The Structure of Simple Organic Liquids [and Discussion]

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The structure of simple organic liquids

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The structure of non-associated molecular liquids is examined in the light of recent experimental results in X-ray, neutron, and light scattering. These data, along with recent theoretical models of liquid structure, point to a simple picture where size and shape are the most important features in determining the structure of a dense liquid.

In this paper we shall examine the structure of simple organic liquids, excluding hydrogen bonded liquids such as H_2O and other strongly associated systems. Thus we are concerned with unassociated liquids such as CCl_4, CS_2 and benzene. We shall examine the experimental and theoretical attempts to understand the static structure of liquids (that is, if a liquid could suddenly be frozen with all molecules retaining their instantaneous positions, what is the relative centre of mass position and orientation of one molecule relative to all other molecules?) In any study of liquid structure we must first examine the simple rare gas liquids which are now fairly well understood. The primary experimental determination of the structure of liquid argon, for instance, is through an interpretation of the radial distribution function, $g(R)$, as obtained from the angular dependence of the intensity of coherently scattered X-rays or neutrons. In the case of X-rays, the incident radiation is unpolarized and the intensity of the coherently scattered radiation from a gas of free atoms is given by (Flygare 1978):

$$\left.\begin{aligned} I(K) &= \frac{e^4 I_0 N}{m^2 R^2 c^4} \left[\tfrac{1}{2}(1 + \cos^2 \theta_s)\right] f(K)^2 = I_e N f K^2, \\ f(K) &= \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} \rho(r, \theta, \phi) \frac{\sin(Kr)}{Kr} r^2 \, dR \sin \theta \, d\theta \, d\phi, \\ K &= (4\pi/\lambda) \sin \tfrac{1}{2}\theta_s, \end{aligned}\right\} \tag{1}$$

where e is the electronic charge, I_0 is the incident intensity, N is the number of scattering atoms, m is the electron mass, R is the scatterer–detector distance, c is the speed of light, and $f(K)$ is the X-ray atomic scattering factor as a function of K, the scattering vector. The scattering is cylindrically symmetric about the incident radiation axis and the scattering angle, θ_s, is the angle between the incident radiation axis and the scatter–detector line. The function $\rho(r, \theta, \phi)$ is the atomic electron density function. The $f(K)$ factors can be measured as indicated above or calculated from the *ab initio* atomic electronic functions. Standard tables of $f(K)$ values are available (International Tables 1962).

In the condensed (liquid) phase of the simple rare gases, the scattering intensity is modified owing to interatomic interference effects, with the scattering intensity now being given by

$$I(K) = I_e N f(K)^2 \left[S(K) + \rho_0 \delta(K)\right]. \tag{2}$$

I_e is defined in equation (1), ρ_0 is the number density of scatterers (atoms in this instance), $\delta(K)$ is a delta function in K and contributes to the forward scattering. $S(K)$ is the liquid

[67]

structure factor (Egelstaff 1967) arising from interatomic interference. $S(K)$ is related to the radial distribution function, $g(R)$, by the Fourier transform,

$$g(R) = 1 + \frac{1}{2\pi^2 R \rho_0} \int_0^\infty K[S(K) - 1] \sin (KR) \, \mathrm{d}K; \qquad (3)$$

$g(R)$ is the probability of finding a particle at R if there is another particle at $R = 0$ (the origin); $g(R)$ is normalized to unity at large distances. Similar expressions are evident for neutron scattering. The liquid structure factor for Ar at $T = 84$ K, and the resultant $g(R)$ are
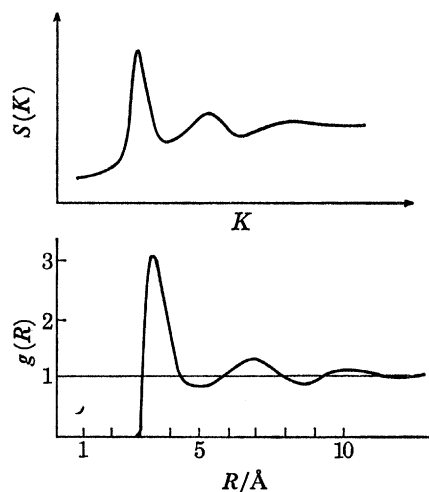

FIGURE 1. Liquid structure factor, $S(K)$, for neutron or X-ray scattering in liquid Ar at $T = 84$ K. The corresponding radial distribution function, $g(R)$ is shown in the lower diagram.

