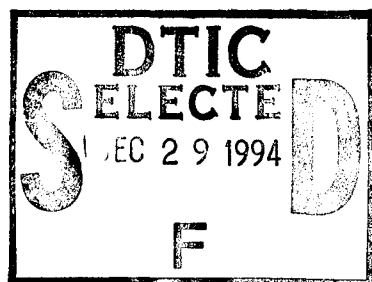


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A DENSITY FUNCTIONAL/MOLECULAR DYNAMICS  
STUDY OF THE STRUCTURE OF LIQUID NITROMETHANE

by

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# A DENSITY FUNCTIONAL/MOLECULAR DYNAMICS STUDY OF THE STRUCTURE OF LIQUID NITROMETHANE

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## Abstract

A molecular dynamics simulation of liquid nitromethane has been carried out, in which a density functional (DF) procedure was used to compute the properties needed to establish the intermolecular force field. The latter was subsequently updated by further DF calculations. The first and second shells of neighbors are found to be at radii of about 6 Å and 11 Å from a given nitromethane molecule. OH partial pair correlation functions are determined, and indicate the presence of C-H····O hydrogen bonding.

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Nitromethane, a prototypical energetic compound, is a liquid at room temperature, with a boiling point of 101.2°C at one atmosphere pressure.<sup>1</sup> The polar nature of the molecule is reflected in its dipole moment, 3.46 D, and in the dielectric constant of the liquid, 35.87 at 30°C.<sup>1</sup> Quite significant intermolecular interactions can therefore be anticipated in the liquid phase, perhaps including C-H·····O hydrogen bonding. (It is now well-established that carbon can be a hydrogen bond donor.<sup>2-5</sup>) The elucidation of such interactions would be important both in furthering the understanding of the structures of polar liquids in general and also in helping to interpret experimental studies of nitromethane in particular.<sup>6-10</sup>

We have accordingly undertaken a combined density functional (DF)/molecular dynamics (MD) study of liquid nitromethane at 300° K and a density of 1.139 g/cm<sup>3</sup>. We use a DF procedure, applied to a single molecule, to compute the properties needed to establish the intermolecular force field and then begin an MD simulation. This is stopped occasionally and a new DF-updated force field is obtained, using now a typical configuration of several molecules. This continues until self-consistency is attained in the force field, which is then appropriate to the specific conditions of temperature and density. Since no experimental data are required as input, this approach can be applied as well to compounds which have not yet been synthesized or for which measurements have not been carried out.

The molecular properties needed to create the initial force field are the optimized geometry, force constants and atomic charges. Once the MD simulation is underway, the periodic DF calculations on the nitromethane clusters are single point runs to determine new charges; the geometries used are those that have evolved during the previous MD simulation. Our approach can be viewed as an improvement over MD techniques that use a non-varying force field (which may be derived from *ab initio*, semi-empirical or experimental data) and in the direction of the procedure of Car and Parrinello, which directly combines the DF and MD equations so that no force field need be explicitly created.<sup>11</sup> While the latter approach is certainly a very desirable one, it is limited at present to relatively small systems.

The density functional calculations were carried out with Gaussian 92/DFT,<sup>12</sup> using the Becke exchange<sup>13</sup> and Lee-Yang-Parr correlation<sup>14</sup> functionals and the 6-31G\*\* basis set. Atomic charges were obtained by fitting them to the computed molecular electrostatic potential while simultaneously preserving the dipole moment.<sup>15</sup> The resulting charges were: N:0.660; O: -0.377; C: -0.266; H: 0.120. The CHARMM program was used for the molecular dynamics simulations<sup>16</sup> and analysis programs were developed *in situ*. 216 nitromethane molecules were distributed uniformly and with random orientations in a cubic box with dimension 26.79 Å, chosen to reproduce the experimental density.<sup>1</sup> Periodic boundary conditions were used. The dynamics were performed with the Verlet algorithm.<sup>17</sup>

Before beginning the simulation, a classical optimization of the orientations and geometries of the molecules was carried out. The resulting average geometry was very similar to that produced by the DF calculation, the largest difference being a shortening of the C-N bond by 0.02 Å. In the early stages of the simulation, the temperature of the system was increased by 10°K every 1 ps (2000 steps); later this became 10° K every 2.5 ps (5000 steps). Once the final temperature of 300°K was reached, the system was allowed to equilibrate for 20 ps. During the final portion of the equilibration, the potential energy and the temperature showed only minor fluctuations.

Some time after equilibration had been finished, at 52 ps after the beginning of the simulation, a cluster of nine nitromethane molecules was selected for the DF update of the force field. This cluster consisted of a central molecule and its first shell of neighbors. The new charges found for the central molecule (and adopted for all 216) were: N: 0.717; O: -0.406; C: -0.331; H: 0.142. A subsequent DF analysis after 20 ps (40,000 steps) showed no significant further changes in atomic charges. Once the system had adjusted to the modified charges, desired properties were determined by taking samples at various regular intervals, using a step time of 0.5 fs.

