelstaff, P. A. *Adv. Chem. Phys.* **1983**, *53*, 1.

(10) Egelstaff, P. A. *Can. J. Chem.* **1988**, *66*, 598.

(11) Etters, R. D.; Kobashi, K.; Belik, J. *Phys. Rev.* **1985**, *1332*, 409

(12) See, for example: Le Sar, R.; Etters, R. D. *Phys. Rev. B* **1988**, *37*, 5364.

(13) See: Shi, X.; Bartell, L. S. *J. Phys. Chem.*, in press (paper I of this series).

(14) Evans, D. J.; Watts, R. O. *Mol. Phys.* **1976**, *31*, 83.

(15) Evans, D. J.; Watts, R. O. *Mol. Phys.* **1976**, *32*, 93.

(16) Claessens, M.; Ferrario, M.; Ryckeart, J.-P. *Mol. Phys.* **1983**, *50*, 217.

(17) Jorgensen, W. L.; Modura, J. D.; Swenson, C. J. *J. Am. Chem. Soc.* **1984**, *106*, 6638.

(18) Steinhauser, O. *Chem. Phys.* **1982**, *73*, 155.

(19) Anderson, J.; Ullo, J. J.; Yip, S. *J. Chem. Phys.* **1987**, *86*, 4078.

(20) Linse, P. *J. Am. Chem. Soc.* **1984**, *106*, 5425.

(21) Bartell, L. S.; Roskos, R. R. *J. Chem. Phys.* **1966**, *44*, 457.

0002-7863/88/1510-7006$01.50/0

For the above reasons it is clear that the degree of rigor and accuracy feasible in simulations of molecular liquids can be expected to be appreciably less at this stage of development than is the case for monatomic liquids. A number of prior studies of our prototype system, liquid benzene, have been carried out using RISM,[22,23] and MC or MD techniques,[15-19] and these appear to have been successful on the face of it. They leave unanswered some crucial questions, however, which will be reviewed presently. The immediate reason for reexamining the problem at this time is the new availability of structural data for liquid benzene.[24] This information has been derived by electron diffraction for large, cold clusters of benzene generated in supersonic flow. The new diffraction patterns of the supercooled liquid provide more demanding tests of theory than existed previously.

Before comparing results of simulations with experiment, it is worthwhile to formulate criteria for assessing whether a given theoretical treatment can be considered to be realistic. We will suppose for the moment that, except for modest isotope effects, it will be adequate to treat molecules such as benzene as if they were rigid. In such a case a satisfactory theory requires at most the molecular masses and the intermolecular interaction potential energy function in order to compute structural and certain thermodynamic information at a given temperature and pressure. For a treatment to be accepted as realistic, then, we propose that it must be able to generate *from one and the same potential energy function*: (1) the crystal structure, including fair accounts of the effects of temperature and pressure; (2) the crystal binding energy or heat of sublimation; (3) the liquid structure, including effects of temperature; and (4) those liquid thermodynamic properties that are insensitive to internal molecular vibrations. Not included among the above criteria but reasonable candidates for future assessments, when more information and more complete computer programs become available, would be lattice frequencies and more extensive thermodynamic properties of crystals, and the pressure dependence of liquid structure. The above list, however, contains the most important considerations for assessing the success of current computer simulations.

What previous statistical mechanical treatments of benzene[15-17] have concentrated upon is criterion 4 above, a criterion that is insensitive to details of intermolecular interactions. As seen in paper I of the present series, none of the earlier potential energy functions adopted gave a satisfactory account of both of the first two criteria, and insufficient information existed to test criterion 3. Therefore, it is useful to readdress the problem.

Two of the potential benefits of striving for realistic treatments are (i) the development of realistic intermolecular interaction potentials, and (ii) the diagnosis of temperatures and densities of large molecular clusters whose exact thermodynamic state has previously been inferable only rather indirectly.

Previous contributions in this series have included evaluations of various proposed benzene potential functions in terms of criteria 1 and 2, and an attempt to construct an improved potential function (paper I).[13] Included was a detailed analysis of the problem of "classically extrapolating" molar volume and crystal binding energy to absolute zero. Paper II[25] provides a framework to enable a rigorous comparison of theory and experiment according to criterion 3. The present paper presents results for various proposed potential energy laws and enquires whether the treatments can be regarded as realistic.

II. Monte Carlo Computations

The general principles of the Monte Carlo method have been described in several reviews[26,27] and will not be repeated here. Specific details of computations (except for the form of the interaction potential and certain subroutines to calculate auxiliary quantities) closely follow those discussed by Jorgensen et al.[17] All computations on condensed benzene were carried out with $N = 128$ molecules in a cubic box $L \times L \times L$ with periodic boundary conditions imposed and with pressure constrained to be 1 atm. Hence, L was not fixed. Contributions to potential energy arising from distances greater than $L/2$ were obtained by integration, assuming that pair correlation functions had converged to unity beyond $L/2$. The number of molecules adopted and the box shape both frustrated crystallization at low temperatures. For crystalline order to be possible throughout the box would have required N to be a multiple of 4 and the different box sides each to be equal to integral number of orthorhombic lattice constants of benzene. Rates of cooling the equilibrated liquid at 298 K corresponded to 10° decreases in temperature each 100 000 cycles (moving one molecule each cycle) until $T = 198$ K, and 5° decreases each 150 000 to 200 000 cycles after that.[28] Even though this required a not insignificant time of computation, it corresponded to a cooling rate enormous compared with experimental cooling rates in nozzle flow (greater by a factor on the order of 10^6).[29] Translational and rotational displacement steps were 0.17 Å and 4° until a temperature of 175 K was reached, after which steps were decreased somewhat. Acceptance rates[17] began at 0.5 and fell to 0.4.

Table I. Parameters in Potential Functions[a] $\sum A_n r_{ij}^{-n}$

type, i,j	$10^{-3} A_{12}$	A_{10}	A_6	A_2	A_0
LJ6[b]					
CC	14 237.0		−5119.6		
LJ12-2[c]					
CC	2 923.9		−2383.8	35.10	−1.40
CH	384.2		−469.7	−35.10	1.40
HH	27.74		−77.9	35.10	−1.40
(12-10-6-2)[d]					
CC	6 023.21	−2 937.5	−1971.5	32.00	−1.267
CH	612.47	−69 047.2	187.6	−32.00	1.267
HH	−33.86	23 490.1	−984.4	32.00	−1.267

[a] Units: r in Å, energy in kJ/mol. For $r > 5$ Å, $A_0 = 0$ and $A_2 = 0$. [b] Parameters from ref 17, six-site model with interactions at carbon atoms, $r_{CC} = 1.40$ Å. [c] Reference 13, 12-site model using $r_{CC} = 1.403$ Å, $r_{CH} = 1.032$ Å. [d] Reference 13, 12-site model using $r_{CC} = 1.400$ Å, $r_{CH} = 1.030$ Å.