shown in figure 1. The scale of the $S(K)$ curve depends on whether neutrons or X-rays are used and their corresponding wavelengths. The resultant $g(R)$ is the same in either case. The data show that the position of the nearest neighbours is quite well defined but that the positional averages become rapidly randomized beyond the first shell of neighbours. The number of nearest neighbours, n, can be obtained by integrating over a sphere,

$$n = 4\pi\rho_0 \int_0^{R_0} g(R) \, R^2 \, \mathrm{d}R, \qquad (4)$$

where R_0 is the first minimum (from the left) in the $g(R)$ curve in figure 1. The $S(K)$ and $g(R)$ curves shown in figure 1 are fairly typical of atomic liquids; there are approximately 12 nearest neighbours and the number distribution becomes rapidly uniform after the shell of 12 nearest neighbours. Thus it is evident that the correlation between atomic centres is short range, only being well defined in the first shell of nearest neighbours.

The radial distribution function in liquids can be calculated by a knowledge of the atom–atom pair potential function which, for rare gas atoms, is usually taken as the Lennard-Jones function given by

$$V(r) = 4\epsilon[(d/r)^{12} - (d/r)^6], \qquad (5)$$

where d is a parameter related to the potential minimum located at $r_0 = (2)^{\frac{1}{6}} d$ with well depth of ϵ. The parameter d is the $V(r = d) = 0$ crossing point of the function. The calculation of the

radial distribution function from the Lennard-Jones potential is a well known but difficult procedure in statistical mechanics (McQuarrie 1976; Hanson & McDonald 1976; Watts & McGee 1976). It is now well known that the structures of the rare gas liquids as reflected in $g(R)$ are satisfactorily explained on the basis of pairwise additions of interactions according to the Lennard-Jones potential. A careful examination of $g(R)$ in figure 1 and the known Lennard-Jones parameters in equation (5) for argon from molecular beam experiments (Levin & Bernstein 1974) show that the average internuclear distance of the nearest neighbour distance in liquid argon centres around r_0. However, in spite of our rather thorough understanding of the rare gas liquids and the statistical mechanical techniques of calculating $g(R)$ from a knowledge of the Lennard-Jones potential, the calculations are very difficult and it is even more difficult to extend these calculations to molecular liquids where longer range attractive forces (electrostatic dipole–dipole and others) are certainly present.

More recently, perturbation theories (McQuarrie 1976; Hanson & McDonald 1976; Watts & McGee 1976) have been developed to evaluate $g(R)$ from the pairwise interaction potential. In these theories the potential energy is separated into parts where the dominant term serves as a reference point for the development of the zero order basis, with the remaining part of the potential serving as a perturbation. One particularly successful perturbation approach by Weeks *et al.* (1971) works well at high density and has important consequences for an understanding of the structure of non-associated molecular liquids. This theory, first developed for the liquid rare gas systems with the Lennard-Jones potential, regards the potential from $r = 0$ to $r_0 = 2^{\frac{1}{6}} d$ in equation (5) as the zero order or reference part of the system, with the remaining part of the potential on the larger side ($r \geqslant r_0$) of the minimum serving as the perturbation. These ideas trace back to van der Waals's original ideas on the structure of atomic liquids as being determined largely by the repulsive part of the potential function. The success of the theory of Weeks *et al.* (1971) shows that the radial distribution function $g(R)$, and what we have called here 'liquid structure', are largely determined by the repulsive part ($r < r_0$) of the Lennard-Jones potential function. These results, along with earlier molecular dynamics calculations on argon (Verlet 1968), which showed that the $g(R)$ could be fitted by hard sphere atoms with temperature and density dependent diameters, convince us that the hard sphere (or repulsive) model is a valid description of the liquid state of rare gases. This is a remarkable conclusion since it simplifies our understanding of atomic liquids largely to a hard sphere picture. The model presented here is limited to high density liquids, high density being greater than twice the critical density of the fluid. However, this requirement does include most unassociated liquids at temperatures near and below their boiling points. These above conclusions concerning the relative atomic positions in a liquid will clearly break down at low densities as in the gas phase where well known van der Waals dimer, trimer, and other monomer species can be formed with energies of stabilization from $\frac{1}{10}$ to $\frac{1}{2} kT$ (Ewing 1975). The structure of the Ar_2 dimer, for instance, will be determined by the complete Lennard-Jones pair potential in equation (5), whereas in the liquid state the atoms are forced together by the thermodynamically most favourable packing of the atoms in the dense medium. Of course, one expects that the thermodynamic properties of the liquid, the boiling and melting points, would be determined from the attractive parts of the potential function. Thus, a complete theory of the liquid state would require a knowledge of the entire pair potential in equation (5). However, it now seems clear that the structures of atomic liquids are determined primarily by the part of the potential function which is on the $r \leqslant r_0$ side of the potential minimum, the repulsive part.