Figure 1 shows the CC, CN and NN pair correlation functions as determined from the production runs. These show that, for a given nitromethane molecule, the first shell of neighbors is within a radius of about 6 Å, and the second shell is within about 11 Å. Of particular interest are the OH correlations, shown in Figure 2. For any pair of nitromethane molecules, there are 12 possible O...H interactions. The total OH pair correlation function is the average of all of these, resulting in the essentially unstructured curve near the bottom of Figure 2. We were able to resolve this into its 12 components (not readily achievable experimentally) that correspond to the 12 possible O...H intermolecular distances between two nitromethane molecules. The first peak of the first OH partial pair correlation function occurs at about 2.3 Å; this is clearly indicative of C-H...O hydrogen bonding in liquid nitromethane,<sup>2,3</sup> a point which has been the subject of speculation in the past.<sup>10</sup>

The self-consistent force field procedure that we have applied in this study provides a more realistic and yet computationally efficient means of treating large systems. In addition, the use of partial pair correlation functions permits a much more detailed analysis of the structure of fluids than is possible with the total pair correlation function.

### Acknowledgement

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## Captions for Figures

Figure 1. Calculated CC, NN and CN pair correlation functions for liquid nitromethane at 300 °K and a density of 1.139 g/cm<sup>3</sup>

Figure 2. Calculated OH total (thick curve) and partial pair correlation functions for liquid nitromethane at 300 °K and a density of 1.139 g/cm<sup>3</sup>. The 12 partial pair correlation functions correspond to the possible O·····H intermolecular distances between two nitromethane molecules.