Because of the desirability of analyzing certain quantities not treated in the original MC program, coordinates of the carbon interaction sites were saved at least every 2000 cycles. Routines were written[25] to extract from these accumulations of coordinates (a) the pair correlation functions of C···C, C···H, and H···H intermolecular distances, even for interaction models with only six interaction sites per molecule (this was done by computations grafting atomic positions onto a framework of interaction sites); (b) electron diffraction patterns corresponding to spherical clusters approximately $L/2^{1/2}$ in diameter and hence larger than the usual cutoff at $L/2$ (see paper II for details and a justification);[25] (c) the ring orientational correlations embodied in the $\lambda(r_{mm})$ functions introduced by Evans and Watts,[15] where r_{mm} is the distance between molecular centers; and (d) the mean-square displacements of centers of masses of the molecules per cycle for inferring order-of-magnitude self-diffusion rates.

To facilitate later discussion we define functions in item c more explicitly by introducing the quantities

$$\lambda_i = \mathbf{a}_i \cdot \mathbf{r}_{ij}$$

$$\lambda_j = \mathbf{a}_j \cdot \mathbf{r}_{ij}$$

$$\lambda_{ij} = \mathbf{a}_i \cdot \mathbf{a}_j$$

where $\mathbf{a}_k$ is a unit vector perpendicular to the plane of molecule k, and $\mathbf{r}_{ij}$ is the unit vector in the direction of the line joining the centers of mass of molecules i and j, following the convention of vector directions making $0 \leq \lambda_i \leq \lambda_j \leq 1$. Because these quantities can be evaluated for each intermolecular separation encountered, the distribution functions $\lambda_i(r_{mm})$, $\lambda_j(r_{mm})$, and $\lambda_{ij}(r_{mm})$ can be accumulated and normalized by dividing by the center-of-mass to center-of-mass radial distribution function, $4\pi r^2 \bar{\rho} g_{mm}(r)$. In some ways this conventional normalization makes the λ functions less discriminating than would division by $4\pi r^2 \bar{\rho}$, for it exaggerates the importance of highly unfavorable configurations whose $g_{mm}(r)$ is small (especially face-to-face stacked configurations that are

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(22) Lowden, L. J.; Chandler, D. *J. Chem. Phys.* **1974**, *61*, 5228.

(23) Narten, A. H. *J. Chem. Phys.* **1977**, *67*, 2102.

(24) Valente, E. J.; Bartell, L. S. *J. Chem. Phys.* **1984**, *80*, 1451.

(25) Bartell, L. S. *Acta Chem. Scand.*, in press (paper II of this series).

(26) Woods, W. W. In *Physics of Simple Liquids*; Temperley, H. N. V., Rowlinson, J. S., Rushbrooke, G. S., Eds.; North-Holland: Amsterdam, 1975.

(27) Valleau, J. P.; Whittington, S. G.; Valleau, J. P.; Torrie, G. M. In *Modern Theoretical Chemistry*; Berne, B. J., Ed.; Plenum: New York, 1977; Vol. 5.

(28) After this procedure was carried out, minor adjustments to the potential parameters were made and the runs were continued at the individual temperatures.

(29) A crude correspondence between time and cycle number was formulated that, when applied to the data of ref 34, reproduced self-diffusion coefficients within a factor of 2 to 4.

suppressed when quadrupole moments are invoked).

III. Potential Functions Investigated

For reasons of ignorance and economics, as discussed in the Introduction, representations of intermolecular interactions were restricted to comparatively simple forms neglecting many-body effects except insofar as they contribute to the net crystal packing energy and volume (two parameters that were used to scale the potential functions). A more detailed discussion of the compromises made in constructing the functions is given in paper I.[13] It seemed appropriate to carry out MC computations on the following model interaction functions whose parameters are summarized in Table I: (1) a six-site Lennard-Jones (12-6) potential, hereafter referred to as LJ6, with parameters due to Jorgensen[17] (in the following the index *n* in LJ*n* refers to the number of interaction sites); (2) a 12-site Lennard-Jones potential representing a rescaled and simplified version of the widely used crystallographer's potential of Williams and Starr,[30] and hereafter referred to a LJ12-2 (if it contains truncated r^{-2} terms to mimic Coulomb forces) or LJ12 (if the charge terms are absent); and (3) a 12-site potential including site–site terms of form r^{-12}, r^{-10}, r^{-6}, and r^{-2} to approximate a rescaled version of the potential of Karlström et al.,[31] hereafter referred to as (12-10-6-2).

A number of other model potentials were also studied. Because they demonstrated little merit, their results will not be presented in detail.

Although the LJ6 model had already been found to be incapable of meeting criteria 1 and 2 for realistic modeling[13] (see Introduction), it has been used with some success in MC and MD computations to simulate thermodynamic properties of liquid benzene.[15-17] It was worthwhile to find whether it could also account for the *structure* of liquid benzene inasmuch as claims had been made that it gave reasonable agreement with prior X-ray studies of that fluid. It was impossible to compare results of the previous MC or MD simulations with the new electron diffraction results. This is due to the fact that the new experimental results are for a much colder liquid and that electrons "see" the hydrogens much more strongly than do X rays. No accounting of hydrogen sites had been made in the prior runs.

The LJ12-2 potential, on the other hand, gave an excellent account of the crystal structure and packing energy.[13] Therefore it was initially supposed that it would suffice for the other criteria as well because it seemed to capture the essence of the molecular details. If the coulomb (or quasi-coulomb) term was left out, it was already well known that the crystal packing deteriorated seriously.[13,30,32,33] Whether this mattered for the liquid was unknown.

Linse[20] has already reported results of MC computations based on the potential of Karlström et al. (the KLWJ potential) and the results exhibited promising aspects. The potential itself, however, gave too high a binding energy and made the molecules too small. This introduced problems to be discussed later. Furthermore, the form of the potential required square roots to be taken at each step, a time-consuming operation. Therefore, a less costly approximation was constructed, the (12-10-6-2) potential, rescaling the well-depths and atomic sizes.[13] Criteria 1 and 2 were then well met.

IV. Results

One of the most important goals of the present work was to find out whether Monte Carlo computations could characterize the highly supercooled microdrops of benzene generated in supersonic flow. Evidence from several sources indicates that the droplets so formed are appreciably colder than 200 K.[24] It quickly became apparent, however, that at the current state of the art of simulations, no practical way has been found to prevent the system from becoming glassy when the degree of supercooling is high.