At this time we note that we have learned that the structure of dense atomic liquids is largely determined by the repulsive part of the potential function – this is a type of hard sphere theory. Now, what influence does this finding have on our understandings of the structure of unassociated *molecular* liquids? It appears that unassociated molecular liquids composed of molecules with appreciable dipole and quadrupole moments have structures which are still largely determined by the size and shape of the molecules (Chandler 1977). We will try to justify this statement in the remaining parts of this paper.

We first return to a discussion of the determination of the liquid structure by X-ray or neutron scattering. In the case of a low density molecular gas, the intensity of the unpolarized X-rays scattered from the monomeric molecules is given by

$$I_0(K) = I_e N \left\{ \sum_\alpha f_\alpha(K)^2 + \sum_{\alpha \neq \beta} f_\alpha(K) f_\beta(K) \frac{\sin K(r_\alpha - r_\beta)}{K(r_\alpha - r_\beta)} \right\}. \tag{6}$$
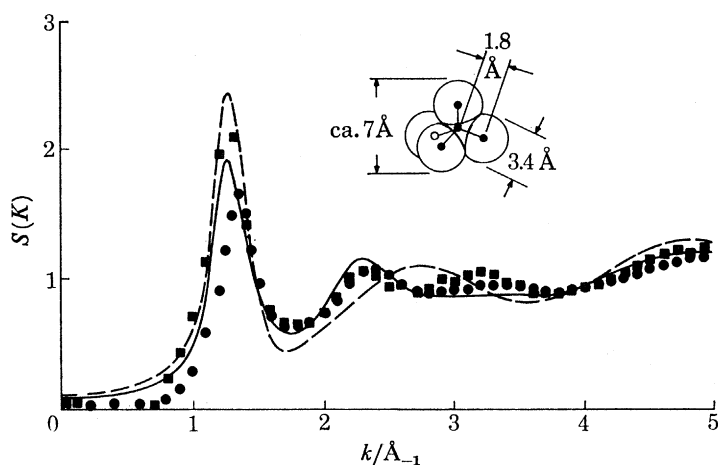

FIGURE 2. Liquid structure factor from neutron scattering in CCl_4. The circles and squares are experimental data, the dashed line is the best fit using a spherical model for CCl_4 (diameter = 5.2 Å) and the solid line is a molecular model of overlapping hard spheres of Cl atoms with diameters of 3.4 Å.

N is the number of scattering molecules, I_e and $f_\alpha(K)$ are defined in equation (1), $f_\alpha(K)$ is the free atom scattering factor for the αth atom in the molecule. The second term in equation (6) leads to an interference term and an oscillation in $I(K)$ due to interatomic interference effects between the different atoms in the single gas phase scattering molecule. If the molecules are now condensed to the liquid state, the corresponding intensity scattered (at K) is given by

$$I(K) = N' (I_0(K)/N) [S(K) + \rho_0 \delta(K)], \tag{7}$$

where $(I_0(K)/N)$ is defined in equation (6), N' is the number of molecules scattering in the liquid, and $S(K)$, the liquid structure factor, is defined from equation (2). The molecular liquid structure factor, $S(K)$ in equation (7) can be obtained from the experimental $I(K)$ curve for the molecular liquid by dividing by $(I_0(K)/N)$ obtained for the low density gas. Thus, the $S(K)$ so obtained is the liquid structure factor and arises from atomic interferences between atoms on different molecules. The liquid structure factor, $S(K)$, for CCl_4 as determined by neutron scattering is shown in figure 2 where the squares (Narten 1976) and circles (Egelstaff et al. 1971) are from different experimental data. Remembering that the $S(K)$ data in figure 2 arise from interatomic interferences between atoms on different molecules, we note that the