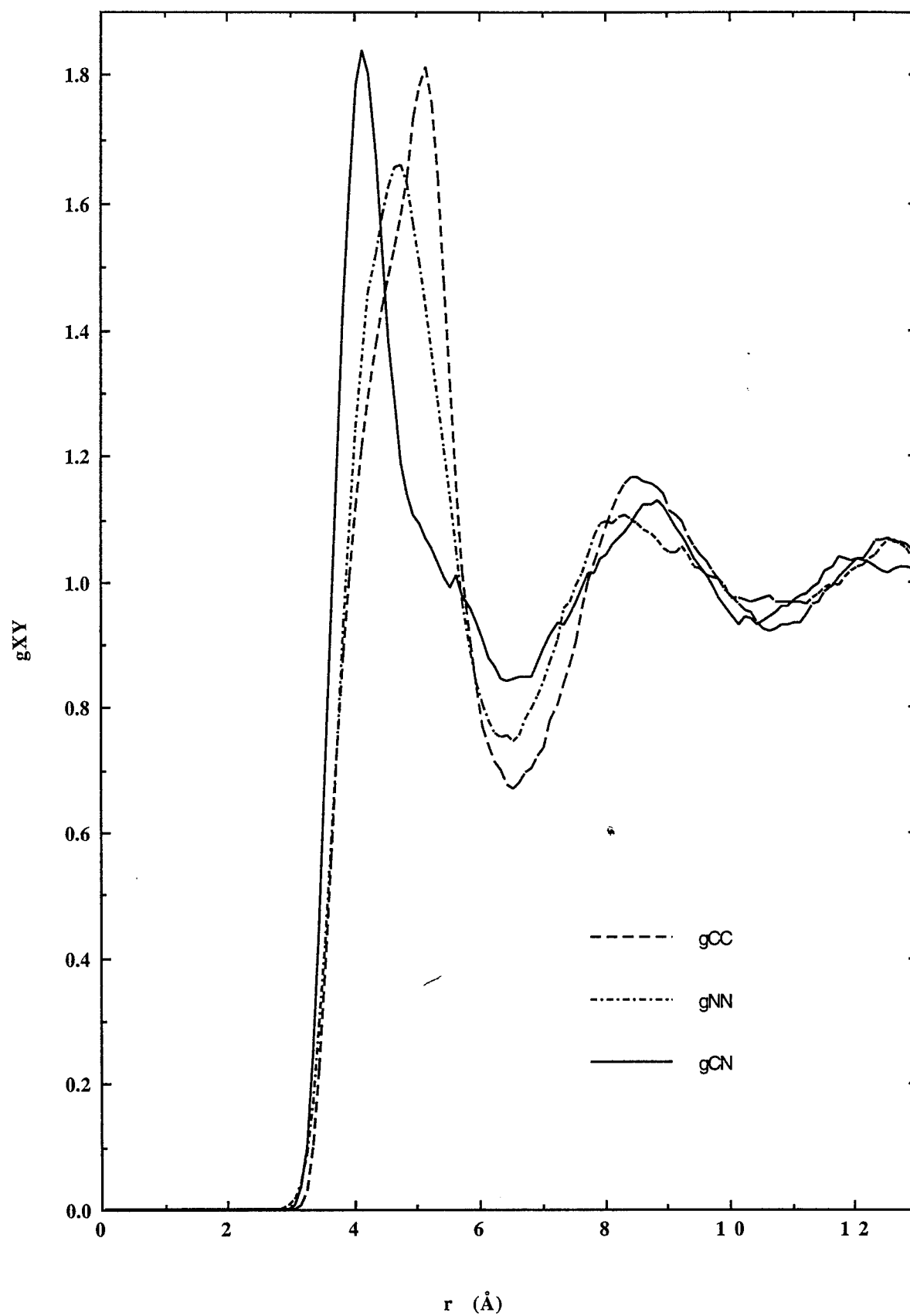


Figure 1.

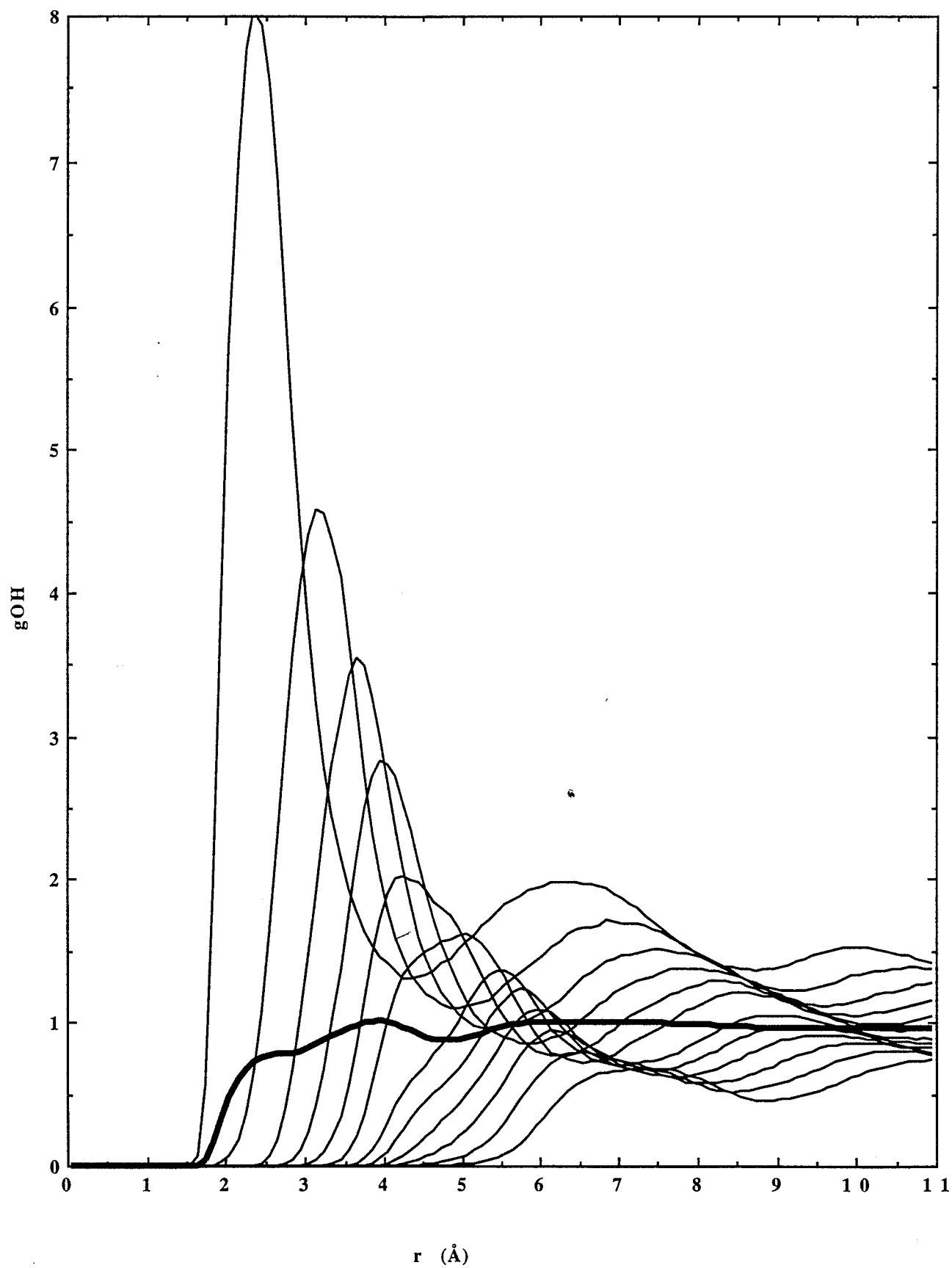


Figure 2.