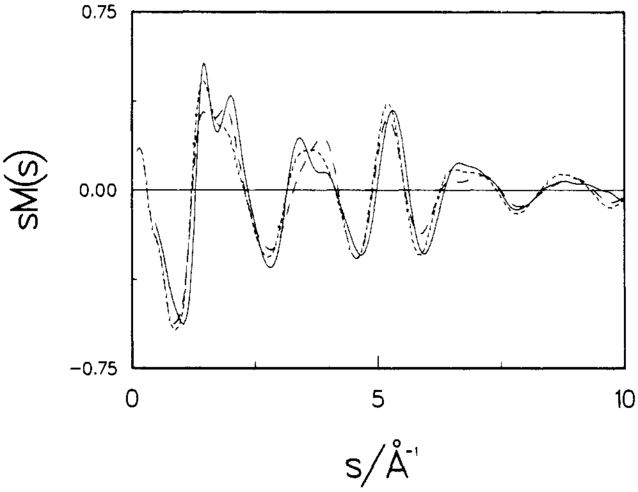

Figure 1. Reduced electron diffraction intensity curves adjusted to correspond to *intermolecular* interference features of benzene clusters 18 Å in diameter (see ref 25): solid curve, experiment; dashed curve, LJ12-2 "crystallographers'" model; and dotted curve, (12-10-6-2) "quantum dimer" model, MC computations at 160 K.

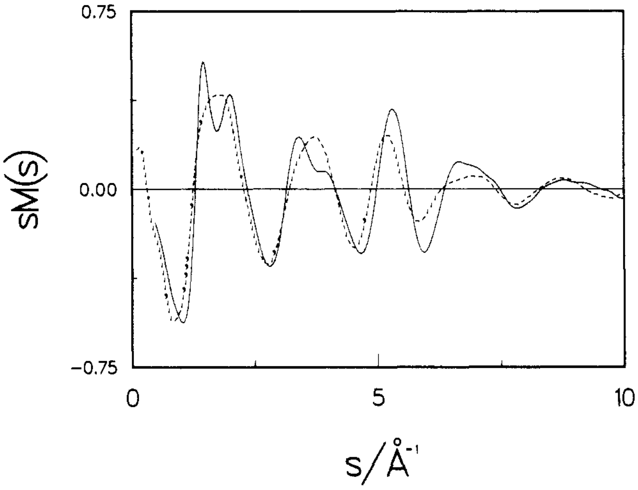

Figure 2. Solid curve as in Figure 1; dotted curve, LJ12, computed for "crystallographer's" model with partial charges deleted, 160 K.

At 298 K, mean-square displacements of molecules in the simulations increased linearly with cycle number, demonstrating the substantial self-diffusion characteristic of a true liquid. At low temperatures, on the other hand, mean-square displacements of molecules leveled off in long runs, as would be expected for a solid. This well-known behavior in MC and MD computations is a consequence of the precipitous cooling rates dictated by feasible computation times. Evidence to be cited later suggests that the cold microdrops actually observed in diffraction experiments are true liquids,[34,35] not amorphous solids. For this reason and, in addition, for the practical reason that few experimental measurements of properties of supercooled benzene exist, it is not possible to make fully rigorous comparisons between theory and experiment. Nevertheless, results appear to provide useful clues. Therefore, after calling attention to the above difficulties, we present the principal results obtained in the computations and compare, where possible, with results of diffraction and calorimetric experiments.

Figure 1 compares the reduced electron-diffraction intensity functions representing the *intermolecular* interference terms. These differ in minor ways, to be discussed later, from the conventional liquid structure functions commonly treated. Illustrated is a comparison between experiment and MC computations for

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(30) Williams, D. E.; Starr, T. L. *Comput. Chem.* **1977**, *1*, 173.

(31) Karlström, G.; Linse, P.; Wallqvist, A.; Jönsson, B. *J. Am. Chem. Soc.* **1983**, *105*, 3777.

(32) Dzyabchenko, A. V. *Zh. Strukt. Khim.* **1984**, *25* (3), 85.

(33) Dzyabchenko, A. V. *Zh. Strukt. Khim.* **1984**, *25* (4), 57.

(34) Fox, J. R.; Andersen, H. C. *J. Phys. Chem.* **1984**, *88*, 4019.

(35) Jonsson, H.; Andersen, H. C. *Phys. Rev. Lett.* **1988**, *60*, 2295.

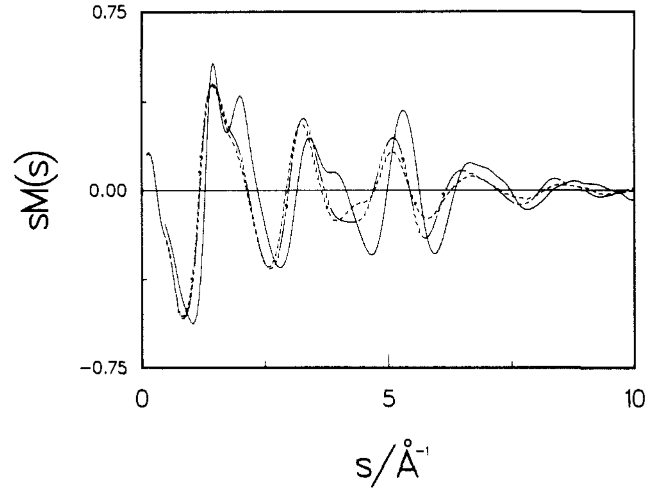

Figure 3. Solid curve as in Figure 1; dot-dashed curve for 130 K; and dotted curve for 180 K computed with six-site model potential of ref 17.

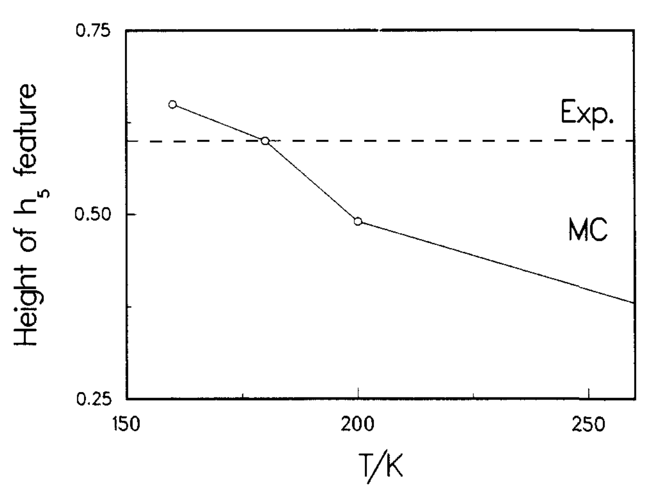

Figure 4. Trough-to-peak amplitude of diffraction feature at 5.3 Å^{-1} calculated for various temperatures according to (12-10-6-2) model potential: dashed line, experimental amplitude.

the LJ12-2 and (12-10-6-2) potentials. Note that considerably more detail attributable to molecular packing is shown than in conventional MC/MD studies[15-17] (which commonly display the sum of intra- and intermolecular interference terms, the latter of which quickly tend to vanish in comparison with the former). Figures 2 and 3 make corresponding comparisons between experiment and computation based on the LJ12 and a representative six-site potential.