data for the liquid structure factor for CCl_4 are similar to the data in figure 2 for the atomic Ar liquid. Fourier transformation of $S(K)$ in figure 2 to give a $g(R)$ function shows again that there are about 12 nearest neighbours and then the correlations fall off rapidly. However, there is also orientational information present in $S(K)$ in figure 2. With the use of the successful Weeks *et al.* theory for atoms, Lowden & Chandler (1974) have calculated $g(R)$ and $S(K)$ by assuming that CCl_4 is a sphere. The best agreement of this model with theory is shown by the
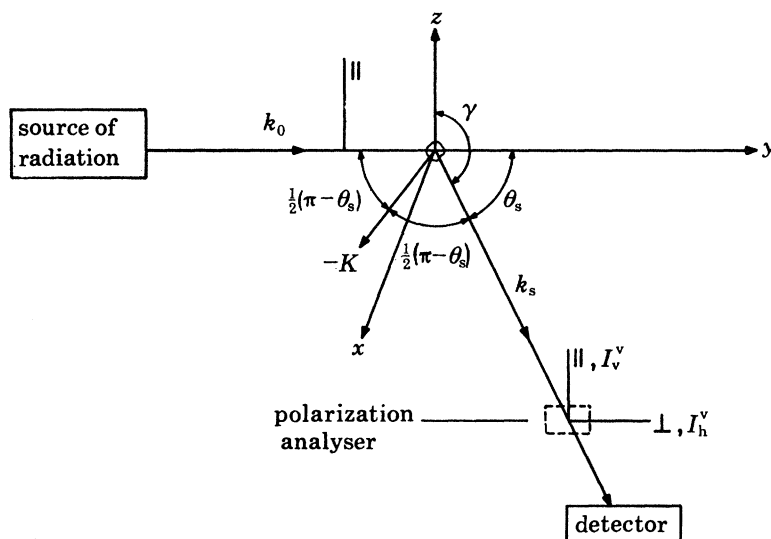

FIGURE 3. Typical light scattering diagram. Scattering vector $K = k_0 - k_s$; $K = (4\pi n/\lambda_0) \sin \frac{1}{2}\theta_s$, $k_0 = 2\pi n/\lambda_0$.

dotted line in figure 2 where the hard sphere diameter is found to be 5.2 Å.† There are significant deviations between this atomic 'best fit' model of CCl_4 and the experimental data. The deviations between the 'best fit' dotted line results and the experimental data are a clear sign that the molecular shape of the CCl_4 molecule must be included in any explanation of $S(K)$ or $g(R)$ in liquid CCl_4. In addition, the best spherical model fit described above gave a diameter of only 5.2 Å which is significantly smaller than one normally obtains for the van der Waals diameter of molecular CCl_4, as shown in the inset of figure 2. Thus it is evident that in liquid CCl_4 the molecules are packed so densely that some interlocking of structure is required. The apparent proximity between CCl_4 molecules can be obtained by acknowledging the actual shape of the molecule and then allowing the Cl atom of one CCl_4 molecule to fit into the crevice along the C_3 axis formed by another molecule. By constructing a CCl_4 molecule of overlapping hard spheres, it is possible to show that size and shape indeed determine the structure of liquid CCl_4, and that the local orientation of near neighbour molecules is determined by the most favourable packing of these hard sphere molecules (Chandler 1977; Narten 1976; Lowden & Chandler 1974). The resultant calculated $S(K)$ is shown by the solid line in figure 2 where a Cl diameter of 3.4 Å was used (Lowden & Chandler 1974). This technique employing the reference interaction site model for calculating interatomic correlation between atoms on different molecules has been applied on several molecular liquids (Chandler 1977) including CCl_4 (see above), CS_2, N_2, O_2, Br_2, benzene and acetonitrile. The rather definite

† 1Å = 0.1 nm = 10^{-10} m.

282 W. H. FLYGARE

conclusion from these studies is that both orientational and centre of mass positioning of molecular liquids are largely determined by short range forces. In fact there appears to be very little long range order. The effect of dipole–dipole and other electrostatic interactions (which are absent in atomic liquids) in molecular liquids appears to be merely to change the 'effective' hard sphere radii of the overlapping atoms in the molecule. This conclusion again refers back to our previous discussion of atomic liquids in which we found that the dominant liquid structural features were determined by the repulsive part of the pair potential function. In molecular liquids we find again that the dominant features of the liquid structure are determined by the size and shape of the molecules and the repulsive parts of the pairwise atomic potentials, where each molecule is constructed of overlapping hard sphere atoms. The diameters of the overlapping atoms are fitted parametrically to the liquid structure factors, and they are therefore dependent on the dipole–dipole and other electrostatic interactions that do affect the liquid structure, but apparently only a short range effect is observed.

