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RISM calculation of the structure of liquid chloroform†

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It is shown that the RISM theory of molecular liquids provides an accurate prediction of the measured neutron scattering structure factor of deuterated liquid chloroform.

The purpose of this note is to further document the predictive power of the reference interaction site model (RISM) theory [1] by applying the theory to liquid chloroform. Bertagnolli, *et al.* [2] have recently reported their first neutron diffraction results for deuterated liquid chloroform. The chloroform molecule, $CDCl_3$, possesses a dipole moment; and the static dielectric constant of liquid chloroform is moderately large. The RISM theory ignores the dipolar interactions and attributes the local arrangements of molecules to steric forces which it mimics with hard core interactions centred at various interaction sites within each molecule. As a result, it might be guessed that liquid chloroform is one system for which the RISM theory will fail. However, the calculations presented herein indicate that such expectations are not correct.

We have taken the simplest possible RISM molecule for $CDCl_3$ in which each nucleus is the force centre for an additive hard sphere intermolecular interaction. Thus, there are three parameters in the model; the diameters associated with carbon, deuterium and chlorine. Previous RISM studies of liquid carbon tetrachloride [3] and acetonitrile [1] have fixed the values for these diameters so that they are not adjusted for the present investigation. The numbers taken from the previous publications are $\sigma_{Cl}=3{\cdot}4$ Å, $\sigma_C=3{\cdot}0$ Å, and $\sigma_D=2{\cdot}2$ Å. To complete the model, the intramolecular structure of the chloroform molecule must be specified. We assume it is rigid with tetrahedral bonding, and the bond lengths are given by $L_{CCl}=1{\cdot}76$ Å, $L_{CD}=1{\cdot}10$ Å. This RISM molecule is drawn to scale in figure 1.

We have solved the RISM integral equation for the model using Lowden's FORTRAN programs [4]. The molecular density of the liquid was taken to be $\rho=7{\cdot}48\times10^{-3}$ Å^{-3} which is the experimental value at room temperature and

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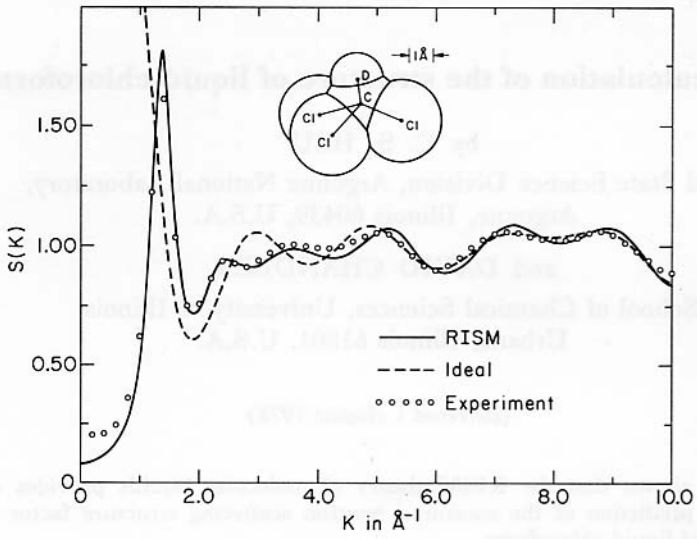

Figure 1. Neutron scattering structure factor, $S(k)$, for liquid chloroform at 20°C and 1 atm pressure, and the RISM molecule representing a $CDCl_3$ molecule. See text for the model parameters. The circles are experimental data (reference [2]); the dashed line is $S_{\text{ideal}}(k)$; and the solid line is the RISM theory result.

1 atm pressure. The solution of the integral equation provides all six distinct atom–atom radial distribution functions, $g_{\alpha\gamma}(r)$, and the associated partial structure factors. An examination of the $g_{\alpha\gamma}(r)$'s indicates that there is considerable interlocking of nearest neighbour molecules. The situation is similar to but quantitatively different than the interlocking in liquid carbon tetrachloride [3]. The r-space distribution functions can be obtained from the authors on request. For the purpose of this note, however, we confine our attention to the normalized neutron scattering structure factor, $S(k)$, formed from the appropriate linear combination of the partial structure factors (see references [1], [3] or [5] for convention). The neutron scattering lengths which determine the weights in the combination are $0{\cdot}665 \times 10^{-12}$ cm, $0{\cdot}667 \times 10^{-12}$ cm and $0{\cdot}958 \times 10^{-12}$ cm, for C, D and Cl, respectively. The theoretical results are compared with experiment and the uncorrelated molecular structure factor, $S_{\text{ideal}}(k)$, in figure 1.

The agreement between the RISM theory and experiment, obtained without adjustable parameters, indicates that to a good approximation the local structure of liquid chloroform is determined by packing or steric effects. Thus, liquid chloroform is a normal non-associated liquid [5]. It is probably improper to imagine that the preferred arrangements of neighbouring molecules in this liquid are appreciably affected by specific attractive interactions (if they exist) or long ranged dipolar forces.

References

[1] Hsu, C. S., and Chandler, D., 1978, *Molec. Phys.*, **36**, 215, and references cited therein.

[2] BERTAGNOLLI, H., LEICHT, D. O., and ZEIDLER, M. D., 1978, *Molec. Phys.*, **35,** 199.
[3] LOWDEN, L. J., and CHANDLER, D., 1974, *J. chem. Phys.*, **61,** 5228.
[4] LOWDEN, L. J., RISM, RISMGR, RISMSK : Program number QCPE306 ; Quantum Chemistry Computer Exchange, Indiana University, Bloomington, Indiana 47401, U.S.A.
[5] CHANDLER, D., 1978, *A. Rev. phys. Chem.*, **29,** 441.