It is clear from these figures that, if a reasonably realistic potential is used, the MC intermolecular diffraction features closely resemble experiment. This suggests the possibility of deducing the experimental cluster temperature from the MC computations. There is a strong damping of the features as scattering angle increases, and the damping increases as the mean-square displacements of molecules from their favored positions increases. This, of course, is why diffraction patterns of benzene at room temperature reveal less detail than patterns of the supercooled liquid. The height of the feature at 5.3 Å^{-1}, in particular, is an especially favorable indicator of temperature, as noted in an earlier work.[24] Figure 4 shows that the calculated feature agrees with the observed feature at about 175 K, a temperature agreeing with earlier rough and ready estimates.[24]

Pair correlation functions for CC, CH, HH, and center-of-mass to center-of-mass (mm) intermolecular pairs at different temperatures are shown in Figures 5–7 for calculations based on the (12-10-6-2) potential. For comparison, the corresponding functions for cold benzene based on the LJ6 model are plotted in Figure 8. Correlations in molecular orientation embodied in the $\lambda(r)$ functions are displayed in Figure 9. Because this representation is only weakly dependent upon temperature and potential function, partly for reasons noted in section II, only the 160 K results are given, and these only for the (12-10-6-2) potential.

In evaluating various representations of potential functions characterizing condensed benzene, the microscopic properties as revealed by diffraction patterns (criteria 1 and 3 of section I) are

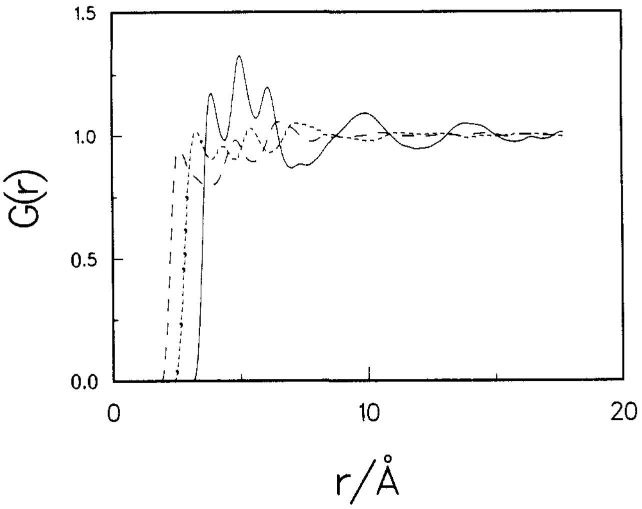

Figure 5. Pair correlation functions calculated for supercooled benzene at 160 K according to (12-10-6-2) model potential: solid curve, CC pairs; dotted, CH; dashed, HH.

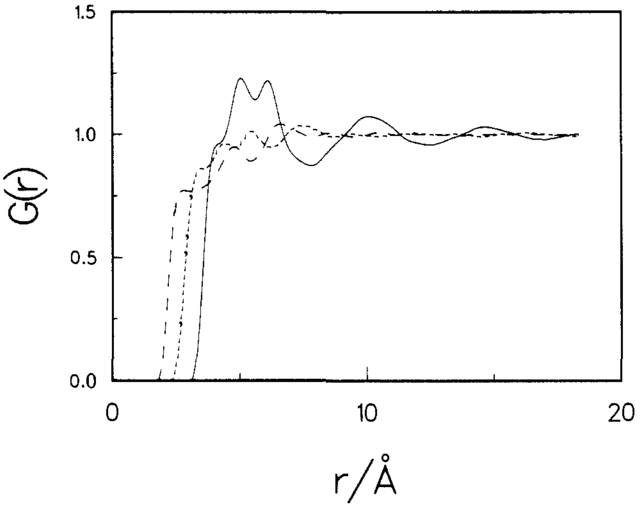

Figure 6. Pair correlation functions as in Figure 5 except at 298 K.

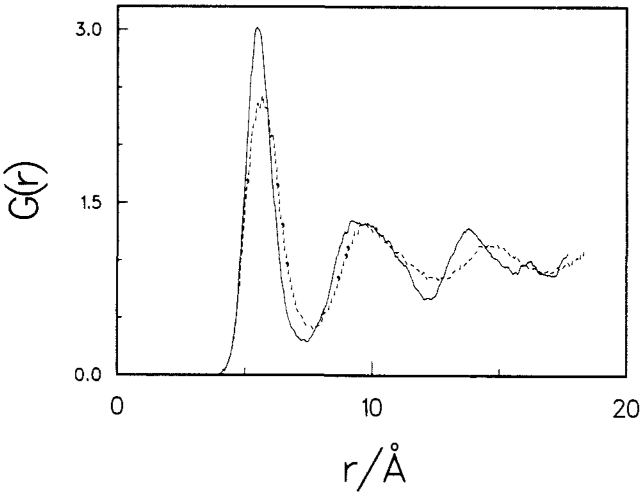

Figure 7. Center-of-mass to center-of-mass pair correlation functions calculated for benzene according to (12-10-6-2) model potential: solid curve for 160 K; dashed for 298 K.

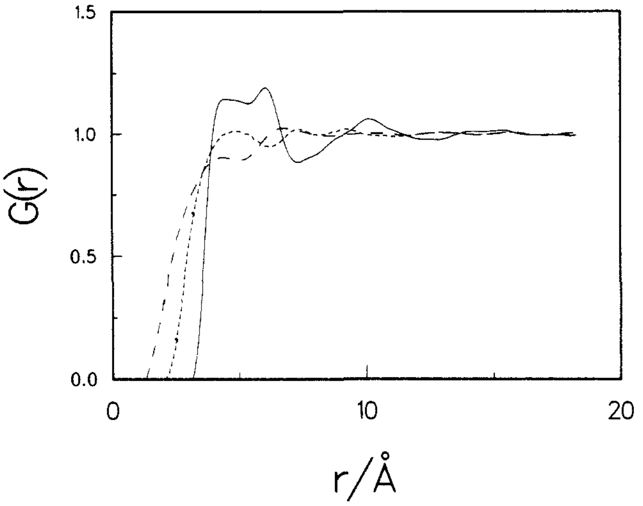

Figure 8. Pair correlation functions as in Figure 5 except that the six-site model of ref 17 was adopted. Note that the initial features of the six-site model at 160 K are more blurred than those of the 12-site (12-10-6-2) model at 298 K.