Orientational pair correlations can be measured by Rayleigh light scattering. A typical light scattering experiment is arranged as shown in figure 3, where monochromatic z–y polarized incident radiation is scattered and either the polarized ($\parallel$) or depolarized ($\perp$) scattered light is observed (Flygare 1978; Berne & Pecora 1976). In the case of a pure liquid of cylindrically symmetric molecules, the spectrum of Rayleigh depolarized scattering in the limit where Debye rotational diffusion is evident, is given by (Flygare 1977)

$$I_h^v(\omega) = \frac{\omega^4(\alpha_{aa}-\alpha_{bb})^2\, Nf(n)g_2}{15R^2\pi c^4} \left\{ \frac{(1/\tau)}{(\omega-\omega_0)^2+(1/\tau)^2} \right\}, \qquad (8)$$

$$g_2 = 1 + \langle \tfrac{1}{2} \sum_j (3\cos^2\theta_{ij}-1)\rangle.$$

$\alpha_{aa}-\alpha_{bb}$ is the polarizability anisotropy where a is the symmetry axis of the cylindrically symmetric scatterer, R is the scatterer–detector distance, N is the number of scatterers, $f(n)$ is some function of the refractive index, n, related to the local radiation field at the scatter, g_2 is the static structure factor where the brackets indicate an average over all particles j relative to the origin particle i. $\omega_0 = k_0 c$ is the frequency of the incident monochromatic laser and τ is the relaxation time of the scattering system. τ is related to the single particle relaxation time, τ_{sp} by $\tau = g_2\tau_{sp}$. The value of τ_{sp} can be measured by the width of the depolarized Raman scattered light. Thus, g_2 can be measured by comparing the line widths of depolarized Raman and Rayleigh spectra or by a measurement of the total intensity of depolarized Rayleigh scattered light. Quite a large number of $g_2 = \tau/\tau_{sp}$ have been measured in symmetric top molecules according to the above methods (Flygare 1977; Bauer et al. 1976; Patterson & Griffiths 1975). The g_2 values range from 1.0 in benzene to about 2.0 in bromoform. There appears to be no relationship between g_2 and the magnitude of the dipole moment (Patterson & Griffiths 1975), and this indicates that g_2 is a function of the size and shape of the molecule.

Also g_2 has been measured by the integrated intensities by first measuring the local field factor, $f(n)$, in equation (8) (Gierke & Flygare 1974). Molecules that are like liquid crystals have shown the expected large values for g_2 even in the isotropic phase (Alms et al. 1974). An interesting study has been reported of cross correlation between the benzene–hexafluorobenzene and mesitylene–hexafluorobenzene pairs by examining both spectral widths and the integrated intensities (Bauer et al. 1975). The g_2 cross correlation values are 2.0 for benzene–hexafluorobenzene and 1.0 for the other pair. The correlation was very short lived – on the

order of picoseconds – as was evident from a spectral fit of the depolarized scattered light. If the benzene–hexafluorobenzene were in a tight binding dimer structure with no correlation between dimers, the observed spectra would be composite of benzene, hexafluorobenzene and the dimer, with the dimer part of the spectra being narrower owing to the slower rotational correlation time of the dimer relative to the benzene and hexafluorobenzene monomers. No evidence for the narrower line was observed. This result is also consistent with the data in pure liquids; the correlation is very short lived, shorter than the rotational correlation times of 1–10 ps. Bertucci *et al.* (1977) have made a systematic study of orientational pair correlations in a series of substituted benzenes, where the size and shape of the molecule remains relatively constant but the dipole moment varies from near 0.0 D in toluene up to nearly 4.0 D in nitro-benzene. The orientational pair correlations in these substituted benzenes do scale as the square of the electric dipole moments. However, the temperature dependence of the orientation correlation factors was negligible. This was found earlier in symmetric tops (Patterson & Griffiths 1975) and is confirmed again by the careful study of the temperature dependence of g_2 in CS_2 by Madden (this Symposium).

The small temperature dependence of the orientational pair correlations as described above indicates that long range interactions are not important in determining these correlations. Thus, we conclude that short range interactions primarily involving the repulsive part of the molecule–molecule interaction potential are important in determining the orientational pair correlations. It is quite clear that the orientational pair correlations, as measured by the light scattering experiment, can include interactions up to a distance of the inverse scattering vector which is in excess of 500 nm for these experiments. However, the temperature dependence points to a more localized order of the correlations, perhaps only the first shell of nearest neighbours which would be most affected by the sharp repulsive part of the molecule–molecule pair potential.