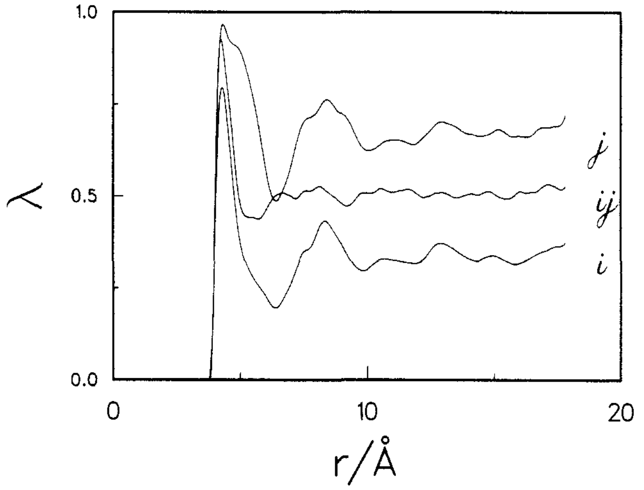

Figure 9. Ring orientational correlations $\lambda(r_{mm})$ of Evans and Watts[15] calculated for benzene at 160 K according to (12-10-6-2) potential function. Comparison with those in ref 16 and 20 shows modest sensitivity to temperature and potential function but extreme sensitivity to phase (crystal vs. supercooled liquid).

particularly helpful but incomplete. Macroscopic properties (criteria 2 and 4) are required as well. Among them were selected the molar volume and heats of sublimation and evaporation. These are given in Table II for the solid at 0 K and for the liquid at several temperatures as calculated according to a series of model potentials. For comparison are listed "experimental" values, including entries for the (hypothetical) motionless state of the crystal derived in paper I[13] and for the highly supercooled liquid as extrapolated from values for the normal liquid by the analytical representations of Yaws.[36] Because no true experimental values exist for such entries, tabulated values are subject to appreciable uncertainty.

Finally, the presentation of diffraction results would be incomplete if attention were not called to a technical problem. The most appropriate liquid diffraction pattern to analyze in detail is the so-called structure function, $sH_d(s)$, defined and discussed in paper II.[25] The fact that the alternative reduced intensity function $sM_{cl}(s)$ is plotted in Figures 1-3 instead is purely for convenient visual assessment. Because $sM_{cl}(s)$ is damped progressively more relative to $sH_d(s)$, as scattering angle gets *small*, it is easier to portray in a single figure the details of the most important features with this representation. Fourier analysis is, however, degraded by the effect of incoherent scattering. For reference, the functions $sH_d(s)$ and $sM_{cl}(s)$ as derived from experiment[37] are compared in Figure 10.

Table II. Properties of Normal and Supercooled Benzene[a] at Various Temperatures from Classical Simulations According to Model Potentials. Results at 0 K for Crystal

	model			
property	LJ6[b]	LJ12-2[c]	(12-10-6-2)[c]	"expt"
$\Delta H_v(298)$	33.9	37.6	33.6	33.6[d]
$\Delta H_v(200)$			39.0	37.9[e]
$\Delta H_v(180)$	37.4	42.9	40.3	38.7[e]
$\Delta H_v(160)$		44.5	41.0	39.4[e]
$\Delta H_{sub}(0)$	40.7	(52.3)[f]	(52.3)[f]	52.3[g]
$V(298)$	89.4	85.3	86.5	89.5[d]
$V(200)$			78.2	81.1[e]
$V(180)$	83.5	76.4	76.9	79.6[e]
$V(160)$		75.3	75.8	78.3[e]
$V(0)$	72.7	(67.4)[f]	(67.4)[f]	67.4[h]

[a] Heats of vaporization in kJ/mol, volumes in cm^3/mol. [b] Model of ref 17. [c] Models of Table I. [d] Reference 36. [e] From equations of ref 36 extrapolated far beyond the stated range of validity. [f] Model potential adjusted to reproduce this value. [g] References 16 and 30. [h] Estimated result of "classical extrapolation" to vibrationless crystal at 0 K according to ref 13.

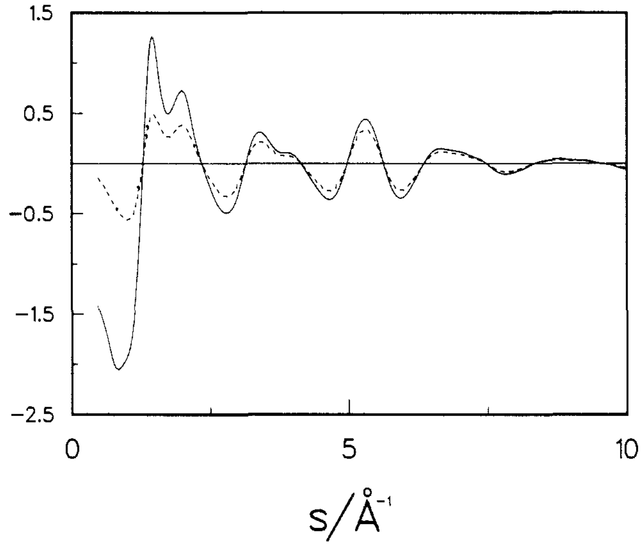

Figure 10. Comparison between experimental *intermolecular* interference features $sH_d(s)$ (solid) and $sM_{cl}(s)$ (dashed), for benzene. The former corresponds to interference intensities divided by *elastic* atomic intensities whereas division in the latter is by *elastic plus inelastic* atomic intensities.

V. Discussion

On Crudeness of Model. Before discussing results of computations for benzene, it is reasonable to enquire whether there is any likelihood of satisfying the four criteria in section I in the face of the severe limitations imposed on the model interaction potentials that are explored. Can results of a simulation realistically account for microscopic and macroscopic properties of both the liquid and solid phases if the potential deviates appreciably from the correct representation? The answer, of course, depends upon the level of precision demanded. One helpful illustration is provided by the argon system where it is simple to carry out calculations with deficiencies in the potential corresponding to those expected for benzene.

Calculations for argon were performed with Lennard-Jones (LJ) interactions, excluding many-body interactions, with LJ parameters adjusted to fit the molar volume and packing energy of the solid. The question is whether such a potential, mediocre in form but

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(36) Yaws, C. L. *Physical Properties, a Guide*; McGraw-Hill: New York, 1977.

(37) Data from ref 24 were transformed as discussed in ref 25.

adjusted to absorb errors for the solid, can account for properties of the liquid to within a few percent. It is well-known that the LJ function is too shallow and broad beyond its minimum, and too steep inside its minimum. In fitting the net binding energy of the condensed phase, then the LJ function places far too much emphasis on interactions beyond nearest neighbors, the coefficient of its "long-range" r^{-6} term being 60% higher than the correct value.[38] Yet, through compensations associated with the parameter adjustment, computations extended to liquid argon do account, to within 1 to 3%, for ΔH_v and $\bar{V}$ near the melting point. In the case of benzene, where not even the form of the pair interaction energy is known very well, errors of a few percent would be considered acceptable in the present context. Details of our argon computations[39] are not listed here because many similar computations have been published in the past.

Regarding Glass Formation. As mentioned in section IV, MC simulations led to a glassy phase when sample temperatures dropped substantially below the freezing point of benzene. It is important to establish, then, whether the clusters generated in supersonic flow are also glasses or whether they are true supercooled liquids. It is known that the glass transition temperature $T_g(10)$ for samples cooled at the conventional rate of 10°/min is approximately 121 K for benzene.[40,41] It is also known that the glass transition temperature, in general, is raised when cooling rates are increased.[42,43] Direct measurements of cooling rates for clusters in supersonic jets are not available. It is possible to make quite reasonable estimates of cooling rates, however, by carrying out computer simulations of nucleation and cluster growth in a medium of expanding carrier gas. Benzene clusters, when nearly full grown, are believed to be comparatively warm, perhaps 260 K when produced under typical conditions.[44] If such clusters were to cool by evaporation into a vacuum, their cooling rate would be nearly proportional to their vapor pressure.[45] The rate would rapidly drop from over $\sim 10^8$ to $\sim 10^7$ K s^{-1} at 220 K to $\sim 10^5$ K s^{-1} at 180 K. In the presence of an expanding carrier gas in nozzle flow, the rate can be appreciably enhanced, especially at the lower end of the accessible temperature range where the vapor pressure approaches 10^{-6} bar.[46]

Angell et al.[42,43] have shown how to estimate the dependence of the glass transition temperature T_g on the cooling rate. These investigators report that various classes of liquids ranging from "fragile" to "strong" exhibit characteristic patterns of structural relaxation times as a function of $T_g(10)/T$. Therefore, because relaxation times pertaining to a system as it undergoes a glass transition are inversely proportional to the cooling rate, it is possible to derive an approximate value of T_g from the cooling rate. If benzene is taken to be a fragile liquid similar to toluene or *o*-terphenyl (to cover a range of possibilities corresponding to Figure 1 or 2 of ref 43), a cooling rate of 10^{12} K/s comparable to that in our MC runs, would lead to a glass transition at 160–190 K. Below 250 K in the simulations, self-diffusion became too low to be demonstrably that of a liquid.[47] On the other hand, in experiments on clusters the most extreme cooling rates that could be encountered, $\sim 10^8$ K/s, only happen at $\sim$260 K, well above the 139–144 K range at which a glass would be formed at this cooling rate. At the lowest observed cluster temperatures the structural relaxation becomes the most sluggish, of course. But as this temperature range is approached, the cooling rate falls below 2×10^6 K/s. At 2×10^6 K/s, T_g drops to about 135 K, only 14° above the experimental glass temperature and some 40° lower than the estimated cluster temperature. Therefore, the clusters are believed to be liquid.

Viability of Six-Site Models. Although a six-site model can give a good account of the thermodynamic properties of liquid benzene[16,17] (criterion 4), it is evident that it is far inferior to the 12-site models in meeting the other criteria. Speculation that it might satisfactorily model the quite random structure of the liquid, even if it cannot model the crystal, is unfounded. This can be seen in Figures 3 and 8. The molecules slip around too easily in the cages formed by their neighbors. At 160 K their pair correlation functions are more washed out than the corresponding 12-site functions at room temperature. If a point quadrupole is placed at the ring centers, the heat of sublimation is improved but the implied structures remain inadequate. The face-to-face stacking which the quadrupole moment was introduced to destabilize is excessively destabilized. A modified six-site model with six 12-6 sites but with 12 point charges at C and H sites to reproduce the experimental quadrupole moment can be adjusted to give a good binding energy and crystal structure, particularly if the radial site position is optimized.[13] It might yield satisfactory liquid properties, as well. It was not tested in MC runs, however, because it offers no significant computational advantage over full 12-site models and is less realistic.

Necessity of Partial Charges. Paper I[13] corroborated and extended prior results[20,30–33] showing that partial charges of a magnitude implied by the experimental quadrupole moment are essential to reproduce the experimental crystal structure. On the other hand, several simulations[15,16] of liquid structure at room temperature made with potentials devoid of electrostatic charges were interpreted as being in more or less satisfactory agreement with experimental diffraction studies. To settle the issue for liquids, an electron diffraction pattern was calculated for an LJ12 potential function derived by deleting charges[48] from an LJ12-2 function that successfully accounted for the crystal structure and gave an enormously better account of the liquid than did the six-site model. As can be seen in Figure 2, the chargeless LJ12 model gives an unsatisfactory description of the supercooled liquid. The apparent acceptability of previous chargeless models was partly due to the fact that the diffraction detail of the warm liquid examined was too smeared by thermal motion to be very revealing and partly due to the insensitive basis upon which the comparison was made.

Quantum Model vs. Crystallographer's Model. The (12-10-6-2) potential is a simplified representation of Karlström's quantum result for a benzene dimer,[31] with parameters rescaled to reproduce the binding energy and molar volume of crystalline benzene and thereby to include some aspects of many-body interactions. It has been shown not to be satisfactorily transferable to other hydrocarbon crystals.[13] By contrast, the LJ12-2 potential is a simplified representation of the potential of Williams and Starr,[30] whose parameters not only anticipated the partial charges later found in a measurement of the molecular quadrupole moment[49] but also modeled the two crystal phases of benzene excellently and, in addition, were successful in reproducing the crystal structures of a wide variety of other organic compounds. In our opinion, our simplification of the potential of Williams and Starr scarcely affects the results of the present computations (except to correct them for effects of thermal motion as described in Paper I[13]). Clearly, then, the LJ12-2 model would be highly preferable to the (12-10-6-2) model, on the basis of its wider applicability in crystallography, provided the two models performed comparably in computations on the liquid. As Figures 1–3 show, both are far superior to the others examined in simulating liquid structure,

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(38) Guggenheim, E. A.; McGlashan, M. L. *Proc. R. Soc.* (*London*) **1960**, *255*, 456. Guggenheim, E. A. *Applications of Statistical Mechanics*; Clarenden: Oxford, 1966.

(39) Sharkey, L. R.; Bartell, L. S.; unpublished research. Calculations for liquid and solid at 1 atm were repeated for consistency and to check the present routine.

(40) Dubochet, J.; Adrian, M.; Teixeira, J.; Alba, C. M.; Kadiyala, R. K.; MacFarlane, D. R.; Angell, C. A. *J. Phys. Chem.* **1984**, *88*, 6727.

(41) Angell, C. A.; Sare, J. M.; Sare, E. J. *J. Phys. Chem.* **1978**, *82*, 2622.

(42) Angell, C. A.; Torell, L. M. *J. Chem. Phys.* **1983**, *78*, 937.

(43) Angell, C. A.; Dworkin, A.; Figuiere, P.; Fuchs, A.; Swarc, H. *J. Chim. Phys.* **1985**, *82*, 773.

(44) Bartell, L. S. *Comm. Chem. Phys.*, in press.

(45) Gspann, J. In *Physics of Electronic and Atomic Collisions*; Datz, S., Ed.; Hemisphere: Washington, 1976.

(46) Bartell, L. S. *Chem. Rev.* **1986**, *86*, 491.

(47) Angell, C. A.; Clarke, J. H. R.; Woodcock, L. V. *Adv. Chem. Phys.* **1981**, *48*, 398.