Thus, it appears that this evidence supports the concept of local order for the liquid structure. The effect of the dipole–dipole and other multipole–multipole interactions is to modify the repulsive part of the potential function for the closely packed molecules. It is not surprising then that the liquid structure $g(R)$ functions obtained from X-ray or neutron scattering can be fitted with a hard sphere model when we require the sphere diameter to be modified because of the dipole–dipole (and other electrostatic interactions) modification of the repulsive part of the molecule–molecule pair potential. From this we conclude that molecular liquid structures (unassociated systems) are largely determined by the size and shape of the molecules.

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Discussion

A. D. Buckingham, F.R.S. I have some reservations about your conclusion that local structure in the liquid is determined by the short range repulsive forces that are responsible for the shape of the molecule. It runs counter to our notions of complex formation. There is evidence that electrostatic forces can also play a significant role in determining orientational correlations. For example, the shapes of benzene and hexafluorobenzene are similar, yet the liquid mixture behaves quite differently from the pure components in light scattering (Bauer *et al.* 1975), magnetic birefringence (Le Fèvre *et al.* 1969) and thermodynamics (Gaw & Swinton 1968). It is tempting to deduce that the electrostatic forces favour a face-to-face configuration in the mixture, but hinder it in the pure components. Similarly in pure 1,3,5-trifluorobenzene, or in *s*-triazine, the face-to-face configuration, staggered by 60°, might be favoured by electrostatic forces. The qualitative difference between the crystal structures of benzene (Cox *et al.* 1958) and hexafluorobenzene (Boden *et al.* 1973) on the one hand, and of *s*-triazine (Wheatley 1955) and the 1:1 complex of hexafluorobenzene and mesitylene (Dahl 1971) on the other hand (the structure of crystalline C_6H_6—C_6F_6 has apparently not been determined), is further evidence of the significance of electrostatic forces. It is tempting to predict that the dimer of 1,3,5-trifluorobenzene is not dipolar (unlike $(C_6H_6)_2$ (Janda *et al.* 1975)) and that the packing of the molecules in the crystal is similar to that in *s*-triazine.

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M. R. Battaglia (*Theoretical Chemistry Department, University of Cambridge, Cambridge CB2 1EW, U.K.*). Would Professor Flygare like to speculate on the dependence of g_2 on the molecular quadrupole moment in quadrupolar liquids – such as benzene and hexafluorobenzene – just mentioned by Professor Buckingham?

Although these two molecules have the same symmetry, and approximately the same size, their local structure appears to be quite different. Contrary to any intuitive prediction based on either hard core or electrostatic considerations, the estimates (Battaglia 1978) of g_2 (from light scattering) are qualitatively different for benzene and hexafluorobenzene – 0.9 and 1.4 respectively.

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W. H. FLYGARE. The issues raised here are discussed in my paper. More details involving short range electrostatic interactions are given in another paper (Flygare *et al.* 1977) which deals in detail with the nitrobenzene orientational pair correlations. The dipole–dipole electrostatic interactions do influence the short range repulsive part of the potential function. The result of this is to modify the 'effective' diameters of the atoms in the molecules. Therefore, the conclusions involving these systems are not inconsistent with my model.

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H. A. POSCH (*Institut fur Experimentalphysik*, 1090 *Wien, Strudlhofg.* 4, *Austria*). Only indirect information on orientational correlation between neighbouring molecules may be gained from generalized Kirkwood $g^{(l)}$ factors. Not only nearest neighbours contribute significantly to $g^{(l)}$, but also molecules in shells much further out. Clearly, the statistical weight of particles in outer shells is proportional to r^2. Although orientational correlations between these molecules and the central particle are usually small, their contribution to $g^{(l)}$ is enhanced owing to the statistical weight. This has been demonstrated by Neumann & Steinhauser (1978) in their recent molecular dynamics study of liquid CS_2. It is interesting to note that centre of mass correlations $g(r)$ die away already in the second shell whereas orientational correlations extend at least up to 1 nm.

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W. H. FLYGARE. I have not seen Neumann & Steinhauser's unpublished work and am therefore unable to comment on their analysis. I have tried to address the point Dr Posch raised in my paper and, as I mentioned, the small temperature dependence of g_2 points to short range effects.