(48) Model of ref 13. When the charges were deleted the remaining coefficients were rescaled to reproduce the crystal packing energy.

(49) Battaglia, M. R.; Buckingham, A. D.; Williams, J. H. *Chem. Phys. Lett.* **1981**, *78*, 421.

and the LJ12-2 model is only slightly inferior to the (12-10-6-2) model in this regard. The critical distinction is in the computed heats of vaporization listed in Table II. Here the LJ12-2 model gives an excessive value while the (12-10-6-2) model acquits itself very well. From this simple example it is tempting to conclude that, in some respects, liquids pose a more discriminating test of potential functions than do crystals because molecules in a liquid are not constrained quite so rigidly to special orientations in their mutual contacts. Even though it is less attractive because of its lack of transferability, the (12-10-6-2) model appears to capture the specific characteristics of benzene–benzene interactions in the liquid significantly better than does the LJ12-2 model. It also yields a T-shaped dimer, the shape attributed to the dimer from its polarity,[50] whereas the crystallographer's model does not.[51]

One worrying aspect of the (12-10-6-2) model in its original form is the rather abrupt truncation of the r^{-2} term at 5 Å. While the function is continuous, its derivatives at 5 Å are not. After all of the tabulated results in the present paper had been computed, a version with the r^{-2} term truncated at 12 Å was tried, retaining the old potential parameters except for A_2 and $A_0 = A_2/144$ Å^2. Augmenting A_2 to 58.68 kJ Å^2/mol to compensate for the relaxed truncation yielded crystal packing results for cell constants and molecular orientations in close accord with those obtained with the more severe truncation. They also yielded MC results for 500 000 cycles at 298 K which deviated from the results in Table II by little more than the statistical noise.

Comparison with Linse's MC Results. One striking feature of the present calculations is that the pair correlation functions of the supercooled liquid more nearly resemble those of Linse's crystals[20] than those of his liquids! This is partly a real effect of the high degree of supercooling but partly an artifact of Linse's calculations. Two aspects of the Karlström-Linse (KLWJ) potential are involved. First, the binding energy of the KLWJ potential is too great by 20%. When the potential is rescaled to give the correct binding energy, the corresponding temperatures of the Monte Carlo simulations drop 20%. Therefore, it is appropriate to shift Linse's temperature scale by this amount in making comparisons. This makes his lower-temperature liquid run correspond to a temperature 21° below the bulk freezing point. The second aspect of the KLWJ potential is more important and has consequences in the opposite direction. That is, the molar volume at 0 K is about 11% too small. If Linse's computations had been for atmospheric pressure this would have made only a modest difference in results. Instead, his calculations were carried out at the experimental density. Because the associated volume was over 11% higher than the equilibrium volume, the implied pressure was *negative* and very large, and the molecules filled the surplus of space allotted them by executing larger amplitudes of motion than would have been allowed at 1 atm. Therefore, Linse's crystal at 258 K (215 K rescaled) gives much more diffuse atom–atom pair correlation functions than does our supercooled liquid which itself displays only slightly more blurred functions than Linse's crystal at 120 K (100 K, rescaled). On the other hand, the center-of-mass to center-of-mass pair correlation functions $g_{\mathrm{mm}}(r)$ of both of Linse's crystal simulations clearly resolve the 5 to 6 Å doublet that merges into a single peak in our supercooled liquid. This function is, unfortunately, not an experimental observable in diffraction experiments. Nevertheless, it is available in simulations and is informative about structural order. In this respect it was more discriminating than the atom–atom pair correlation functions.

One reason the KLWJ potential had originally appeared to be interesting to investigate lay in the heats of vaporization it yielded in MC simulations.[20] When Linse's energies and temperatures were rescaled as described above, the heats of vaporization (see Table II) turned out to be somewhat too small, a deviation *opposite* to the one observed for the "crystallographic" potential, suggesting that some compromise might lead to an improvement over both. Our rescaled, simplified (12-10-6-2) version of the KLWJ potential, however, immediately yielded satisfactory heats of vaporization without need for further compromise, and it is not unlikely that the rescaled KLWJ potential might also, if runs were made at an imposed pressure of 1 atm. The small heat of vaporization obtained in Linse's runs may in large measure be due to the high negative pressure of the simulation which, in pulling the molecules somewhat apart, reduced the energy required to complete the vaporization.

Other Inferences about Structure and Molecular Motions. Another comparison is invited by availability of the center of mass function $g_{\mathrm{mm}}(r)$. Temperley[52] has suggested that benzene molecules in a liquid "may...be expected to behave nearly as spheres" as a consequence of their rotational motions. In this regard it is of interest to note that the crystal structure of benzene[53] is such that if the oblate molecules were steadily inflated to a spherical shape, the lattice would transform smoothly to the cubic-closest-packed structure characteristic of rare gas solids and many metals. Clearly, of course, the molecular interaction potentials are decidedly anisotropic, a fact strongly confirmed by Figures 5, 6, and 9, as well as the potential function itself. Yet, in a sense, Temperley's suggestion is borne out in the appearance of $g_{\mathrm{mm}}(r)$ (Figure 7) which bears some resemblance to that of amorphous metals[54] and the "polyicosahedral" amorphous clusters of argon discussed by Farges et al.[55] Steinhardt et al.[56] and Jonsson and Andersen[35] have also called attention to the tendency of LJ atoms to form icosahedral aggregates in supercooled liquids and glasses. In Farges' polyicosahedral structures, $g(r)$ displays a strong first peak at r_1 for atoms in contact, followed by a peak for next-nearest neighbors at $1.7r_1$, a smaller one at $2.0r_1$, and a more prominent peak at $2.5r_1$. Dense random packing of spheres leads to somewhat similar pair correlation functions as discussed by Cargill.[57] As an amorphous solid melts, the subsidiary peak at $2.0r_1$ ultimately merges with that at $1.7r_1$. Runs for supercooled benzene as exemplified by Figure 7 exhibited the three major peaks mentioned at very nearly the values expected for the packing of spherical objects, and most cold runs gave a weak shoulder at $2.0r_1$. Despite its marked asphericity, benzene mimics a sphere in its statistical center-to-center distribution.

A further feature of Figure 7 is to be noted. The first peak shows no inner shoulder at small r. Such a shoulder appears in simulations that include no electrostatic interaction to destabilize the face-to-face stacking of benzene rings that are favored by van der Waals attractions.[15,16] By inhibiting the closest approach of benzene molecules to each other, the quadrupole moment, roughly speaking, plays down manifestations of flatness of the molecules in their packing arrangements.

Another comparison sheds light on aspherical aspects of benzene, the orientational correlations. It has already been mentioned that the $\lambda(r_{\mathrm{mm}})$ functions typified by those in Figure 9 are not strongly discriminating in their portrayal of correlations between orientations of benzene rings in liquids. That is, these functions do not undergo marked changes with temperature or potential function, even when the potential function is an unacceptable six-site model. Nevertheless, the $\lambda(r_{\mathrm{mm}})$ for the liquid are entirely different from those of the *solid* calculated by Linse.[20] At distances beyond the first peak in $g_{\mathrm{mm}}(r)$, the solid $\lambda(r_{\mathrm{mm}})$ functions confirm a well-ordered distribution of orientations of planes, whereas the liquid functions imply near chaos. In the face of the striking similarity between the atom–atom pair correlation functions for the solid and the supercooled liquid then, it can be inferred that while the orientations of the planes of the rings are poorly ordered in the liquids, the orientations of the rings about

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(50) Janda, K. C.; Hemminger, J. C.; Winn, J. S.; Novick, S. E.; Harris, S. J.; Klemperer, W. *J. Chem. Phys.* **1975**, *63*, 1419.

(51) Williams, D. E. *Acta Crystallogr., Sect. A* **1980**, *36*, 715.

(52) Temperley, H. N. V. In ref 26, p 21.

(53) Cox, E. G.; Cruickshank, D. W. J.; Smith, J. A. C. *Proc. Soc. London, Ser. A* **1958**, *247*, 1. For a precise new crystal structure of C_6D_6, see: Jeffrey, G. A.; Ruble, J. R.; McMullan, R. K.; Pople, J. A. *Ibid.* **1987**, *414*, 47.

(54) Lauriat, J. P. *J. Non-Cryst. Solids* **1983**, *55*, 77.

(55) Farges, J.; de Feraudy, M. F.; Raoult, B.; Torchet, G. *J. Chem. Phys.* **1983**, *78*, 5067.

(56) Steinhardt, P. J.; Nelson, D. R.; Ronchetti, M. *Phys. Rev.* **1983**, *1328*, 784.

(57) Cargill, G. S., III *Solid State Phys.* **1975**, *30*, 227.

their 6-fold axes are well-ordered, for molecules in contact, until the temperature gets quite warm (compare Figures 5 and 6). Although this behavior seems at first glance to be at odds with that in the solid where the results of an NMR study[58] and Linse's analysis both indicate that there is "a larger rotational freedom around the C_6 axis than that around a C_2 axis", the orientational preference is distinct from rotational diffusion.

VI. Conclusions

We conclude by summarizing the most important inferences drawn about the system of supercooled benzene and enumerating significant aspects of the present treatment, not all of which have been wholly resolved.

Available evidence indicates that the liquid-like clusters produced by homogeneous nucleation in supersonic expansion in prior research are true liquid microdrops, of the order of 200 Å in diameter[59] and, at ~175 K, supercooled to a degree far beyond that yet attained in the bulk (mp 278.7 K). This supercooling considerably enhances the detail observable in the pair correlation functions, and the diffraction patterns thereby offer a more discriminating test of molecular interaction potentials and of liquid theory than could be achieved in earlier structural studies of liquids.[23,60,61]

While the short-range structure of cold liquid benzene closely resembles that of the crystal, the MC results suggest that the distribution of molecular centers is very like that in amorphous metals and polyicosahedral clusters of rare gas atoms too small to adopt the bulk fcc structures.[55] The strong peaks displayed in the spectrum of intermolecular distances originally derived from the electron diffraction data but absent in RISM computations[24,62] show up prominently in the Monte Carlo simulations. Their close resemblance to the corresponding features in Linse's Monte Carlo calculations for crystalline benzene constitutes the evidence that the short-range packing in the cold liquid is very similar to that in the solid. The specific interactions that govern this structure in both phases are the partial charges that are also manifested in the electric quadrupole moment. Small, at only ~1/7 electron surplus on C, deficit on H, these charges nevertheless dominate *short-range* interactions (and play almost no role at long range). Simulations deleting these charges give unacceptably poor accounts of the crystal and liquid structures. This result is not altogether consistent with suggestions in the literature to the effect that liquid structure is dictated almost entirely by steric (harshly repulsive) forces.[63] Of course, for stable (warm) liquids the influence of the specific (nonsteric) interactions becomes less conspicuous.

The present work definitively narrows the form of interaction potentials that are acceptable for benzene, rejecting six-site and chargeless models, but it in no sense establishes a fully optimized potential function for benzene. It does indicate that the crystallographer's model which is extremely successful in predicting crystal structures is at best mediocre in accounting for liquid properties. A (12-10-6-2) potential has been constructed that comes closer to satisfying all four criteria (outlined in section I and the abstract) to be met by a realistic treatment than does any other potential introduced so far. Its parameters, which were adjusted to fit only dimer and crystal properties, also reproduce the heat of vaporization of the liquid excellently, and come within 14% of accounting for the increase in volume from the (hypothetical) motionless state of the crystal to the liquid at 25 °C. Yet, the residual 3% error in the molar volume of the liquid at 25 °C and the small, systematic differences between experimental and calculated structure functions for the supercooled liquid betray imperfections in the Monte Carlo simulations.

Discrepancies in the structure function may, at least in part, arise from the fact that the Monte Carlo sample had become glassy instead of remaining liquid as the sample was cooled.[35] A human lifetime of Cray XMP/48 computations would not be able to cool the sample as slowly in simulations as in the supersonic experiments and avoid the glass transition. Other potential shortcomings include the simplified representation of the unknown actual interaction function, the classical nature of the treatment, and the neglect of intramolecular vibrations. A resolution of the discrepancies is a problem for the future. Meanwhile, significant progress has been made in the understanding of the system investigated and, despite its flaws, the present treatment is the most realistic to date on a system as complex as benzene.

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Registry No. Benzene, 71-43-2.

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(58) Andrew, E. R.; Eades, R. G. *Proc. R. Soc. London, Ser. A* **1953**, *218*, 537.

(59) Cluster diameter estimated from simulations in ref 44 which were, in turn, calibrated against simulations for solid clusters which can be checked experimentally.

(60) Narten, A. H. *J. Chem. Phys.* **1968**, *48*, 1630.

(61) Bartsch, E.; Bertagnolli, H.; Schulz, G.; Chieux, P. *Ber. Bunsenges. Phys. Chem.* **1985**, *89*, 156.

(62) The computations of ref 24 indicating a lack of detail in the RISM pair correlation functions for benzene had been carried out neglecting partial charges. When results of ref 13 emphasized the importance of charges in the packing structure of benzene, the RISM computations were repeated with charges included (Valente, E. J., unpublished research, 1988). The RISM pair correlation functions remained almost featureless in comparison with the Monte Carlo results.

(63) Chandler, D. *Acc. Chem. Res.* **1974**, *7*, 246; *Annu. Rev. Phys. Chem.* **1978**, *29*, 441. It should be said that the dominating effect of harsh repulsions was demonstrated most compellingly for atomic systems, and strongly associated liquids were excluded. Benzene was explicitly included among systems expected to be dominated by steric effects, but that was before the detailed forces governing benzene interactions had been widely recognized.